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Santa Barbara

Catalytic Upcycling of Polyolefins to Alkylaromatics

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy
in Chemistry

by

Jiakai Sun

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March 2024

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March 2024

Catalytic Upcycling of Polyolefins to Alkylaromatics

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by

Jiakai Sun

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7. **Sun, J.**, Dong, J., Gao, L., Zhao, Y.-Q., Moon, H., Scott, S. L., “Catalytic Upcycling of Polyolefins,” *Chem. Rev.* (invited), in review.
6. Lamb, J. V., Lee, Y.-H., **Sun, J.**, Byron, C., Uppuluri, R., Kennedy, R. M., Meng C., Behera, R. K., Wang, Y.-Y., Qi, L., Sadow, A. D., Huang, W., Ferrandon, M. S., Scott, S. L., Poeppelmeier, K. R., Abu-Omar, M. M., Delferro, M., “Supported Platinum Nanoparticles Catalyzed Carbon-Carbon Bond Cleavage of Polyolefins: Role of the Oxide Support Acidity,” *ACS Appl. Mater. Interfaces*, **2024**, accepted.
5. **Sun, J.**,[#] Lee, Y.-H.,[#] Yappert, R.D., LaPointe, A.M., Coates, G.W., Peters, B., Abu-Omar, M. M., Scott, S. L., “Bifunctional tandem catalytic upcycling of polyethylene to surfactant-range alkylaromatics,” *Chem*, **2023**, 9(8), 2318-2336.
4. Lee, Y.-H.,[#] **Sun, J.**,[#] Scott, S. L., Abu-Omar, M. M., “Quantitative Analyses of Products and Rates in Polyethylene Depolymerization and Upcycling,” *STAR Protocol*, **2023**, 4, 102575.
3. Zhang, F., Zeng, M., Yappert, R. D., **Sun, J.**, Lee, Y.-H., LaPointe., A. M., Peters, B., Abu-Omar. M. M., Scott, S. L., “Polyethylene Upcycling to Long-chain Alkylaromatics by Tandem Hydrogenolysis/Aromatization,” *Science*, **2020**, 379, 437-441.
2. Wang, J.-W.,[#] **Sun, J.**,[#] Liu, D.-C., Jiang, L., “Visible-light-driven CO₂ reduction catalyzed by a dinuclear nickel complex,” *Eur. J. Inorg. Chem.* **2020**, 47, 4450-4453.

1. Wang, J.-W., Huang, H.-H., **Sun, J.**, Zhong, D.-C., Lu, T.-B., “Syngas production with a highly-robust nickel(II) homogeneous electrocatalyst in a water-containing system,” *ACS Catal.* **2018**, 8, 7612-7620.

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2. Lee, Y.-H., Heuston, A., **Sun, J.**, Scott, S. L., Abu-Omar, M. M., “Polyethylene-derived Surfactants from Reactive Separation of Hydrocarbons Mixture via Sulfonation,” in preparation.

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1. Process for catalytic upcycling of hydrocarbon polymers to alkylaromatic compounds, Inventors Mahdi M. Abu-Omar, Manhao Zeng, Susannah Scott, Fan Zhang, **Jiakai Sun**, Yu-Hsuan Lee, International patent WO 2022/015971, filed 7/15/21, issued 1/20/22.
2. Efficient and selective upcycling of polyethylene to alkylbenzenes under moderate hydrogen pressure, Inventors **Jiakai Sun**, Susannah L. Scott, Yu-Hsuan Lee, Mahdi M. Abu-Omar, US Provisional Patent Application 63/502,520, filed 5/16/23.

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The essential effect of support acidity on the tandem conversion of polyethylene to alkylaromatics. **Jiakai Sun**, Yu-Hsuan Lee, Mahdi Abu-Omar, Susannah Scott. 27th North American Catalysis Society Meeting; May 2022; New York, NY. (Oral Presentation).

ABSTRACT

Catalytic Upcycling of Polyolefins to Alkylaromatics

by

Jiakai Sun

Plastics, a pivotal product of the last century, have dramatically transformed industries ranging from healthcare and food safety to textiles, electronics, and construction, making consumer goods more accessible worldwide. Plastic production has soared from its early days, and is projected to continue growing significantly. This increase is primarily due to polyolefins like polyethylene (PE) and polypropylene (PP), which make up about half of all plastic production. However, this manufacturing boom has led to a massive surge in plastic waste, with poor waste management practices causing significant environmental issues. A small portion of this waste is recycled, mainly through mechanical methods that degrade quality.

Chemical recycling to monomers is effective for condensation polymers but less so for polyolefins due to their strong carbon-carbon bonds, often resulting in low-value products. Upcycling is a possible alternative for managing polyolefin waste. The aim is to selectively cleave specific C-C bonds in polyolefins, converting them into building blocks that can be used as feedstocks for chemical manufacturing.

Catalytic conversion of waste polyolefins to value-added alkylaromatics could contribute to carbon recycling. Tandem catalytic conversion by platinum supported on γ -alumina converts various polyethylene (PE) grades into valuable long chain alkylaromatics and alkylnaphthalenes (average $\sim C_{30}$, dispersity $D = 1.1$) with high yields, in the absence of added solvent or molecular hydrogen. Coupling exothermic hydrogenolysis with endothermic aromatization renders the overall transformation thermodynamically accessible despite the moderate reaction temperature of 280 °C.

Compared to tandem hydrogenolysis/aromatization of PE catalyzed by Pt/ γ -Al₂O₃ at 280°C, both a five-fold enhancement in the rate of C-C bond scission and a doubling of the molar yield of alkylaromatics were realized using a more acidic Pt/F-Al₂O₃ catalyst instead. Bifunctional (metal/acid) catalysts also generate alkylaromatic products with lower average carbon numbers (ca. C₂₀), similar to conventional anionic surfactants. Since physical mixtures of weakly acidic Pt/ γ -Al₂O₃ or non-acidic Pt/SiO₂ with strongly Brønsted acidic Cl-Al₂O₃ or F-Al₂O₃ are also effective, the tandem reaction does not require nano-scale intimacy between metal and acid active sites. Kinetic studies using triacontane (*norm*-C₃₀H₆₂) as a model for PE show that the Pt-catalyzed dehydrogenation/hydrogenation reactions are quasi-equilibrated, while the acid-catalyzed C-C bond scission and skeletal transformations (isomerization and cyclization) determine the overall rates of depolymerization and aromatic formation.

Different from hydrocracking, aromatic formation must be conducted without high pressure H₂. Depolymerization can be performed without adding any external H₂, depending instead on redistribution of PE-derived H₂ to value-added alkylbenzenes. However, moderate external H₂ pressures (1-8 bar) significantly enhance the depolymerization rate and alkylbenzene yield (maximum yield at 4 bar H₂). The rate of C-C bond scission is pseudo-

zeroth-order. It increases with external $P(\text{H}_2)$ at lower pressures (< 10 bar), then decreases at higher pressures. Modifying the traditional hydrocracking mechanism to include competitive adsorption of aromatics explains the $P(\text{H}_2)$ dependence of the rate. Dynamic control of the reactor atmospheres can further increase the alkylbenzene yield, especially in the desired molecular weight range for anionic surfactants.

Depolymerization and upcycling are promising approaches to managing plastic waste. However, quantitative measurements of reaction rates and analyses of complex hydrocarbon product mixtures arising from the depolymerization of polyolefins constitute significant challenges in this emerging field. The methods for recovery and analysis of all products arising from batch depolymerization of polyethylene are detailed. The quantitative analyses of reaction rates and selectivity for alkanes and aromatic products are described. This protocol can be extended to depolymerization of other plastics such as polypropylene, and to characterization of other product mixtures (including long-chain olefins).

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Chapter 1. Introduction

Note: This chapter was adapted from sections of the following publication.

Publication: **Sun, J.**, Dong, J., Gao, L., Zhao, Y.-Q., Moon, H., Scott, S. L., “Catalytic Upcycling of Polyolefins,” *Chem. Rev.* (invited), in review.

1.1. Catalytic Upcycling Strategies for Polyolefins

Plastics are unquestionably one of the most important technologies of the last century. They have transformed sectors as diverse as health care, food safety, textiles, electronics, transportation, machinery, and construction, and they have made a vast array of consumer goods more broadly accessible to people in all sectors of society. Since the early days of mass production, the global production of plastics has soared, from 2 Mt in the 1950s to nearly 400 Mt today.¹ On the current trajectory, it is possible that by 2050, the world will produce 500 Mt plastics each year. The plastics industry is predicted to consume as much of 20 % of oil production while generating 15 % of annual carbon emissions.²

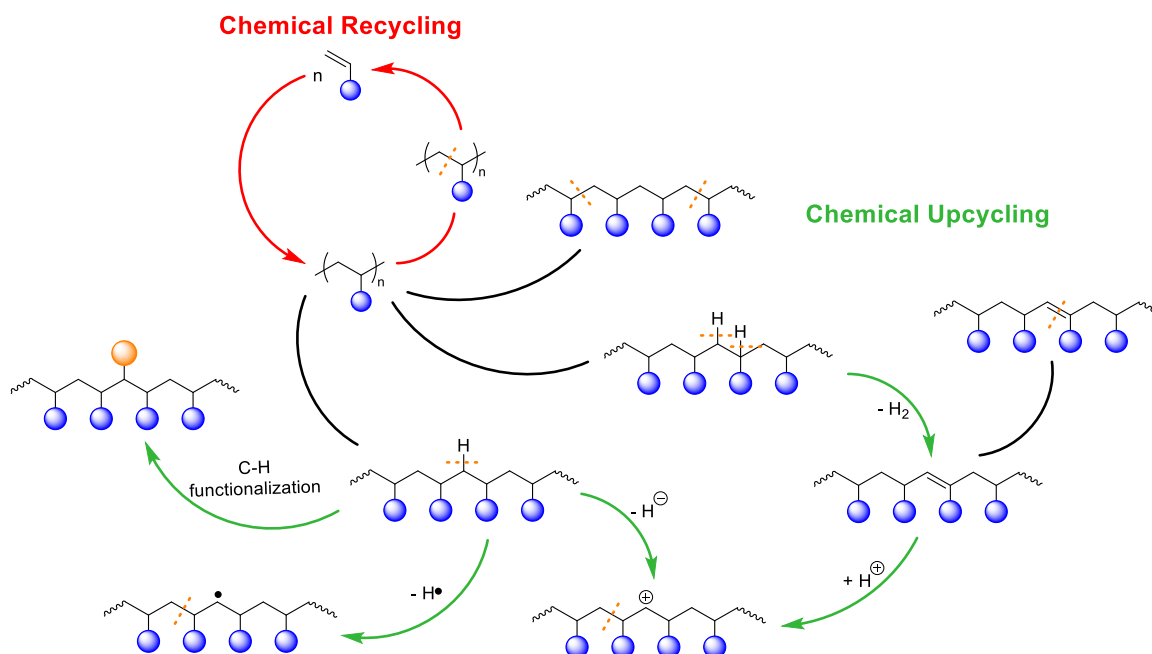
The commodity polyolefins (POs), which are polymers of simple alkenes, include polyethylene (PE) and polypropylene (PP). These two polymers represent the largest fraction of modern plastics. For example, in 2021, PE accounted for approximately 27 % of plastic production, including low-density polyethylene (LDPE) and high-density polyethylene (HDPE), while PP constituted about 20 %.³ Thus POs effectively represent half of all plastic production.

This immense manufacturing success, combined with the low cost of POs, has led to a proliferation of short-term uses and a corresponding surge in waste, with 353 Mt plastic waste

generated in 2019 alone.⁴ Unfortunately, much of this waste is not responsibly managed. According to a report monitoring the fate of plastic waste, approx. 23 % ends up in landfills.³ Around 42 % is incinerated, which can be a strategy for energy recovery but which releases CO₂ into the environment. The problem is compounded by emissions of gases other than CO₂, due in part to the intimate mixing of polymers with other materials.³ Conventional recycling has not thus far proven to be a viable solution to address these issues.⁵

Plastic waste can be recycled mechanically, chemically, or through hybrid chemomechanical processes.^{6,7} Mechanical recycling involves remanufacturing waste into new products, without disassembling the polymer chains. This process is most effective for recycling material of known composition and high purity (i.e., industrial scrap), rather than post-consumer waste. Even then, it usually compromises the mechanical properties (e.g., strength, toughness) of the original polymer. Chemical recycling requires at least partial depolymerization into monomers or oligomers, which can be repolymerized or repurposed after appropriate chemical separation.⁸ This method is most readily applied to heteroatom-containing polymers like polyesters, such as polyethylene terephthalate (PET), with its hydrolysable ester linkages.⁹ It is not generally used for polyolefins, whose backbones consist solely of strong and relatively inert C-C bonds.⁵ Depolymerization of polyolefins can in principle be performed at elevated temperatures. Although these reactions are spontaneous above the polymer ceiling temperature,¹⁰ in practice, thermal depolymerization is only effective for polystyrene. PE and PP pyrolyze before reaching their ceiling temperatures, resulting in a complex and low-value mixture of gases, low-quality liquids, and coke.¹¹

Upcycling is a possible alternative for managing polyolefin waste.^{8,12} The aim is to selectively cleave specific C-C bonds in polyolefins, converting them into building blocks that can be used as feedstocks for chemical manufacturing. It requires a suitable catalyst, and often involves the use of co-reactants. **Scheme 1.1** illustrates differences between chemical recycling and upcycling, including key intermediates in the upcycling process. Unlike chemical recycling, which necessitates breaking a large fraction of the C-C bonds in the polyolefin backbone, chemical upcycling often targets a small fraction of these bonds. This selective cleavage reduces the energy requirement and makes the reactions more thermodynamically accessible.



Scheme 1.1. Comparison of polymer backbone cleavage in chemical recycling and upcycling. Blue balls represent polyolefin side-chains (H and CH₃). The orange ball represents a new functional group.

Hydrogenolysis is one upcycling strategy. It uses a metal catalyst to break C-C bonds and add H₂ to cap the new chain ends. However, hydrogenolysis can break every C-C bond, producing methane whose low value does not qualify the process as upcycling. Another strategy begins with C-H bond cleavage to give a reactive site. For instance, forming a C=C bond by polymer dehydrogenation opens up the possibility of chain cleavage via alkene metathesis, or protonation to give a carbocation that is susceptible to chain cleavage by β -scission in the (hydro)cracking. Direct carbocation formation in polyolefins (i.e., without first forming a C=C bond) can be achieved by heterolytic C-H bond cleavage, as in hydride abstraction by a Lewis acid. Alkyl radicals can be formed by homolytic C-H bond cleavage, as in H atom abstraction by a reactive oxygen species. In the presence of excess oxidant, the polymer can be converted to higher value oxygenates, or combusted to low value CO_x. Obviously, converting polyolefins to CO_x is also not considered upcycling. Installing other functional groups, such as aromatic rings, could convert post-consumer plastic into a new polymer, or into different types of chemical feedstocks with higher value.

This dissertation focuses on the direct conversion of polyolefins to alkylaromatics through tandem aromatization/hydrocracking (the overall reaction redistributes hydrogen). The current knowledge of (hydro)cracking and aromatization, both on small hydrocarbons and polymers, will be discussed in the introduction.

1.2. Catalytic Cracking and Hydrocracking of Polyolefins

1.2.1. Key Concepts

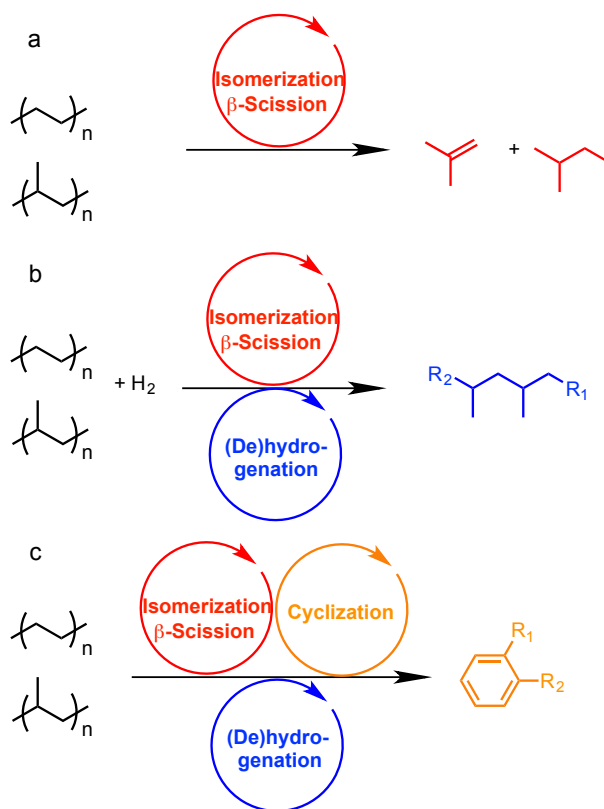
According to the IUPAC Goldbook, cracking refers to thermal or catalytic decomposition of a hydrocarbon into chemical species of smaller molecular weight.¹³ Because chemical feedstocks typically have much smaller carbon numbers than polymers, cracking is a promising strategy to generate recycled chemical feedstocks from polyolefins.

Thermal cracking in the absence of O₂ is also known as pyrolysis. The pyrolysis of POs generates mostly *n*-alkanes, 1-alkenes, and alkadienes at high temperatures (>500 °C).¹³ The endothermic reaction is proposed to follow a radical mechanism. Many others have discussed the impact of reaction conditions and reactors on the product distribution and reaction mechanisms, as well as the technical challenges.^{14–20} Catalytic cracking shares similar reaction conditions with pyrolysis, but differs in the use of a solid acid catalyst (**Scheme 1.2**).²¹ The catalytic cracking of POs typically requires lower temperatures (but still >400 °C) compared to pyrolysis, and it generates a mixture of *iso*-alkanes, alkenes, cycloalkanes, and aromatics.^{22–26}

Hydrocracking is a form of catalytic cracking that occurs in presence of a high pressure of H₂. In addition to the acid component, the catalyst contains a component with a (de)hydrogenation function (**Scheme 1.2**).¹³ Hydrocracking of POs generates *iso*-alkanes. Since the reaction is exothermic, it can be performed at even lower temperatures than catalytic cracking. The lower energy requirement and simpler product distribution of hydrocracking has attracted much interest for polymer upcycling. The following section focuses primarily on

(relatively) low temperature hydrocracking of POs, although some efforts in the area of catalytic cracking will also be discussed.

In addition to catalytic cracking and hydrocracking, POs can be converted, in the absence of external H_2 or under low P_{H_2} , and in the presence of acidic, and especially bifunctional catalysts, into higher-value aromatics by hydrogen redistribution (**Scheme 1.2**). This strategy will be discussed in **Section 1.3**.



Scheme 1.2. Overall processes for (a) catalytic cracking, (b) hydrocracking, and (c) hydrogen redistribution, showing the individual catalytic reactions involved.

1.2.1. Key Definitions

In *hydrocracking*, the net reaction is *hydrogenolysis*, in which H_2 adds across a carbon-carbon (C-C) or carbon-heteroatom (C-X) single bond, resulting in its cleavage.¹³ In the hydrocracking literature, *hydrocracking* and *hydrogenolysis* are sometimes used interchangeably to refer to the overall cleavage of C-C single bonds.²⁷ However, in hydrocracking, the catalyst is bifunctional (metal/acid) and C-C bond cleavage is usually achieved via an initial dehydrogenation step to form an alkene whose protonation leads to a highly reactive carbenium ion. In contrast, hydrogenolysis refers specifically to the C-C bond cleavage that occurs when an alkane interacts directly with a hydrogen-covered metal surface.²⁷ In the following sections, we will adopt the mechanism-based definitions for the hydrocracking and hydrogenolysis of both small molecule alkanes and polyolefins.

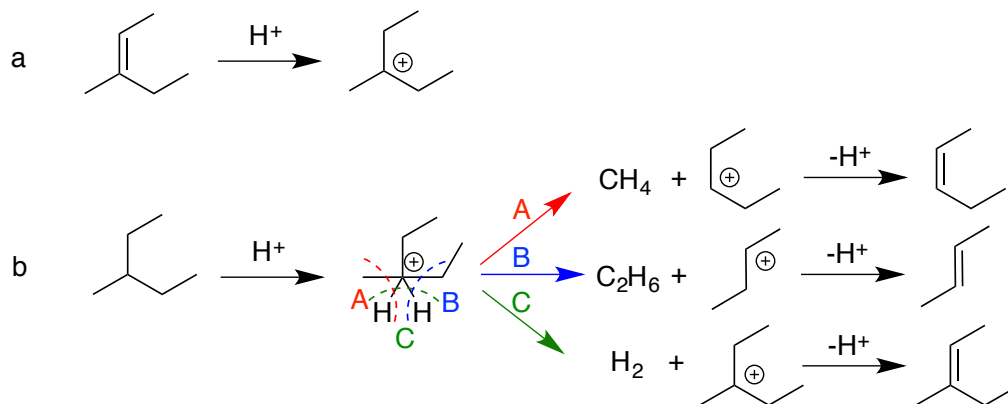
1.2.2. Mechanistic Considerations

Because the catalysts used in catalytic cracking and hydrocracking both contain acid sites, the proposed mechanisms exhibit many similarities.

1.2.2.1. Catalytic Cracking Mechanism

Our current understanding of catalytic cracking was summarized in a review by Corma and Orchillés.²⁸ The reaction is proposed to proceed in three stages: (1) initiation by formation of a carbenium ion; (2) skeletal rearrangement of the carbenium ion, leading to C-C bond scission to give an alkene and a new carbenium ion, and hydride abstraction from another alkane; (3) deprotonation of the carbenium ion to form an alkene.²⁸

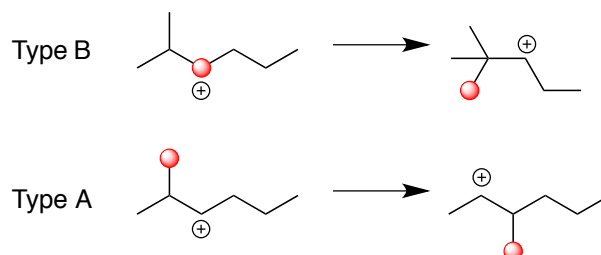
In the initiation step starting from an alkene, a Brønsted acid site (BAS) protonates an alkene to form a tri-coordinate carbenium ion (**Scheme 1.3a**). If the reactant is an alkane, the initiation step is widely believed to be catalyzed by BAS. The first carbocation is formed by the reaction with a BAS at a C-H bond to give H₂ and a carbenium ion. Haag and Dessau suggested that alkane cracking can also be initiated by reaction with a BAS at a C-C bond, initially forming a five-coordinate carbonium ion whose protolytic cracking gives either an alkane or H₂, and a carbenium ion (**Scheme 1.3b**). Formation of carbenium ions has also been proposed to occur directly, by abstraction of hydride ions from alkanes by Lewis acid sites (LAS).^{28,29}



Scheme 1.3. (a) Protonation of 3-methyl-2-pentene to give a tri-coordinate carbenium ion and (b) protolytic cracking of 3-methylpentane and *n*-hexane via a penta-coordinate carbonium ion.²⁸

Carbenium ions can undergo either type A or type B isomerization, **Scheme 1.4**. The former, being faster, involves classical alkyl and hydride shifts and results in changes in the

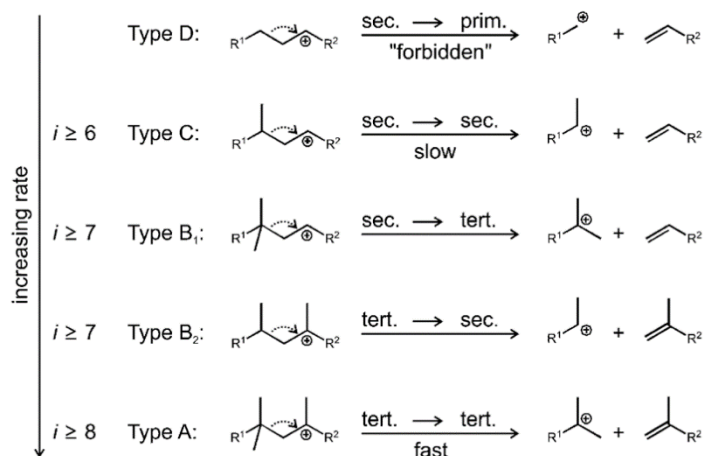
position of branches but not their number. The latter changes the number of branches via protonated cyclopropane intermediates.^{28,30}



Scheme 1.4. Type A and B isomerization. The red circles indicate the carbon atoms that undergo skeletal isomerization.

After possibly multiple isomerization events, the carbenium ions undergo various β -scission reactions. They are classified as Types A, B, C, or D, with reaction rates decreasing in this order, due to the relative stabilities of the carbenium ions (**Scheme 1.5**). Type A β -scission requires a tertiary carbenium ion with three branches in an α,γ,γ -arrangement; heterolytic C-C bond cleavage leads to a disubstituted alkene and a new tertiary carbenium ion. A Type B β -scission requires a secondary carbenium ion whose cleavage gives a tertiary carbenium (Type B₁), or vice-versa (Type B₂). Both B-types require two branches, in either the γ,γ - (for B₁) or α,γ - (for B₂) positions. Less common Type C and D scissions involve the reaction or formation of highly unstable primary carbenium ions. In these cases, the carbenium ions may undergo rearrangement to a more favorable configuration for β -scission faster than they undergo C-C bond cleavage.²⁷ While polyolefins have more than enough carbon atoms

to undergo any of these scission reactions, their branch frequency and pattern will influence the rates of β -scission under hydrocracking conditions.

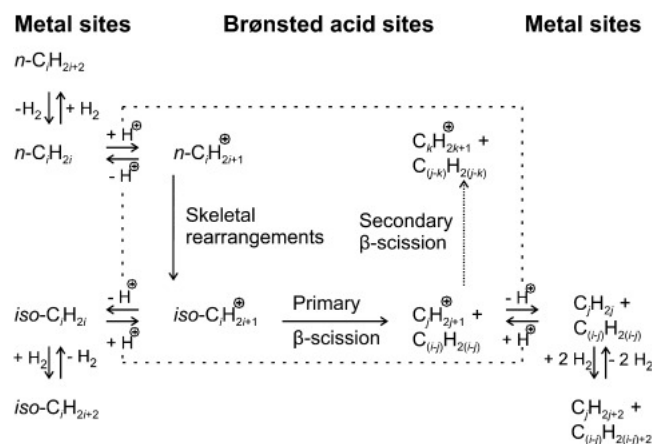


Scheme 1.5. Classification of β -scission reactions for carbenium ions (the value of i refers to the minimum number of carbon atoms required).²⁷

Another proposed reaction in catalytic cracking is hydride abstraction from an alkane by a carbenium ion. This may be the dominant pathway for producing carbenium ions on new alkane chains, considering the slow rate of carbenium ion formation via alkane protonation by BAS. Carbenium ions desorb from BAS by re-forming alkenes, or from LAS by re-forming alkanes.²⁸ If multiple C-C bond scissions occur on a single alkane chain, the major products of catalytic cracking will be alkenes. However, cyclization and aromatization, via hydrogen transfer, can also be acid-catalyzed.²⁶ This aspect will be discussed in **section 1.3**.

1.2.2.2. Bifunctional Hydrocracking Mechanism

The classical alkane hydrocracking mechanism, shown in **Scheme 1.6**, was summarized by Weitkamp.²⁷ The acid-catalyzed steps are similar to those in catalytic cracking. Alkane hydrocracking involves the following sequence of steps: (1) alkane dehydrogenation on metal sites, leading to release of an alkene; (2) diffusion of the alkene to an adjacent Brønsted acid site, where its protonation yields a highly reactive carbenium ion; (3) skeletal isomerization of the carbenium ion, leading to C-C bond scission to give an alkene and a new carbenium ion; (4) deprotonation of the carbenium ion to generate a new alkene; and (5) diffusion of both alkenes to metal sites, where they are hydrogenated to the corresponding alkanes.



Scheme 1.6. Classical mechanism for hydrocracking of n-alkanes on a bifunctional catalyst with metal sites to catalyze alkane dehydrogenation/hydrogenation and Brønsted acid sites to catalyze alkene skeletal isomerization leading to C-C bond cleavage.²⁷

1.2.3. Metal-Acid Balance (MAB)

1.2.3.1. Influence on Hydrocracking Activity

According to the bifunctional mechanism outlined above, the overall reaction depends on the ready availability of both metal and acid sites. Bifunctional catalysts are therefore optimized for their metal-to-acid site balance, which is commonly achieved by adjusting the n_M/n_A ratio. Typically, the cracking activity per acid site (turnover frequency, TOF) increases with this ratio until it reaches a plateau, **Figure 1.1**. In the plateau region, the (de)hydrogenation reactions are quasi-equilibrated on the metal sites, such that the rate is controlled solely by the number of acid sites. This is called the “ideal hydrocracking region”.

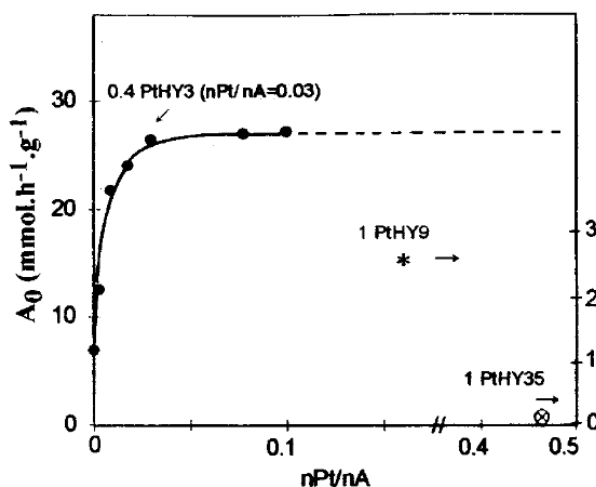


Figure 1.1. MAB dependence of the initial activity (A_0 , normalized by total catalyst mass) for *n*-decane hydrocracking catalyzed by Pt/HY zeolite, at 200 °C. MAB is represented by the ratio of the number of accessible Pt atoms to the number of acid sites (n_{Pt}/n_A). The data labeled PtHY3 were recorded for a constant number of acid sites. Acidity decreases in the order HY3 > HY9 > HY35.³¹

1.2.3.2. Influence on Hydrocracking Selectivity

For longer hydrocarbons (C_iH_{2i+2} , $i > 8$), MAB also influences the regioselectivity of C-C bond cleavage. Low n_{Pt}/n_A ratios result in mostly C_3 - C_6 products, while high ratios give a random distribution of hydrocarbons across the entire range of carbon numbers, **Figure 1.2**.

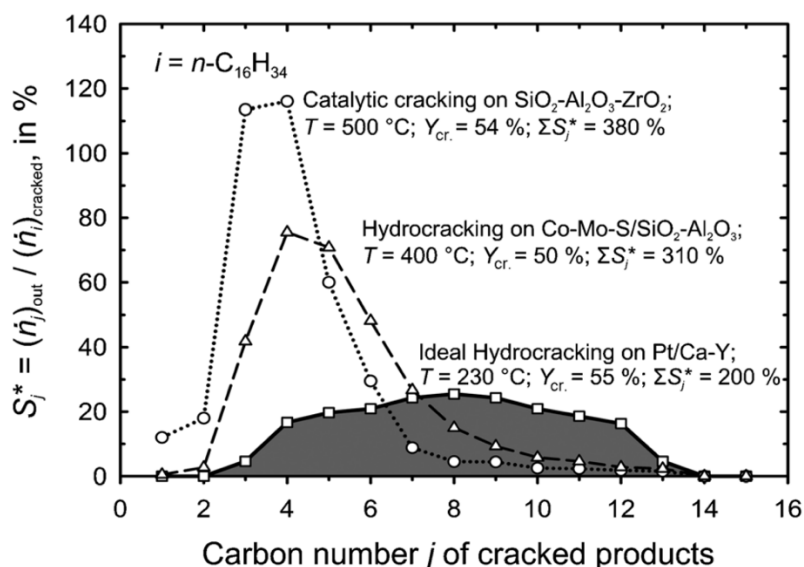


Figure 1.2. Molar distribution of hydrocarbon products from the catalytic cracking or hydrocracking of *n*-hexadecane. The results are typical for catalysts with no hydrogenating component ($SiO_2-Al_2O_3-ZrO_2$), a weak hydrogenating component (sulfided $Co-Mo-S/SiO_2-Al_2O_3$), or a strong hydrogenating component ($Pt/Ca-Y$ zeolite), at similar yields of cracked products ($Y_{cr.} \approx 50 \%$). S_j^* is the modified cracking selectivity, defined as moles of hydrocarbons with j carbon atoms per mol *n*-hexadecane converted.²⁷

The difference in regioselectivity is a consequence of metal-catalyzed dehydrogenation/hydrogenation. A high MAB leads to a high alkene concentration, resulting

in competitive adsorption of alkenes on the acid sites. Consequently, C-C bond scission tends to be more random for a high-MAB catalyst, resulting in a bell-shaped distribution of hydrocarbon chain lengths. Conversely, a low-MAB catalyst generates more C₃-C₆ hydrocarbons because the low alkene concentration results in more persistent alkene-acid site interactions, allowing for consecutive C-C bond scission events on the same hydrocarbon chain.

1.2.4. Examples of Polyolefin Catalytic Cracking

The first report of catalytic cracking of a PO by a solid acid dates to the 1980s.³² Using silica-alumina as the catalyst at 480 °C, PP was converted predominantly to alkenes (44 wt%), *iso*-alkanes (35 wt%), and aromatics (11 wt%). Since then, many such studies have appeared. Several reviews summarize the effect of catalyst variables (acidity, pore structure), reaction conditions, reactor type, reaction kinetics and mechanisms.^{22,26,33,34} Nevertheless, some of these topics are mentioned below for comparison purposes. In the 1990s, the use of MgCl₂×AlCl₃ was first reported in the catalytic cracking of PE at 370 °C, giving mostly gases (88 wt%) as products.³⁵ A couple of examples of the use of other salts as well as chloroaluminate ionic liquids have since been summarized in a review.²⁶

More recently, lower temperatures have been used in the catalytic cracking of POs to target more valuable products. Metal-free H-MFI zeolite (0.4 g, Si/Al = 40) was reported to crack PE (1 g, M_w = 4,000 g/mol, $\bar{D}$ = 1.9) to C₃-C₇ (37 wt%, mostly *n*-alkanes, *iso*-alkanes, *iso*-alkene, alkenes) in 17 h at 200 °C.³⁶ More than 90 wt% of the polymer was converted, as

judged by the mass of residual solid hydrocarbon. However, the mass balance was poor: 50 wt% of the total mass was not collected.

Selectivity for desired carbon numbers and hydrocarbon product types can be better controlled. The use of ZSM-5 nanosheets (0.1 g, Si/Al = 21) was reported to convert PE (0.5 g, described as having an average molecular weight 150,000 g/mol without indicating M_n , M_w or D) in a quartz tube at 280 °C under flowing H₂ into C₁-C₇ hydrocarbons (75 wt%).³⁷ Among these products, the majority (84 wt%) were C₃-C₆ alkenes. The amount of coke was undetectable.

Catalytic cracking can be coupled with other reactions to make desired products selectively at even lower temperatures. The use of a chloroaluminate ionic liquid [C₄Py]Cl-AlCl₃ ([C₄Py]Cl:AlCl₃ molar ratio 1:2, 3 mmol) catalyst with tert-butyl chloride (TBC, 0.05 mmol, 0.005 g) as initiator, dissolved in 3 mL CH₂Cl₂, was reported to fully convert a low molecular-weight PE (0.2 g, M_w = 4,000 g/mol, D = 1.9) by its reaction with isopentane (0.8 g) to liquid *iso*-alkanes (C₄ to C₃₀, ~200 wt% relative to starting PE) at 70 °C.³⁸

1.2.5. Examples of Polyolefin Hydrocracking

Hydrocracking of POs first began to attract attention in the 1990s. In contrast to pyrolysis¹⁴ and catalytic cracking³⁹ approaches, typically conducted at temperatures above 400 °C and producing complex hydrocarbon mixtures including alkenes, aromatics, and alkanes, PO hydrocracking is typically performed at lower temperatures and generates highly saturated hydrocarbon liquids. These liquids can be used directly as transportation fuels or as fuel oil. A review described the effects of variables such as temperature, H₂ pressure, reaction time,

presence and type of catalyst, and the nature of the plastic feed on the hydrocracking of both virgin and waste plastic materials.⁴⁰

In early studies, PO hydrocracking was generally conducted at 350-450 °C with 20-150 bar H₂ (pressure measured at room temperature), similar to the hydrocracking of light alkanes. The hydrocracking catalysts were similar too: metal NPs dispersed on an acidic support. The supports were often amorphous oxides such as silica-alumina, crystalline zeolites such as HZSM-5, or acid-modified oxides such as sulfated zirconia. The hydrogenating component was a noble metal (Pd or Pt), or a non-noble metal from group 6 (Mo or W), group 9 (Co), or group 10 (Ni). Intrinsic catalytic activity was not necessarily apparent at the high reaction temperatures, where mass transport can limit the overall reaction rate. Furthermore, the catalysts experienced significant coke build-up, leading to rapid deactivation.⁴¹ Therefore, more recent studies have focused on reactions conducted at lower temperatures. An explosion of recent interest has resulted in numerous new catalyst designs.

As polymer upcycling has attracted more interest in recent years, researchers have started to investigate hydrocracking at even lower temperatures (200-300 °C), and with more advanced characterization of the catalysts and reaction products. The current state-of-the-art for an efficient bifunctional catalyst or a mixture of catalysts involves converting a polyolefin (ca. 10× the total catalyst mass) into mostly *iso*-alkanes (C₄-C₃₀) within several hours at ca. 250 °C under ca. 20 bar H₂.

For example, the hydrocracking of LDPE ($M_w = 150,000 \text{ g mol}^{-1}$, $\bar{D}$ not specified) was reported to be catalyzed by either Pt/USY or Pt/HBeta (10 wt% relative to LDPE), at 275-330 °C under 20 bar H₂.⁴² C₄-C₆ *iso*-alkanes were formed in high yields within 1 h, resulting in

>95 wt% of the polymer being recovered as either gas- or liquid-phase hydrocarbons. At a similar temperature (250 °C) and H₂ pressure (30 bar), the conversion of LDPE (2.0 g, $M_w = 250,000 \text{ g mol}^{-1}$, $\bar{D}$ not specified) was reported to be catalyzed by a physical mixture of Pt/WO₃/ZrO₂ (0.1 g) and HY zeolite (0.1 g) to predominantly *iso*-alkanes (85 wt%) within 2 h, but the products were in the gasoline (C₅-C₁₂) and diesel (C₉-C₂₂) ranges.⁴³

Highly dispersed MoS_x-HBeta (0.1 g) was investigated as a noble metal-free catalyst to hydrocrack various polyolefins.⁴⁴ After 16 h at 180 °C with a low molecular weight PE wax ($M_w = 3,000 \text{ g mol}^{-1}$, $\bar{D}$ not specified), a catalyst loading of 20 wt% relative to polymer, and 25 bar H₂, branched alkanes (C₄-C₁₂) were recovered in 96 wt% yield. At 250 °C under 20 bar H₂, the reactions of HDPE, LLDPE, LDPE, and PP (1 g, all with $M_w = 300,000 \text{ g mol}^{-1}$, $\bar{D}$ not specified) gave branched liquid alkanes (mostly C₄-C₁₆, isomers not specified) in >85 wt% yield after 6 h.

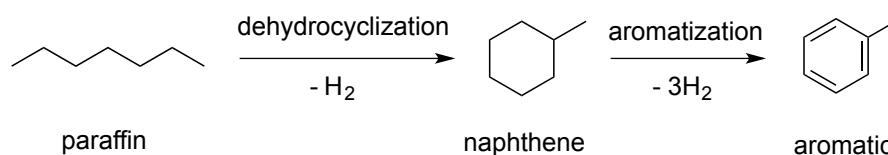
PP hydrocracking was reported to be catalyzed by Ru, Ni, or Pt nanoparticles supported on anatase prepared by a sol-gel route (Ru, Ni, or Pt/TiO₂-A-SG, 0.07 metal/nm²).⁴⁵ At 260 °C, the Ru/TiO₂-A-SG catalyst converted PP (isotactic, $M_w \sim 250,000 \text{ g/mol}$, $\bar{D} = 3.7$) about three times faster than Ru/CeO₂, when normalized by surface Ru sites. In addition, Ru/TiO₂-A-SG showed lower selectivity towards undesired CH₄ ($S_{\text{CH}_4} = 3 \text{ wt\%}$) compared to Ru/CeO₂ (21 wt%), slightly higher selectivity towards desired liquid products (C₆₋₄₀, $S_{\text{liquid}} = 78 \text{ wt\%}$) compared to Ru/CeO₂ (72 wt%), and higher isomerization activity (62% of C₁₀ products are *iso*-alkanes), compared to Ru/CeO₂ (40%).

1.3. Hydrogen Redistribution of Polyolefins

1.3.1. Mechanism of Aromatics Formation

1.3.1.1. Catalytic Reforming

Monocyclic aromatic hydrocarbons such as benzene, toluene, and xylenes (the mixture known as BTX) are important chemical building blocks. In 2020, the global demand for BTX was ca. 108 million metric tons (MMT), and it is projected to increase at an annual growth rate of 5% in coming years.⁴⁶ The conventional route for producing BTX involves catalytic reforming of naphtha (which consists of mostly C₆-C₁₀ alkanes), typically at ca. 500 °C. The major reactions include alkanes dehydrocyclization to cycloalkanes, and the further dehydrogenation of the cycloalkanes to aromatics. Both reactions generate H₂ as a byproduct, **Scheme 1.7**. Since the use of polyolefins to make aromatics shares much in common with these processes, we first briefly review what is known about the catalytic reactions involving smaller hydrocarbons.

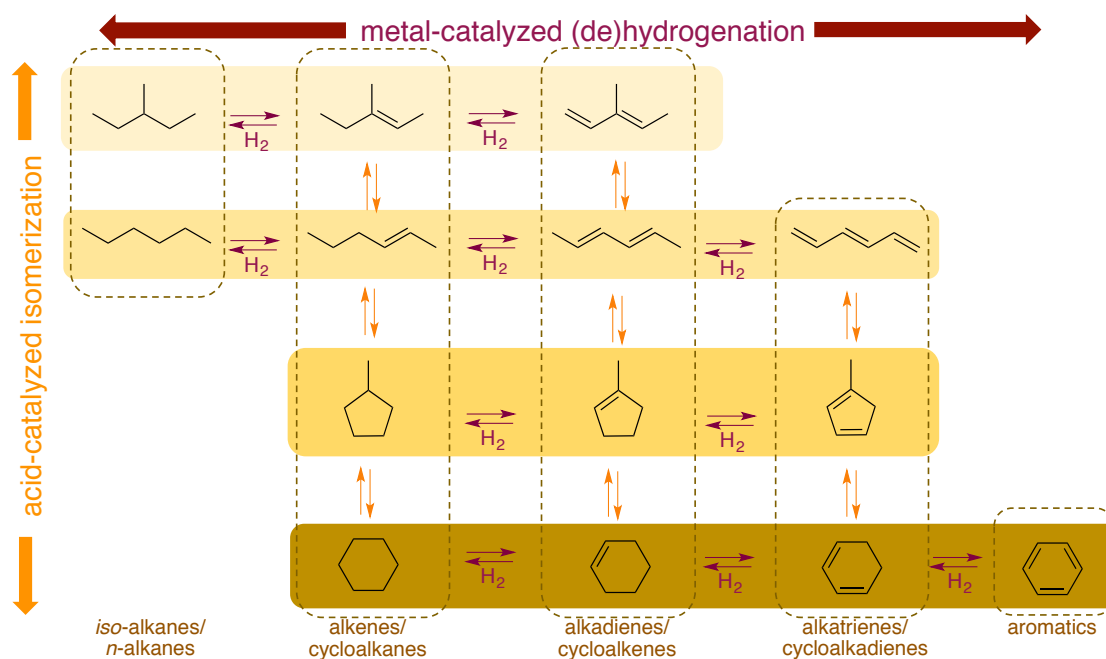


Scheme 1.7. The two main reactions in naphtha catalytic reforming.

Traditional catalysts for naphtha reforming are bifunctional, consisting of Pt nanoparticles supported on an acidic alumina.⁴⁷ Similar to the hydrocracking mechanism, the metal sites are proposed to catalyze (de)hydrogenation, while the acid sites are proposed to catalyze skeletal transformations, including isomerization, cyclization of an alkene to cycloalkane, and C-C bond scission (**Scheme 1.8**). Cyclization is a key reaction because it leads to the formation of

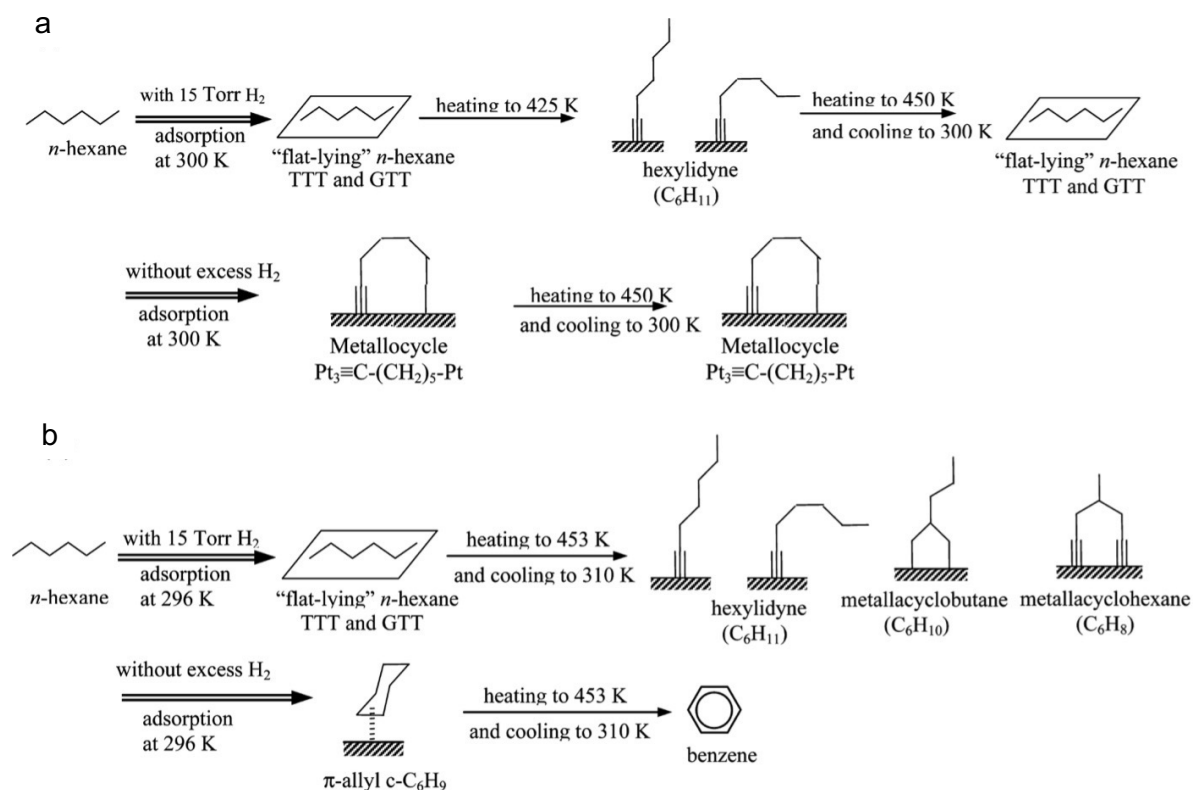
aromatic rings. Initially, the cyclization of an alkene or alkadiene can lead to either a five- or six-membered ring.⁴⁸ Although only the latter can be dehydrogenated to give an aromatic directly, the ring expansion of five-membered rings is believed to be rapid under reforming conditions.^{49–54}

Skeletal isomerization of *n*-alkanes is desirable in catalytic reforming because *iso*-alkanes have higher octane numbers, which is important in gasoline. However, C-C bond scission is undesirable, because it generates light gases which have much lower value. In general, catalytic reaction rates decrease in the following order: (de)hydrogenation > isomerization > dehydrocyclization ~ C-C bond scission.



Scheme 1.8. Proposed reaction mechanism for bifunctional catalytic reforming, involving alkane (de)hydrogenation, isomerization, and dehydrocyclization. Redrawn from ref 55.

Monofunctional catalysts are also used commercially in catalytic reforming. For example, the Aromax[®] catalyst, Pt/KL (where KL is potassium-exchanged zeolite L), converts *n*-hexane to benzene selectively at ca. 500 °C.⁵⁶ The non-acidic nature and specific pore geometry of KL contributes to the selectivity, as well as to resistance to coke formation and Pt sintering.^{57–60} Metal sites on single-crystal surfaces have been observed to catalyze isomerization and cyclization of *n*-alkanes, in the absence of acidity.^{61,62} For example, adsorption geometries and surface reactions of *n*-hexane on Pt(100) and Pt(111) surfaces were investigated using sum frequency generation vibrational spectroscopy. Initially, *n*-hexane adsorbs in a “flat-lying” conformation (**Scheme 1.9**). Increasing the surface temperature causes dehydrogenation of the “flat-lying” species to hexylidyne. In the absence of low pressure H₂, several other adsorbates can coexist: a metallacyclic Pt₃≡C-(CH₂)₅-Pt on Pt(100) and a π-allylic form of cyclo-C₆H₉ on Pt(111). The latter is significant because it leads directly to benzene.

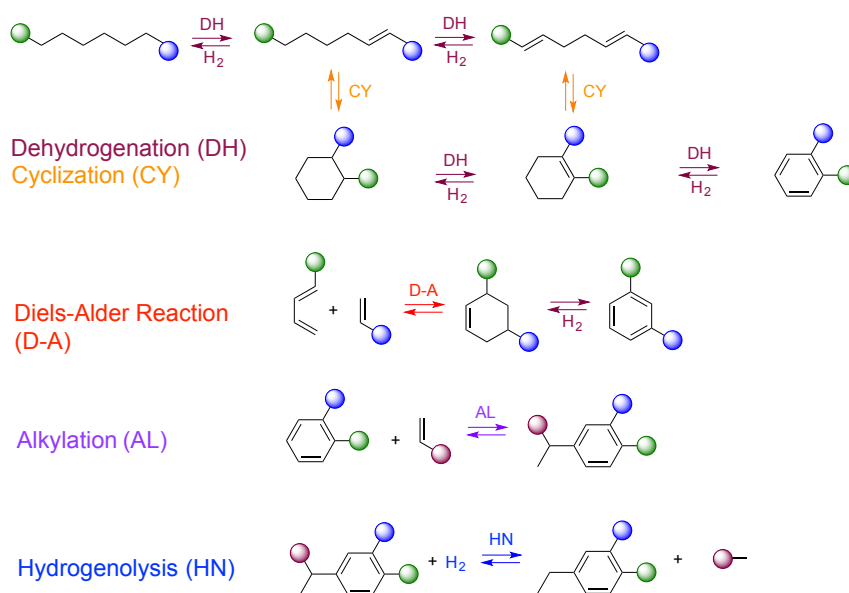


Scheme 1.9. Surface species observed on (a) Pt(100); and (b) Pt (111), both exposed to 1.5 Torr *n*-hexane in the presence or absence of H₂ (15 Torr).⁶²

1.3.1.2. Polyolefin Conversion to Molecular Alkylbenzenes

Because various hydrocarbon types, including alkenes, isolated and conjugated alkadienes, can coexist during PO depolymerization, there are two possible mechanisms for aromatic formation. The first proposes that a benzene ring is formed on an alkyl chain derived from the cracking of PE by cyclization of an alkene or alkadiene, similar to the mechanism for small hydrocarbons in **Scheme 1.8**. Another possibility is that an alkene reacts with a alkadiene (both derived from PE cracking) via a Diels-Alder reaction, forming an unsaturated ring as a cycloaddition product.⁶³

In principle, aromatic ring formation can occur on either long or short alkyl chains, depending on the choice of catalyst and reaction conditions. In addition, aromatic rings can be alkylated by alkenes present in the reaction mixture and alkyl substituents on aromatic rings can be shortened by C-C bond scission, yielding alkylaromatics with a range of molecular weights, **Scheme 1.10**.



Scheme 1.10. Some of the proposed reaction pathways in the conversion of polyethylene to alkylaromatics. The colored circles represent alkyl chains of varying lengths.

1.3.2. Monofunctional Catalysts

A preliminary techno-economic analysis showed that producing gasoline from POs through hydrocracking is not likely to be profitable at a small plant scale (e.g., 5 kton/year).⁶⁴ Unfortunately, plastic waste is highly dispersed, and its collection, sorting and transportation

to a processing site incurs significant costs. Aromatics may be more attractive depolymerization targets due to their higher intrinsic value relative to fuels.⁶⁵

Unlike naphtha catalytic reforming, which employs monofunctional metal catalysts or metal-acid bifunctional catalysts, the most commonly reported catalysts for producing aromatics from alkenes are solid acid catalysts, particularly zeolites. Zeolites are known to effectively generate small aromatics (C₆-C₈, BTX) by catalytic cracking of PE and PP under an inert atmosphere at temperatures between 400 and 500 °C. Their activity and aromatic selectivity are attributed to their strong acidity and shape-selective micropores, respectively.²⁶

Catalyst acidity is important in maximizing the aromatic yield in depolymerization, presumably via a mechanism similar to that described in **Scheme 1.8**, but without the metal function. For example, decreasing the acidity of ZSM-5 (1.5 g), by increasing the SiO₂/Al₂O₃ ratio (from 23 to 80) or NaOH treatment, demonstrated a reduction in aromatic selectivity in the liquid products obtained from catalytic cracking of LDPE (10.0 g, molecular weight unspecified) to decrease at ca. 450 °C under N₂.⁶⁶

An amorphous, mesoporous silica-alumina (SA, 0.200 g) was also used to convert a low molecular weight PE (0.130 g, $M_w = 3.52 \times 10^3$ g/mol, $D = 1.9$) to alkylaromatics (carbon numbers unspecified) at 280 °C under Ar.⁶⁷ The silica content (from 1.5 to 30 wt%) was varied while maintaining a similar surface area (ca. 200 m²/g) and mesoporous diameter (ca. 10 nm). Both the rate of chain scission and the formation of aromatics were observed to correlate with the number of BAS. The fraction of polyaromatic products also increased with the number of BAS, measured at similar aromatics content (ratios of aromatic protons to total protons, $H_{\text{arom}}/H_{\text{total}}$). SA produced similar amounts of CHCl₃-soluble hydrocarbons, similar $H_{\text{arom}}/H_{\text{total}}$

in these products, and similar molecular weight distribution for the total hydrocarbons (as evidenced by GPC-RI) compared to Pt/Al₂O₃, although the molecular weight distribution of the aromatic products was not necessarily the same as for other types of hydrocarbons. Nevertheless, this study indicated that strongly acidic catalyst can also produce significant amounts of aromatics, similar to a weakly acidic catalyst with a strong dehydrogenation function.

The zeolite microstructure also plays a role in determining the carbon number distribution of the aromatic products. For example, ZSM-5 with a 10-membered ring channels whose pore diameter is ca. 0.5 nm was been reported to produce primarily C₇-C₈ aromatics from the catalytic cracking of LDPE (viscosity-average molecular weight, $M_w = 298,000$ g/mol, $D = 4.6$) at 480 °C under N₂, while C₁₀-C₁₁ aromatics were the main products from HY,⁶⁸ whose 12-membered ring channels have a diameter of 0.7 nm.⁶⁹

Activated carbon was reported to convert PE in a fixed bed-flow reactor at 526 °C. Molten PE (viscosity-average molecular weight, $M_v = 1.3 \times 10^4$ g/mol, D unspecified) was fed through a capillary under N₂ pressure. In addition to alkanes (C₁-C₁₀, 56 wt%) and alkenes (C₂-C₈, 6 wt%), a significant amount of BTX aromatics (37 wt%) was formed. Under the same conditions, the aromatic yield was only 10 wt% when silica-alumina (13.5% Al₂O₃) was the catalyst.⁷⁰ Due to the low yield of branched alkanes, the authors proposed that the reaction mechanism over activated carbon involved radicals rather than carbocations.

Treating carbon derived from wood chips with H₃PO₄ was demonstrated to enhance the formation of aromatics in a dual-stage fixed-bed reactor. In the initial stage, PE (10 g, molecular weight unspecified) was pyrolyzed at 550 °C under N₂, becoming alkanes and

alkenes (carbon number unspecified). In the second stage, these compounds were exposed to the catalyst (4 g) at 600 °C. The aromatic (C₇-C₁₀) yield of the products increased from 0 to 24 wt% when the phosphorus-to-wood chip (carbon source) mass fraction (P/WC) increased from 0 to 40 %.⁷¹

1.3.3. Metal-Assisted Hydrogen Redistribution

1.3.3.1. Making Methylated Aromatics

The transformation of polyolefins to a mixture of small molecule alkanes and aromatics is a disproportionation, requiring a redistribution of hydrogen. Acid sites alone are typically not efficient in catalyzing (de)hydrogenation, therefore metal sites are usually involved. For example, Pt/Al₂O₃ is used in naphtha catalytic reforming to make BTX, while Ga/ZSM-5 is the catalyst in the Cyclar process which converts LPG (liquefied petroleum gas, a mixture of propane and butanes) into BTX.^{72,73}

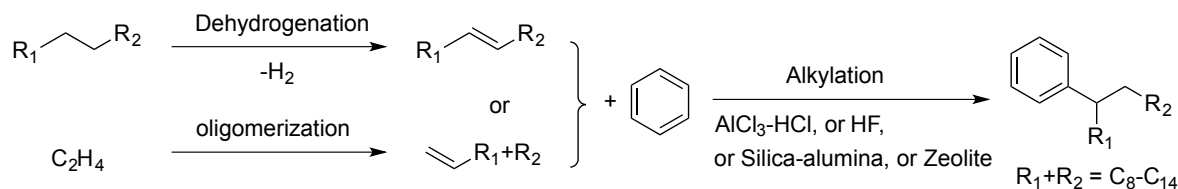
Several studies have investigated the use of supported metal catalysts for the conversion of PE to small molecule aromatics in fixed-bed tubular reactors under a continuous flow of inert gas (e.g., He or N₂) at ca. 500 °C. Molten PE was fed through a capillary under inert gas. The effect of metal addition, e.g., Pt, Fe, and Mo, to supports like activated carbon, alumina, and silica-alumina gave higher activity compared with corresponding support alone in the conversion of PE ($M_v = 1.3 \times 10^4$ g/mol, D unspecified) to aromatics at 526 °C.⁷⁴ Use of a H-gallosilicate resulted in higher selectivity to aromatics (BTX, 60 wt%) from LDPE (molecular weight not specified), compared to just 34 wt% with Al-containing HZSM-5 at 525 °C ($W/F = 0.12$ h, where W is the mass of catalyst, and F is the mass flow rate of molten LDPE through

an inlet capillary).⁷⁵ Ion-exchanging HZSM-11 with Zn^{2+} resulted in aromatics ($\text{C}_6\text{-C}_9$) in 53 wt% yield at 500 °C, compared to 27 wt% with HZSM-5.⁷⁶ Similarly, Pt/ZSM-5 (1.4 wt% Pt, Si/Al = 38) was reported to reduce the onset temperature for forming BTX aromatics from 310 to 270 °C compared with the zeolite alone in the reaction of PE ($M_w = 4,000$ g/mol, $D = 2.4$) under flowing He, where a physical mixture ($m_{\text{PE}}/m_{\text{catalyst}} = 1:6$) of PE and catalyst was loaded into a stainless cup inside the micropyrolyzer.⁷⁷

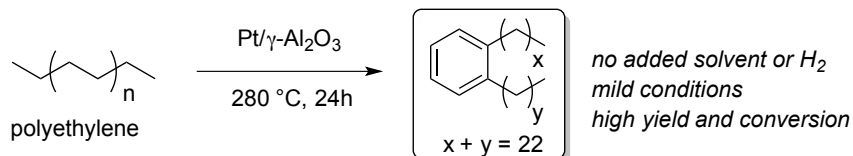
1.3.3.2. Making Long-Chain Alkylaromatics

Alkylbenzenes with alkyl chains considerably longer than methyl (surfactant-range linear alkylbenzenes, or LABs, with carbon numbers $\text{C}_{16}\text{-C}_{22}$) are the direct precursors of linear alkylbenzene sulfonates, used commercially as biodegradable surfactants.⁷⁸ Global LAB production was 1.4 million tons in 2018, with demand estimated to increase at an annual rate of 4.7% from 2020 to 2027.⁷⁹ The principal synthesis route is the alkylation of petroleum-derived benzene with a petroleum-derived alkene (derived either from dehydrogenation of an alkane or, from ethylene oligomerization), in the presence of an acid catalyst ($\text{AlCl}_3\text{-HCl}$, HF, silica-alumina, or a zeolite), **Scheme 1.11a**. In other words, the method is bottom-up.^{80–83}

a Current route to linear alkylbenzene



b One-pot synthesis of linear dialkylbenzenes



Scheme 1.11. Comparison of routes to alkylbenzenes. (a) The current route to linear alkylbenzenes, i.e. the bottom-up method.⁸¹ (b) one-pot tandem process from polyethylene, i.e. top-down approach.⁸⁴

A top-down approach was devised to synthesizing long-chain dialkylaromatics, combining partial depolymerization of PE with H_2 redistribution under Ar (i.e., in the absence of external H_2) in a tandem hydrogenolysis/aromatization process.⁸⁴ **Chapter 2** of this dissertation will discuss this initial finding, with further development covered in **Chapters 3** and **4**.

1.4. Useful Definitions in Polyolefin Upcycling

Catalytic transformations of polyolefins (POs) usually involve a complex series of reactions. For example, C-C bond cleavage can occur on the main polymer chain or a side-chain, as well as on the many hydrocarbon fragments generated during the reaction. Many catalysis terms used in small molecule reactions are still useful, but can benefit from being more precisely defined when they are used to describe polymer-based reactions. In addition,

new terms are needed (see **section 1.4.2** below) to more clearly describe the extent of reaction as well as characteristics of product classes when polymers are deconstructed. In the reports of polyolefin reactions described later in this review, there are many instances of incomplete or inadequate polymer specification and/or product analysis. While we are limited to reporting the information available in published reports to-date, we offer the following guidance for future reports.

1.4.1. Relevant Terms

1.4.1.1. Polyolefin Conversion

The *conversion* (X) is the extent to which a reactant has been transformed into products. Being dimensionless, it is usually expressed as a fraction or percent. In small molecule reactions, a molar basis is usually implied. However, molar conversion is difficult to specify in reactions involving macromolecules, which have a distribution of molecular weights. In polymer upcycling, conversion is commonly defined instead as the ratio of the mass of polymer reacted to the initial charge of polymer, **eq 1.1**. Authors should affirm the mass basis for this calculation in their reports.

$$X = 100 \% * (1 - m_{\text{unreacted polymer}}/m_{\text{initial polymer charge}}) \quad (1.1)$$

For polyolefins, the operational definition in **eq 1.1** is unsatisfactory. It is virtually impossible to determine whether a polymer chain is truly unchanged, or arises from the cleavage of an even longer chain, since the molecular weights of products and reactants

overlap for at least some portion of the upcycling process. Furthermore, each polymer chain must undergo many chain cleavage events to become a small molecule product, and it is rarely defined (or even possible to define) how many such events – one, ten, one hundred – constitute the threshold for considering the chain “converted”. Consequently, polyolefin conversion is commonly calculated in terms of the ratio between the mass of insoluble hydrocarbons and the initial PO charge, **eq 1.2**.

$$X = 100 \% * (1 - m_{\text{insoluble hydrocarbons}}/m_{\text{initial polymer charge}}) \quad (1.2)$$

The assumption (usually unstated) is that insoluble hydrocarbons (or the total mass of insoluble solids less the known mass of solid catalyst) represent exclusively unreacted polyolefin. Clearly, this is not always true. Insoluble hydrocarbons also include partially depolymerized material (lower molecular weight), cross-linked material (higher molecular weight), and coke/coke precursors. Where possible, additional characterization of the hydrocarbon solids is desirable, although the low solubility of POs in general, and the challenges in accessing high temperature gel permeation chromatography (GPC) for PO molecular weight analysis, complicate this goal. In some cases, TGA can be used as a crude measure of the amount of unreacted polymer relative to other carbon-based solids. Unreacted polymer should have the same molecular weight and molecular weight distribution (requiring specification of any two of M_n , M_w , and $\bar{D}$) as the original polymer, and, where relevant (e.g., polypropylene and polystyrene), the same stereoregularity.

1.4.1.2. Yields of Upcycling Products

The *yield* (Y) refers to the amount of product obtained in a chemical reaction, often expressed as the fraction or percent of the theoretical maximum amount of product that could be obtained. Yields may be assessed *in situ* (e.g., GC or NMR yield) or determined after purification (isolated yield), and are reported on either a molar or mass basis. Molar yields (in mol%) are common in molecular chemistry, where they conveniently reflect the reaction stoichiometry. However, chemicals are priced on a mass basis, so mass yields (in wt%) can be more directly relevant to the economic viability of a process. It is essential that authors specify clearly which yield they are reporting.

In reactions involving macromolecules, where there are typically a large number of similar products, the mass yield is usually more straightforward to calculate. The yield of any one type of product or, more often, group of products, is expressed in terms of its mass relative to the initial polymer charge, **eq 1.3**.

$$Y(\text{wt}\%) = 100 \% * m_{\text{product group}}/m_{\text{initial polymer charge}} \quad (1.3)$$

Where products are complex, incompletely characterized mixtures with significant molecular weight dispersity, this operational definition is easy to implement. Molar yields are less common. Where available, they are usually calculated relative to the number of moles of monomers present in the initial charge of polymer. Of course, the hydrocarbon products may not be related in a simple way to the original monomer structure of the polyolefin. **Eq 1.3** is less useful for some types of reaction, including alkane metathesis and oxidation, since the

total product yield may exceed 100 wt% by a significant amount because the mass of co-reactants (e.g., alkanes or O₂) is incorporated into the products.

For alkane metathesis and oxidation, the carbon mass yield is a more useful metric because it reflects the efficiency of carbon incorporation from the polymer into the products. The carbon mass yield of one type of products (or group of products) is expressed in the terms of their polymer-derived carbon mass relative to the carbon mass of the initial polymer charge, **eq 1.4**.

$$Y (\text{wt}\%) = 100 \% * (m_{\text{products carbon}} - m_{\text{co-reactants carbon}}) / m_{\text{initial charge of polymer carbon}} \quad (1.4)$$

If some carbon in the products is derived from a co-reactant instead of the polymer, that carbon should not be counted in the carbon mass yield (although it may be challenging to distinguish carbon based on its origin).

Eq 1.4 does not provide useful information in hydrogenolysis and hydrocracking, because the co-reactant (H₂) does not introduce additional carbon, and the wt% carbon in the products is very similar to the polymer.

Regardless of the method chosen for reporting yields, it is important to assess and report the *mass balance*, i.e., the sum of the masses for all products compared to the initial masses of reactants (polymer and, where relevant, non-polymer). In some reports, an inability to recover one of the product phases (typically, gases or solids) led the authors to assume that the unrecovered phase represents all of the missing mass, and report a mass balance of exactly 100 %. Such assumptions must be stated explicitly.

Often, polyolefin reactions are simply characterized in terms of phase yields: gas, solid, liquid. The definitions of each phase can overlap, depending on the recovery method used for each product phase type. For example, C₄-C₆ hydrocarbons may appear in the gas or liquid phases, or be distributed between them, depending on the conditions (temperature, pressure). The difference between liquid and solid is obviously temperature-dependent for heavier hydrocarbons. Liquid phase definitions based on extraction depend on the nature of the extracting solvent (e.g., CH₂Cl₂) and its temperature, as well as the nature of the hydrocarbon products (e.g., oxygenates are more soluble than hydrocarbons without heteroatoms). Sometimes, a portion of the unreacted polymer is soluble, resulting in an apparent non-zero initial conversion. In all cases, the experimental methods should describe the product recovery and phase definitions precisely.

1.4.1.3. Selectivities to Upcycling Products

In molecular reactions, the *selectivity* (*S*) refers to a molar ratio of different products formed from a given reactant. Here too, defining selectivity is not straightforward for macromolecular reactions since the product mixture is often complex, consisting of multiple product types with overlapping molecular weight distributions. An operational definition for selectivity is the mass ratio relating one type of product (or, more likely, group of products) to all products, **eq 1.5**. It is essential to specify the mass basis, and to indicate what the total amount refers to. For example, the CH₄ selectivity could refer either to the mass of methane relative to the mass of all products, or to the mass of methane relative to all gas products.

$$S = 100\% * (m_{\text{products}}/m_{\text{total}}) \quad (1.5)$$

Clearly, the selectivity is less accurate when the mass balance is poor (i.e., when a significant fraction of the polymer mass is unaccounted for), which is not uncommon in reactions of polyolefins. Just as in molecular transformations, it is essential to compare selectivities for different catalysts and/or different reaction conditions at similar levels of conversion. Comparisons at constant reaction times are potentially misleading, since selectivity can change greatly as a function of conversion.

Selectivity for a particular type of product, such as the selectivity for aromatic compounds among all hydrocarbon products, or the selectivity for hydrocarbons within a certain molecular weight range, such as gasoline-range compounds (C₅-C₁₂) is frequently reported. Another commonly reported selectivity is based on phase yields (gas, liquid, solid products). As described in **section 1.4.1.2**, this requires a clear description of the recovery method for each phase, since some products can appear in different phases, or in more than one phase, depending on the method.

1.4.2. Metrics Specifically for Describing Polyolefin Upcycling

1.4.2.1. Number of C-C Bond Scission Events

In simple reactions of small molecules, the product yield is related directly to the extent of reaction. The relationship is more complex for the partial depolymerization of macromolecules. For example, in the random depolymerization of POs, the mass yield of intermediate-length hydrocarbon chains (for example, C₁₃-C₂₀ as shown in **Figure 1.3**)

increases initially, then decreases as the reaction proceeds. This non-monotonic behavior occurs because POs tend to break first into relatively long-chain hydrocarbons, which are then further converted to shorter chains. Thus the yield of hydrocarbons in any particular molecular weight range is non-linear with respect to the extent of reaction, and its use in activity comparisons can be misleading.

Simply combining the mass yields of different product types does not resolve the problem. It assumes that the total mass yield (which is equal to the PO conversion, if the mass balance is complete) increases until the reaction is complete. However, when the total product yield (or PO conversion) reaches 100 %, depolymerization usually continues, as intermediate products undergo further depolymerization. After this point, the total product yield (or PO conversion) remains constant at 100 %, and is no longer meaningful for describing the extent of reaction.

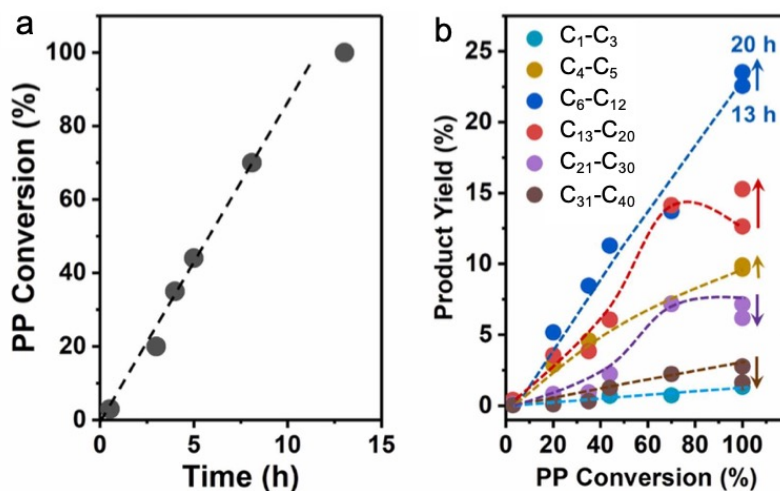


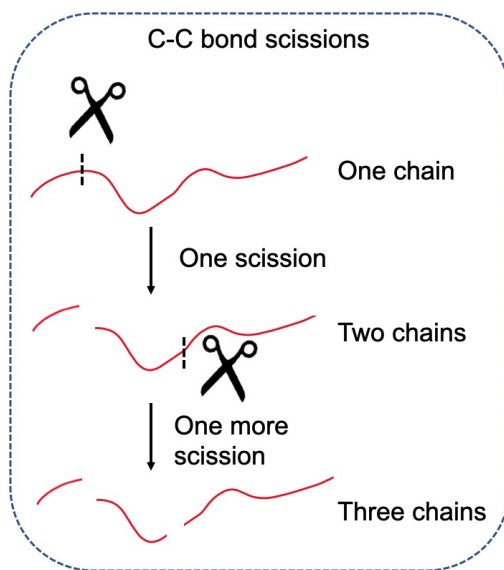
Figure 1.3. Time-dependence of PP hydrocracking: (a) increase in PP conversion with time; and (b) variations in the yields of various hydrocarbon product groups with conversion. Dual

data points at 100 % PP conversion were measured at two reaction times (13 and 20 h), where the colored arrows represent increasing reaction time.⁴⁵

An alternative, and potentially more precise, metric for assessing the extent of depolymerization is the *number of C-C bond scission events* ($n_{\text{C-C scission}}$).^{41,84,85} Each such event generates one new hydrocarbon chain (**Scheme 1.12**), such that the total number of C-C bond scission events ($n_{\text{C-C scission}}$) is given by eq 1.6:

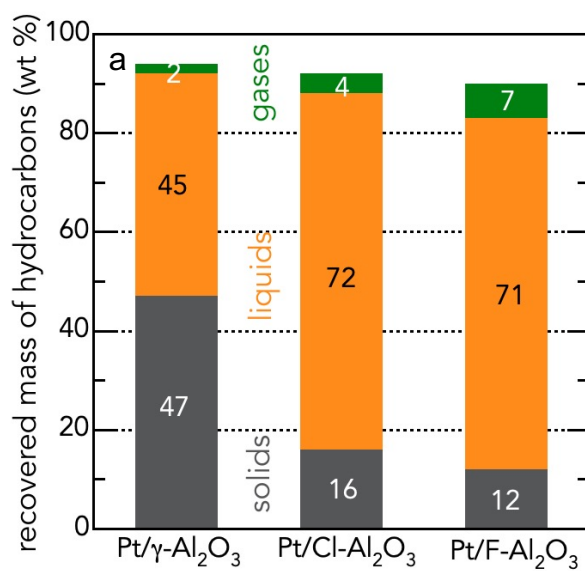
$$n_{\text{C-C scission}} = N(t) - N(0) \quad (1.6)$$

where $N(0)$ and $N(t)$ represent the total number of polymer chains (and chain fragments) present in a batch reactor at time 0 and time t , respectively.



Scheme 1.12. Each C-C bond scission event generates one new hydrocarbon chain, making the number of events equal to the number of new chains.

The value of $n_{\text{C-C scission}}$ is better insight into intrinsic catalytic activity than either conversion or product yield. For example, **Figure 1.4a** shows that using liquid yields makes Pt/ γ -Al₂O₃ appear to be much less active as a catalyst for polyethylene depolymerization than either Pt/Cl-Al₂O₃ and Pt/F-Al₂O₃, while the latter two catalysts have similar activities. However, **Figure 1.4b** reveals that the difference in the average rates of C-C bond scission ($n_{\text{C-C scission}}/t$, where $t = 8$ h in this case) is about a factor of two between Pt/Cl-Al₂O₃ and Pt/F-Al₂O₃, similar to the difference between Pt/ γ -Al₂O₃ and Pt/Cl-Al₂O₃. The misleading conclusions from liquid yields arise because the operational definitions for unreacted solids and liquids include large molecular weight ranges which fail to represent the number of catalytic events accurately (see also **section 1.4.2.2**).



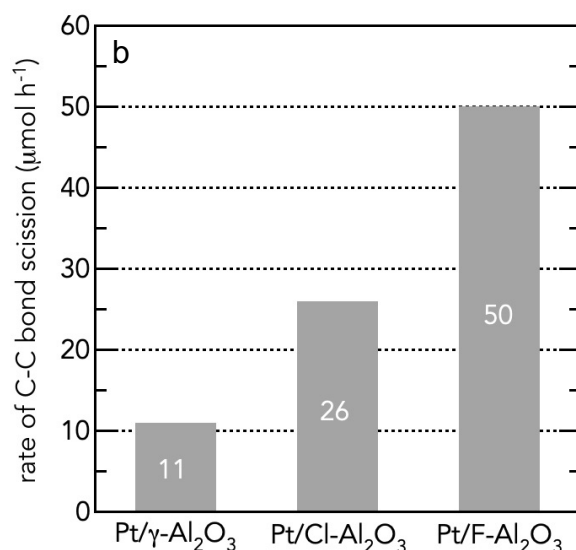


Figure 1.4. Activity comparison of three Pt-based catalysts for polyethylene depolymerization: (a) by mass fractions of hydrocarbons recovered from a batch reactor: green, gases; orange, liquids soluble in hot CH₂Cl₂; black, organic residues insoluble in hot CH₂Cl₂, and (b) by average rate of C-C bond scission (defined as $n_{\text{C-C scission}}/t$).⁸⁵

In the specific case of hydrogenolysis of saturated polyolefins, *H₂ consumption* can be used as an independent assessment of the extent of depolymerization.⁸⁶ Furthermore, the H₂ uptake is usually convenient to measure. Since H₂ consumption occurs concurrently with the cleavage of C-C bonds, both metrics may yield the same result. However, H₂ redistribution processes such as dehydrogenation, cyclization, and aromatization can occur simultaneously with hydrogenolysis, complicating the relationship between C-C bond cleavage and H₂ consumption.^{84,85} Consequently, the *number of C-C bond scission events* is the more general metric.

In oxidative depolymerization of polyolefins, the number of C-C bond scission events can also be calculated using **eq 1.6**, modified by allowing $N(t)$ to represent the total number of molecules of hydrocarbon oxygenates, as well as CO and CO₂. Alkane metathesis involves only chain length redistribution, so the total number of chains does not change and $n_{\text{C-C scission}}$ does not reflect the extent of depolymerization.

1.4.2.2. Degree of C-C Bond Scission

In the field of polymer science, the *degree of polymerization* denotes the number of monomeric units within a polymer.¹³ By analogy, a precise description of the extent of depolymerization is the *degree of scission (DOS)*, defined in **eq 1.7**.

$$DOS = 100 \% \cdot n_{\text{C-C scission}} / n_{\text{initial number of C-C bonds}} \quad (1.7)$$

DOS is a universal metric for reaction progress in depolymerization, and is directly proportional to $n_{\text{C-C scission}}$. The mass distributions for a hypothetical long-chain alkane undergoing random hydrogenolysis are modeled as a function of *DOS* in **Figure 1.5**. When $DOS = 0$, the reactor contains only the starting alkane; when $DOS = 1$, all of the original chains have been converted to CH₄.

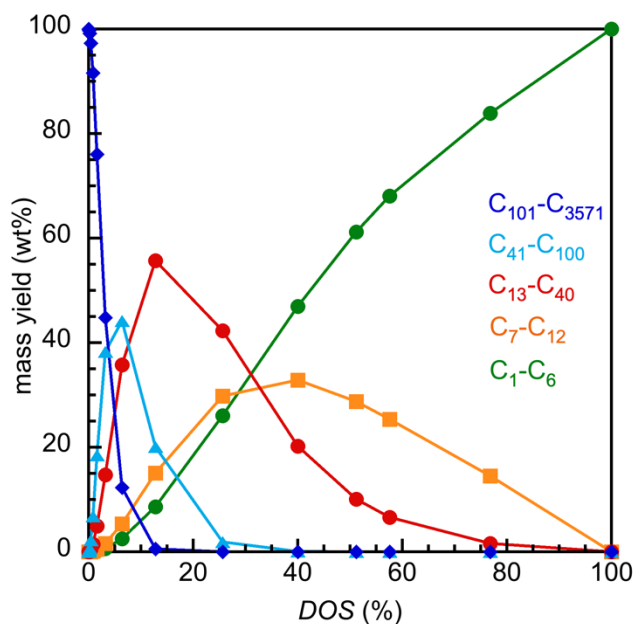


Figure 1.5. Model of the mass distribution of hydrocarbon product groups resulting from the random hydrogenolysis of an atomically-precise *n*-alkane C₃₅₇₁H₇₁₄₄ ($M = 50,000$ g/mol) as a function of its degree of scission (DOS), starting with 2,000 chains. Assuming all C-C bonds have an equal chance of undergoing hydrogenolysis implies that longer chains have a higher likelihood of being cut, in proportion to their length. The mass of H₂ incorporated was not included in the product mass yields.

1.4.2.3. Molecular Weight and Dispersity

Due to the broad product distributions that typically result from PO hydrogenolysis, statistical methods are necessary to compare distributions arising from different experiments. Metrics from the polymer field such as the number-averaged molecular weight (M_n), weight-

averaged molecular weight (M_w), and dispersity ($D = M_w/M_n$) are appropriate to describe the hydrocarbon product distributions obtained in depolymerization reactions.

However, inferring catalytic activity from molecular weight distributions must be done with caution. If all hydrocarbons, including the initial polymer, are included in the product molecular weight distribution, M_n is inversely proportional to $n_{C-C \text{ scission}}$ (or DOS), **eq 1.8**.

$$M_n = \frac{\sum M_i n_i}{\sum n_i} = \frac{m_{PE}}{\sum n_i} = \frac{m_{PE}}{N(0) + n_{C-C \text{ scission}}} = \frac{m_{PE}}{N(0) + n_{\text{initial number of C-C bonds}} \cdot DOS} \quad (1.8)$$

Consequently, M_n initially decreases rapidly, but the rate of decrease slows abruptly with the extent of reaction. This behavior has been reported by a few studies.^{84,87} M_n for a hypothetical long-chain alkane undergoing hydrogenolysis is predicted as a function of DOS in **Figure 1.6**.

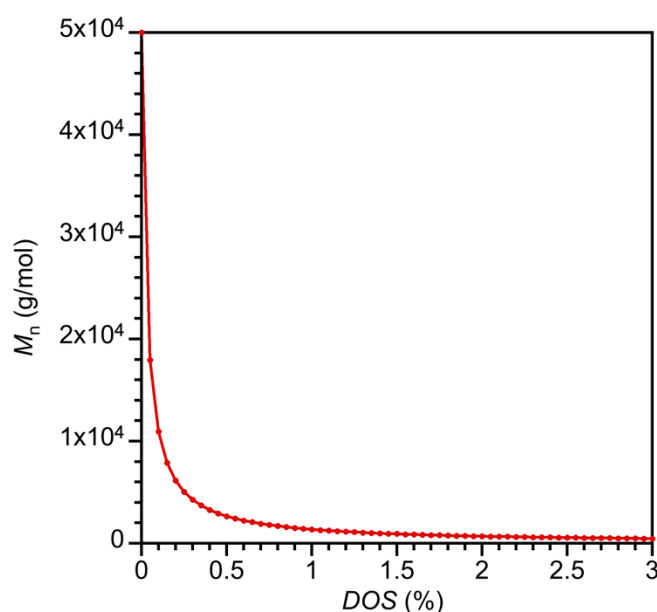


Figure 1.6. Predicted evolution of the number-averaged molecular weight (M_n) as a function of the Degree of Scission (DOS), starting from 2,000 chains of an alkane with the precise formula $C_{3571}H_{7144}$ (i.e., $M = 50,000$ g/mol). The mass of H_2 incorporated was not included in the product mass.

Since the change in M_n is highly non-linear with respect to n_{C-C} scission or DOS , the change in average molecular weight slows dramatically as reaction proceeds. This behavior does not necessarily indicate catalyst deactivation, or selectivity for products in a particular molecular weight range.

1.5. Characterization in Polyolefin Upcycling

1.5.1. Polyolefins as Reactants

For molecular compounds, the name, along with purity and vendor information, adequately represent its form. However, this is not the case for macromolecular materials, whose structures and molecular weights are generally not precise. Providing only the name of a polymer, such as polyethylene or polypropylene, provides information on the empirical chemical composition but is inadequate to record the behavior of a material in a depolymerization reaction. Slightly more specific designations, such as LDPE, indicate the grade of polymer and implies something about the branching frequency. However, other important properties including the average chain length, the chain length distribution, the type and frequency of branches, and where appropriate, the stereoregularity (tacticity), all require further specification. Many of these properties influence reactivity in depolymerization. To

make polymer upcycling reports more reproducible,^{88–90} information beyond the average chain length should be sought and reported. Researchers are encouraged to consult standard works on polymer characterization.^{91,92} Here, we briefly discuss the characterization and specification of macromolecular chain length, because this value is used in the calculation of the number of C-C bond scission events (see **section 1.4.2**).

The most widely used technique to assess macromolecular chain lengths is GPC. The measurement requires a calibration curve made using the elution times of polymer standards with molecular weights ranging from a few hundred to several million g/mol. The elution time of a polymer sample is then used to determine its molecular weight and molecular weight distribution, based on the calibration curve.⁹³ To report the chain length, one must provide two of the following three values: the number-averaged molecular weight M_n , the weight-averaged molecular weight M_w , and the dispersity $D = M_w/M_n$ (see **section 1.4.2.3**). A challenge specific to polyolefins is the low solubility of high molecular weight PE and PP chains, which precludes analysis by room-temperature GPC (typically performed in a solvent like THF or CHCl_3). In such cases, less widely available high-temperature GPC is required, with high-boiling solvents like 1,2,4-trichlorobenzene and decalin.

1.5.2. Polyolefin Upcycling Products

Quantitative analysis is even more challenging for polyolefin upcycling products than for the polyolefin reactant, because (1) the potential range of molecular weights is very wide, from 10^6 g/mol for unreacted ultrahigh molecular weight PE, down to 10^2 g/mol for small molecule products, (2) the number of hydrocarbon product types (e.g., alkanes, alkenes,

cycloalkanes, aromatics) as well as oxygenates (e.g., alcohols, aldehydes, ketones, carboxylic acids) is considerable, and (3) many isomers are possible for each carbon number in a particular product type (branched alkanes, substituted aromatics, etc.).

GC is a convenient way to separate low molecular weight hydrocarbons (C_1 to C_{40}). Qualitative identification and quantitative analysis can be achieved using electron ionization mass spectrometry (EI-MS) and flame ionization detection (FID), respectively. Response factors in EI-MS depend on the hydrocarbon type and the number of carbons, requiring calibration curves. Although FID analyses can assume that common types of hydrocarbons (e.g., alkanes, alkenes, cycloalkanes, and aromatics) have similar response factors, this simplification is not applicable to other types of molecules (e.g., oxygenates).⁹⁴ When the mixture contains a large number of isomers with the same or similar carbon numbers, even identification can be problematic due to insufficient separation. In such cases, adding a second separation dimension (e.g., 2D GC x GC) may be helpful,⁹⁵ although the technique is not yet widely available and requires extensive calibration.

EI, being a hard ionization technique, induces extensive fragmentation during hydrocarbon analysis by EI-MS. In contrast, techniques that use soft ionization methods, e.g., matrix assisted laser desorption ionization-time of flight mass spectrometry (MALDI-TOF-MS), field desorption mass spectrometry (FD-MS), and atmospheric pressure chemical ionization mass spectrometry (APCI-MS) can provide information about the hydrocarbon types present in mixtures, as well as the molecular weight distributions for heavier hydrocarbons (MALDI-TOF: up to 150,000 g/mol, FD-MS: up to 12,000 g/mol, and APCI-MS: up to 1,500 g/mol). However, isomers with the same molecular weight may not be

separated, and product families belonging to the same mass series may overlap (e.g., *n*-alkanes and alkylnaphthalenes). Furthermore, these techniques are generally only semi-quantitative, because compounds with lower molecular weights may be preferentially removed when the sample is prepared under vacuum, while compounds with higher molecular weights may not be soluble enough and/or volatile enough.

For oligomers ($C_{>40}$) and partially converted polymers, GPC can be used to assess the molecular weight distribution. This technique is typically considered reliable for compounds with molecular weights above a few thousand (i.e., $C_{>100}$), where the refractive index is essentially independent of molecular weight.⁹⁶ In a typical polymer upcycling process, waxy oligomers ($C_{\sim 40}$ to $C_{\sim 100}$) and even heavy liquids ($C_{\sim 10}$ to $C_{\sim 40}$) are also present. They may be improperly assessed by GPC, influencing the accuracy of the average molecular weight determination for the entire sample.

$\bar{D}$ values (i.e., M_w/M_n) obtained from GPC measurements are subject to the same limitations. In a non-living polymerization process, the value of $\bar{D}$ increases with molecular weight. It must therefore decrease in a depolymerization process (although an initial increase may be observed before the decreasing trend is established).^{84,87} Since GPC measurements have a low molecular weight ($C_{\sim 10}$) cutoff due to overlap with the solvent peak, measured $\bar{D}$ values can underestimate the complete distribution of products. Careful attention is required when using $\bar{D}$ values obtained from GPC measurements to compare and make claims about product distributions.

To obtain accurate molecular weights, polymer standards must be used with a chemical structure similar to that of the molecules being analyzed. When the chemical structures differ,

the Mark–Houwink equation can be used to convert molecular weights measured with one kind of standard to another.⁹³ For example, linear alkane waxes generated in PE hydrogenolysis can be analyzed by GPC using common PS calibration standards, but the results must be converted to values corresponding to calibration with PE standards. When upcycling generates products with chemical properties that are very different from the original polymer (e.g., PE conversion to long-chain alkylaromatics, or PE oxidation to oxygenated waxes), the change in hydrodynamic volume of the products relative to the standards affects the retention times and makes the extracted molecular weight values less reliable.

Solution-state ^1H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy can give complementary information about the types of protons and carbons present in product mixtures. These methods provide only an overall assessment, since different hydrocarbon types often exhibit overlapping signals (especially ^1H signals). They are also limited to compounds with sufficient solubility. The larger chemical shift range for ^{13}C can be useful, but sensitivity can be an issue due to the low natural abundance (0.1 %) of ^{13}C . Increased sensitivity with ^{13}C isotope labeling requires additional expense and/or synthetic effort. To ensure NMR information is quantitative, the relaxation delay used in the NMR data acquisition needs to be long enough to allow for complete spin-lattice relaxation. The appropriate delay is ascertained by inversion recovery measurements.⁹⁷ In addition, a relaxation agent such as $\text{Cr}(\text{acac})_3$ can be added to reduce the spin-lattice relaxation time and improve the measurement efficiency.⁹⁸ Some characterization of poorly soluble or insoluble solids can be achieved using solid-state magic-angle spinning (MAS) NMR, although the resolution is typically much lower than for solution-state NMR. *Operando* MAS-NMR

equipment is not currently compatible with the elevated temperatures typically required in depolymerization experiments ($> 250\text{ }^{\circ}\text{C}$),⁹⁹ but this technique may be useful in lower temperature studies, and higher temperature compatibility may become available in the future.

A protocol for the quantitative analyses of products and rates in polyethylene depolymerization and upcycling will be discussed in **Chapter 5**.

1.6. References

1. Geyer, R., Jambeck, J.R., and Law, K.L. (2017). Production, use, and fate of all plastics ever made. *Sci. Adv.* 3, e1700782. 10.1126/sciadv.1700782.
2. The New Plastics Economy: Catalysing action
<https://www.ellenmacarthurfoundation.org/the-new-plastics-economy-catalysing-action>.
3. Plastics - the Facts 2022 • Plastics Europe Plast. Eur.
<https://plasticseurope.org/knowledge-hub/plastics-the-facts-2022/>.
4. OECD (2022). Plastic waste in 2019. <https://www.oecd-ilibrary.org/content/data/a92f5ea3-en>.
5. Lange, J.-P. (2021). Managing Plastic Waste—Sorting, Recycling, Disposal, and Product Redesign. *ACS Sustain. Chem. Eng.* 9, 15722–15738. 10.1021/acssuschemeng.1c05013.
6. Al-Salem, S.M., Lettieri, P., and Baeyens, J. (2009). Recycling and recovery routes of plastic solid waste (PSW): A review. *Waste Manag.* 29, 2625–2643. 10.1016/j.wasman.2009.06.004.
7. Martey, S., Addison, B., Wilson, N., Tan, B., Yu, J., Dorgan, J.R., and Sobkowicz, M.J. (2021). Hybrid Chemomechanical Plastics Recycling: Solvent-free, High-Speed Reactive

- Extrusion of Low-Density Polyethylene. *ChemSusChem* *14*, 4280–4290. 10.1002/cssc.202100968.
8. Ellis, L.D., Rorrer, N.A., Sullivan, K.P., Otto, M., McGeehan, J.E., Román-Leshkov, Y., Wierckx, N., and Beckham, G.T. (2021). Chemical and biological catalysis for plastics recycling and upcycling. *Nat. Catal.* *4*, 539–556. 10.1038/s41929-021-00648-4.
9. Smith, R.L., Takkellapati, S., and Riegerix, R.C. (2022). Recycling of Plastics in the United States: Plastic Material Flows and Polyethylene Terephthalate (PET) Recycling Processes. *ACS Sustain. Chem. Eng.* *10*, 2084–2096. 10.1021/acssuschemeng.1c06845.
10. Coates, G.W., and Getzler, Y.D.Y.L. (2020). Chemical recycling to monomer for an ideal, circular polymer economy. *Nat. Rev. Mater.* *5*, 501–516. 10.1038/s41578-020-0190-4.
11. Vollmer, I., Jenks, M.J.F., Roelands, M.C.P., White, R.J., van Harmelen, T., de Wild, P., van der Laan, G.P., Meirer, F., Keurentjes, J.T.F., and Weckhuysen, B.M. (2020). Beyond Mechanical Recycling: Giving New Life to Plastic Waste. *Angew. Chem. Int. Ed.* *59*, 15402–15423. <https://doi.org/10.1002/anie.201915651>.
12. Nicholson, S.R., Rorrer, J.E., Singh, A., Konev, M.O., Rorrer, N.A., Carpenter, A.C., Jacobsen, A.J., Román-Leshkov, Y., and Beckham, G.T. (2022). The critical role of process analysis in chemical recycling and upcycling of waste plastics. *Annu. Rev. Chem. Biomol. Eng.* *13*, 301–324. 10.1146/annurev-chembioeng-100521-085846.
13. A. D. McNaught, A.W. (1997). IUPAC. Compendium of Chemical Terminology, 2nd ed. (the “Gold Book”). (Blackwell Scientific Publications, Oxford) 10.1351/goldbook.C00895.

14. Anuar Sharuddin, S.D., Abnisa, F., Wan Daud, W.M.A., and Aroua, M.K. (2016). A review on pyrolysis of plastic wastes. *Energy Convers. Manag.* 115, 308–326. 10.1016/j.enconman.2016.02.037.
15. Qureshi, M.S., Oasmaa, A., Pihkola, H., Deviatkin, I., Tenhunen, A., Mannila, J., Minkkinen, H., Pohjakallio, M., and Laine-Ylijoki, J. (2020). Pyrolysis of plastic waste: Opportunities and challenges. *J. Anal. Appl. Pyrolysis* 152, 104804. 10.1016/j.jaap.2020.104804.
16. Maqsood, T., Dai, J., Zhang, Y., Guang, M., and Li, B. (2021). Pyrolysis of plastic species: A review of resources and products. *J. Anal. Appl. Pyrolysis* 159, 105295. 10.1016/j.jaap.2021.105295.
17. Jahirul, M.I., Rasul, M.G., Schaller, D., Khan, M.M.K., Hasan, M.M., and Hazrat, M.A. (2022). Transport fuel from waste plastics pyrolysis – A review on technologies, challenges and opportunities. *Energy Convers. Manag.* 258, 115451. 10.1016/j.enconman.2022.115451.
18. Uzochukwu, W., Umunakwe, R., Obasi, H., Ugbaja, M., Cosmas, C., Uche, Eze, W., Henry, C., and Madufor, I. (2021). Plastics waste management: A review of pyrolysis technology. *J Inst Energy* 1, 50–69. 10.3934/ctr.2021003.
19. Dai, L., Zhou, N., Lv, Y., Cheng, Y., Wang, Y., Liu, Y., Cobb, K., Chen, P., Lei, H., and Ruan, R. (2022). Pyrolysis technology for plastic waste recycling: A state-of-the-art review. *Prog. Energy Combust. Sci.* 93, 101021. 10.1016/j.pecs.2022.101021.

20. Xayachak, T., Haque, N., Parthasarathy, R., King, S., Emami, N., Lau, D., and Pramanik, B.K. (2022). Pyrolysis for plastic waste management: An engineering perspective. *J. Environ. Chem. Eng.* *10*, 108865. 10.1016/j.jece.2022.108865.
21. Speight, J.G. (2020). 6 - Catalytic cracking. In *The Refinery of the Future* (Second Edition), J. G. Speight, ed. (Gulf Professional Publishing), pp. 197–226. 10.1016/B978-0-12-816994-0.00006-3.
22. Miandad, R., Barakat, M.A., Aburizaiza, A.S., Rehan, M., and Nizami, A.S. (2016). Catalytic pyrolysis of plastic waste: A review. *Process Saf. Environ. Prot.* *102*, 822–838. 10.1016/j.psep.2016.06.022.
23. Al-Salem, S.M., Antelava, A., Constantinou, A., Manos, G., and Dutta, A. (2017). A review on thermal and catalytic pyrolysis of plastic solid waste (PSW). *J. Environ. Manage.* *197*, 177–198. 10.1016/j.jenvman.2017.03.084.
24. Peng, Y., Wang, Y., Ke, L., Dai, L., Wu, Q., Cobb, K., Zeng, Y., Zou, R., Liu, Y., and Ruan, R. (2022). A review on catalytic pyrolysis of plastic wastes to high-value products. *Energy Convers. Manag.* *254*, 115243. 10.1016/j.enconman.2022.115243.
25. Hussein, Z.A., Shakor, Z.M., Alzuhairi, M., and Al-Sheikh, F. (2021). Thermal and catalytic cracking of plastic waste: a review. *Int. J. Environ. Anal. Chem.* *103*, 5920–5937. 10.1080/03067319.2021.1946527.
26. Serrano, D.P., Aguado, J., and Escola, J.M. (2012). Developing advanced catalysts for the conversion of polyolefinic waste plastics into fuels and chemicals. *ACS Catal.* *2*, 1924–1941. 10.1021/cs3003403.

27. Weitkamp, J. (2012). Catalytic hydrocracking—mechanisms and versatility of the Process. *ChemCatChem* 4, 292–306. <https://doi.org/10.1002/cctc.201100315>.
28. Corma, A., and Orchillés, A.V. (2000). Current views on the mechanism of catalytic cracking. *Microporous Mesoporous Mater.* 35, 21–30. 10.1016/S1387-1811(99)00205-X.
29. Hattori, H., Takahashi, O., Takagi, M., and Tanabe, K. (1981). Solid super acids: Preparation and their catalytic activities for reaction of alkanes. *J. Catal.* 68, 132–143. 10.1016/0021-9517(81)90046-4.
30. Blomsma, E., Martens, J.A., and Jacobs, P.A. (1996). Mechanisms of Heptane Isomerization on Bifunctional Pd/H-Beta Zeolites. *J. Catal.* 159, 323–331. 10.1006/jcat.1996.0094.
31. Alvarez, F., Ribeiro, F.R., Perot, G., Thomazeau, C., and Guisnet, M. (1996). Hydroisomerization and hydrocracking of alkanes. *J. Catal.* 162, 179–189. 10.1006/jcat.1996.0275.
32. Uemichi, Y., Kashiwaya, Y., Ayame, A., and Kanoh, H. (1984). Formation of aromatic hydrocarbons in degradation of polyethylene over activated carbon catalyst. *Chem. Lett.* 13, 41–44. 10.1246/cl.1984.41.
33. Dong, Z., Chen, W., Xu, K., Liu, Y., Wu, J., and Zhang, F. (2022). Understanding the Structure–Activity Relationships in Catalytic Conversion of Polyolefin Plastics by Zeolite-Based Catalysts: A Critical Review. *ACS Catal.* 12, 14882–14901. 10.1021/acscatal.2c04915.

34. Mark, L.O., Cendejas, M.C., and Hermans, I. (2020). The Use of Heterogeneous Catalysis in the Chemical Valorization of Plastic Waste. *ChemSusChem* *13*, 5808–5836. 10.1002/cssc.202001905.
35. Ivanova, S.R., Gumerova, E.F., Minsker, K.S., Zaikov, G.E., and Berlin, A.A. (1990). Selective catalytic degradation of polyolefins. *Prog. Polym. Sci.* *15*, 193–215. 10.1016/0079-6700(90)90028-Y.
36. Tan, J.Z., Hullfish, C.W., Zheng, Y., Koel, B.E., and Sarazen, M.L. (2023). Conversion of polyethylene waste to short chain hydrocarbons under mild temperature and hydrogen pressure with metal-free and metal-loaded MFI zeolites. *Appl. Catal. B Environ.* *338*, 123028. 10.1016/j.apcatb.2023.123028.
37. Duan, J., Chen, W., Wang, C., Wang, L., Liu, Z., Yi, X., Fang, W., Wang, H., Wei, H., Xu, S., et al. (2022). Coking-Resistant Polyethylene Upcycling Modulated by Zeolite Micropore Diffusion. *J. Am. Chem. Soc.* *144*, 14269–14277. 10.1021/jacs.2c05125.
38. Zhang, W., Kim, S., Wahl, L., Khare, R., Hale, L., Hu, J., Camaioni, D.M., Gutiérrez, O.Y., Liu, Y., and Lercher, J.A. (2023). Low-temperature upcycling of polyolefins into liquid alkanes via tandem cracking-alkylation. *Science* *379*, 807–811. 10.1126/science.ade7485.
39. Kunwar, B., Cheng, H.N., Chandrashekar, S.R., and Sharma, B.K. (2016). Plastics to fuel: a review. *Renew. Sustain. Energy Rev.* *54*, 421–428. 10.1016/j.rser.2015.10.015.
40. Munir, D., Irfan, M.F., and Usman, M.R. (2018). Hydrocracking of virgin and waste plastics: A detailed review. *Renew. Sustain. Energy Rev.* *90*, 490–515. 10.1016/j.rser.2018.03.034.

41. Kots, P.A., Vance, B.C., and Vlachos, D.G. (2022). Polyolefin plastic waste hydroconversion to fuels, lubricants, and waxes: a comparative study. *React. Chem. Eng.* 7, 41–54. 10.1039/D1RE00447F.
42. Bin Jumah, A., Anbumuthu, V., Tedstone, A.A., and Garforth, A.A. (2019). Catalyzing the Hydrocracking of Low Density Polyethylene. *Ind. Eng. Chem. Res.* 58, 20601–20609. 10.1021/acs.iecr.9b04263.
43. Liu, S., Kots, P.A., Vance, B.C., Danielson, A., and Vlachos, D.G. (2021). Plastic waste to fuels by hydrocracking at mild conditions. *Sci. Adv.* 7, eabf8283. 10.1126/sciadv.abf8283.
44. Qiu, Z., Lin, S., Chen, Z., Chen, A., Zhou, Y., Cao, X., Wang, Y., and Lin, B.-L. (2023). A reusable, impurity-tolerant and noble metal-free catalyst for hydrocracking of waste polyolefins. *Sci. Adv.* 9, eadg5332. 10.1126/sciadv.adg5332.
45. Chen, L., Moreira, J.B., Meyer, L.C., and Szanyi, J. (2023). Efficient and selective dual-pathway polyolefin hydro-conversion over unexpectedly bifunctional M/TiO₂-anatase catalysts. *Appl. Catal. B Environ.* 335, 122897. 10.1016/j.apcatb.2023.122897.
46. Gong, W.H. (2023). BTX from Lignin. In *Industrial Arene Chemistry* (John Wiley & Sons, Ltd), pp. 1859–1907. 10.1002/9783527827992.ch60.
47. le Goff, P.-Y., Kostka, W., and Ross, J. (2017). Catalytic Reforming. In *Springer Handbook of Petroleum Technology*, C. S. Hsu and P. R. Robinson, eds. (Springer International Publishing), pp. 589–616. 10.1007/978-3-319-49347-3_18.
48. Ilias, S., and Bhan, A. (2013). Mechanism of the Catalytic Conversion of Methanol to Hydrocarbons. *ACS Catal.* 3, 18–31. 10.1021/cs3006583.

49. Campelo, J.M., Garcia, A., Gutierrez, J.M., Luna, D., and Marinas, J.M. (1984). Skeletal isomerization of cyclohexene on Al_2O_3 and $\text{AlPO}_4\text{--Al}_2\text{O}_3$ catalysts. *Can. J. Chem.* *62*, 1455–1458. 10.1139/v84-246.
50. Campelo, J., Garcia, A., Luna, D., and Marinas, J. (1986). Effect of the fluoride ion on the catalytic activity of AlPO_4 in the cyclohexene skeletal isomerization. *J. Catal.* *102*, 299–308. 10.1016/0021-9517(86)90166-1.
51. Alayoglu, S., Aliaga, C., Sprung, C., and Somorjai, G.A. (2011). Size and Shape Dependence on Pt Nanoparticles for the Methylcyclopentane/Hydrogen Ring Opening/Ring Enlargement Reaction. *Catal. Lett.* *141*, 914–924. 10.1007/s10562-011-0647-6.
52. Na, K., Alayoglu, S., Ye, R., and Somorjai, G.A. (2014). Effect of Acidic Properties of Mesoporous Zeolites Supporting Pt Nanoparticles on Hydrogenative Conversion of Methylcyclopentane. *J. Am. Chem. Soc.* *136*, 17207–17212. 10.1021/ja509273h.
53. Alazman, A., Belic, D., Alotaibi, A., Kozhevnikova, E.F., and Kozhevnikov, I.V. (2019). Isomerization of Cyclohexane over Bifunctional Pt-, Au-, and PtAu-Heteropoly Acid Catalysts. *ACS Catal.* *9*, 5063–5073. 10.1021/acscatal.9b00592.
54. Xu, H., Li, Z., Meng, S., Jarvis, J., and Song, H. (2021). Highly selective skeletal isomerization of cyclohexene over zeolite-based catalysts for high-purity methylcyclopentene production. *Commun. Chem.* *4*, 34. 10.1038/s42004-021-00472-8.
55. Paál, Z. (2010). Dehydrocyclization—Heterogeneous. In *Encyclopedia of Catalysis* (John Wiley & Sons). 10.1002/0471227617.eoc071.pub2.

56. Tamm, P.W., Mohr, D.H., and Wilson, C.R. (1988). Octane Enhancement By Selective Reforming of Light Paraffins. In *Studies in Surface Science and Catalysis* (Elsevier), pp. 335–353. 10.1016/S0167-2991(09)60668-6.
57. Derouane, E.G., and Vanderveken, D.J. (1988). Structural recognition and preorganization in zeolite catalysis: Direct aromatization of *n*-hexane on zeolite L-based catalysts. *Appl. Catal.* *45*, L15–L22. 10.1016/S0166-9834(00)82386-6.
58. Mielczarski, E. (1992). Aromatization of *n*-hexane by platinum-containing molecular sieves II. *n*-Hexane reactivity. *J. Catal.* *134*, 359–369. 10.1016/0021-9517(92)90235-A.
59. Azzam, K.G., Jacobs, G., Shafer, W.D., and Davis, B.H. (2010). Aromatization of hexane over Pt/KL catalyst: Role of intracrystalline diffusion on catalyst performance using isotope labeling. *J. Catal.* *270*, 242–248. 10.1016/j.jcat.2010.01.002.
60. Jarvis, J.S., Harrhy, J.H., Wang, A., Bere, T., Morgan, D.J., Carter, J.H., Howe, A.G.R., He, Q., Hutchings, G.J., and Song, H. (2020). Inhibiting the Dealkylation of Basic Arenes during *n*-Alkane Direct Aromatization Reactions and Understanding the C₆ Ring Closure Mechanism. *ACS Catal.* *10*, 8428–8443. 10.1021/acscatal.0c02361.
61. Yang, M., and Somorjai, G.A. (2004). Adsorption and Reactions of C₆ Hydrocarbons at High Pressures on Pt(111) Single-Crystal Surfaces Studied by Sum Frequency Generation Vibrational Spectroscopy: Mechanisms of Isomerization and Dehydrocyclization of *n*-Hexane. *J. Am. Chem. Soc.* *126*, 7698–7708. 10.1021/ja0361446.
62. Bratlie, K.M., and Somorjai, G.A. (2007). A Sum Frequency Generation Vibrational Spectroscopic Study of the Adsorption and Reactions of C₆ Hydrocarbons at High Pressures on Pt(100). *J. Phys. Chem. C* *111*, 6837–6845. 10.1021/jp070968i.

63. Settle, A.E., Berstis, L., Rorrer, N.A., Roman-Leshkóv, Y., Beckham, G.T., Richards, R.M., and Vardon, D.R. (2017). Heterogeneous Diels–Alder catalysis for biomass-derived aromatic compounds. *Green Chem.* *19*, 3468–3492. 10.1039/C7GC00992E.
64. Hernández, B., Kots, P., Selvam, E., Vlachos, D.G., and Ierapetritou, M.G. (2023). Techno-Economic and Life Cycle Analyses of Thermochemical Upcycling Technologies of Low-Density Polyethylene Waste. *ACS Sustain. Chem. Eng.* *11*, 7170–7181. 10.1021/acssuschemeng.3c00636.
65. Yadav, G., Singh, A., Dutta, A., Uekert, T., DesVeaux, J.S., Nicholson, S.R., Tan, E.C.D., Mukarakate, C., Schaidle, J.A., Wrasman, C.J., et al. (2023). Techno-economic analysis and life cycle assessment for catalytic fast pyrolysis of mixed plastic waste. *Energy Environ. Sci.* *16*, 3638–3653. 10.1039/D3EE00749A.
66. Chen, Z., Monzavi, M., Latifi, M., Samih, S., and Chaouki, J. (2022). Microwave-responsive SiC foam@zeolite core-shell structured catalyst for catalytic pyrolysis of plastics. *Environ. Pollut.* *307*, 119573. 10.1016/j.envpol.2022.119573.
67. Pennel, M.L., Maurya, A.K., Ebrahim, A.M., Tassone, C.J., and Cargnello, M. (2023). Activity of Silica-Alumina for the Conversion of Polyethylene into Tunable Aromatics Below Pyrolytic Temperatures. *ACS Sustain. Chem. Eng.* *11*, 12623–12630. 10.1021/acssuschemeng.3c02295.
68. Wang, Y., Zhang, Y., Fan, H., Wu, P., Liu, M., Li, X., Yang, J., Liu, C., Bai, P., and Yan, Z. (2022). Elucidating the structure-performance relationship of typical commercial zeolites in catalytic cracking of low-density polyethylene. *Catal. Today* *405–406*, 135–143. 10.1016/j.cattod.2022.06.024.

69. Xue, Y., Zhou, S., and Bai, X. (2016). Role of Hydrogen Transfer during Catalytic Copyrolysis of Lignin and Tetralin over HZSM-5 and HY Zeolite Catalysts. *ACS Sustain. Chem. Eng.* *4*, 4237–4250. 10.1021/acssuschemeng.6b00733.
70. Uemichi, Y., Ayame, A., Kashiwaya, Y., and Kanoh, H. (1983). Gas chromatographic determination of the products of degradation of polyethylene over a silica—alumina catalyst. *J. Chromatogr. A* *259*, 69–77. 10.1016/S0021-9673(01)87979-6.
71. Sun, K., Huang, Q., Meng, X., Chi, Y., and Yan, J. (2018). Catalytic Pyrolysis of Waste Polyethylene into Aromatics by H₃PO₄ -Activated Carbon. *Energy Fuels* *32*, 9772–9781. 10.1021/acs.energyfuels.8b02091.
72. Springer handbook of petroleum technology (2017). 2nd edition. (Springer Berlin Heidelberg).
73. Giannetto, G., Monque, R., and Galiasso, R. (1994). Transformation of LPG into Aromatic Hydrocarbons and Hydrogen over Zeolite Catalysts. *Catal. Rev.* *36*, 271–304. 10.1080/01614949408013926.
74. Uemichi, Y., Makino, Y., and Kanazuka, T. (1989). Degradation of polyethylene to aromatic hydrocarbons over metal-supported activated carbon catalysts. *J. Anal. Appl. Pyrolysis* *14*, 331–344. 10.1016/0165-2370(89)80008-7.
75. Takuma, K., Uemichi, Y., and Ayame, A. (2000). Product distribution from catalytic degradation of polyethylene over H-gallosilicate. *Appl. Catal. Gen.* *192*, 273–280. 10.1016/S0926-860X(99)00399-3.

76. Renzini, M.S., Sedran, U., and Pierella, L.B. (2009). H-ZSM-11 and Zn-ZSM-11 zeolites and their applications in the catalytic transformation of LDPE. *J. Anal. Appl. Pyrolysis* 86, 215–220. 10.1016/j.jaap.2009.06.008.
77. Wang, W., Yao, C., Ge, X., Pu, X., Yuan, J., Sun, W., Chen, W., Feng, X., Qian, G., Duan, X., et al. (2023). Catalytic conversion of polyethylene into aromatics with Pt/ZSM-5: insights into reaction pathways and rate-controlling step regulation. *J. Mater. Chem. A* 11, 14933–14940. 10.1039/D3TA01917A.
78. de Almeida, J.L.G., Dufaux, M., Taarit, Y.B., and Naccache, C. (1994). Linear alkylbenzene. *J. Am. Oil Chem. Soc.* 71, 675–694. 10.1007/BF02541423.
79. Shokri, A., and Karimi, S. (2021). A Review in Linear Alkylbenzene (LAB) Production Processes in the Petrochemical Industry. *Russ. J. Appl. Chem.* 94, 1546–1559. 10.1134/S1070427221110094.
80. Aitani, A., Wang, J.B., Wang, I., Al-Khattaf, S., and Tsai, T.-C. (2014). Environmental Benign Catalysis for Linear Alkylbenzene Synthesis: A Review. *Catal. Surv. Asia* 18, 1–12. 10.1007/s10563-013-9164-5.
81. Wang, J.-J., Chuang, Y.-Y., Hsu, H.-Y., and Tsai, T.-C. (2017). Toward industrial catalysis of zeolite for linear alkylbenzene synthesis: A mini review. *Catal. Today* 298, 109–116. 10.1016/j.cattod.2017.05.046.
82. Sohn, S., and Do, P. (2023). Linear Alkylbenzenes: An Overview of the Commercial HF and DetalTM Process Unit Alkylation Technology (Case Study). In *Industrial Arene Chemistry* (John Wiley & Sons, Ltd), pp. 729–745. 10.1002/9783527827992.ch25.
83. Kocal, J.A. (1993). Detergent alkylation process using a fluorided silica-alumina.

84. Zhang, F., Zeng, M., Yappert, R.D., Sun, J., Lee, Y.-H., LaPointe, A.M., Peters, B., Abu-Omar, M.M., and Scott, S.L. (2020). Polyethylene upcycling to long-chain alkylaromatics by tandem hydrogenolysis/aromatization. *Science* *370*, 437–441. 10.1126/science.abc5441.
85. Sun, J., Lee, Y.-H., Yappert, R.D., LaPointe, A.M., Coates, G.W., Peters, B., Abu-Omar, M.M., and Scott, S.L. (2023). Bifunctional tandem catalytic upcycling of polyethylene to surfactant-range alkylaromatics. *Chem.* *9*, 2318–2336. 10.1016/j.chempr.2023.05.017.
86. Rorrer, J.E., Ebrahim, A.M., Questell-Santiago, Y., Zhu, J., Troyano-Valls, C., Asundi, A.S., Brenner, A.E., Bare, S.R., Tassone, C.J., Beckham, G.T., et al. (2022). Role of Bifunctional Ru/Acid Catalysts in the Selective Hydrocracking of Polyethylene and Polypropylene Waste to Liquid Hydrocarbons. *ACS Catal.* *12*, 13969–13979. 10.1021/acscatal.2c03596.
87. Celik, G., Kennedy, R.M., Hackler, R.A., Ferrandon, M., Tennakoon, A., Patnaik, S., LaPointe, A.M., Ammal, S.C., Heyden, A., Perras, F.A., et al. (2019). Upcycling Single-Use Polyethylene into High-Quality Liquid Products. *ACS Cent. Sci.* *5*, 1795–1803. 10.1021/acscentsci.9b00722.
88. Bligaard, T., Bullock, R.M., Campbell, C.T., Chen, J.G., Gates, B.C., Gorte, R.J., Jones, C.W., Jones, W.D., Kitchin, J.R., and Scott, S.L. (2016). Toward Benchmarking in Catalysis Science: Best Practices, Challenges, and Opportunities. *ACS Catal.* *6*, 2590–2602. 10.1021/acscatal.6b00183.
89. Scott, S.L., Gunnoe, T.B., Fornasiero, P., and Crudden, C.M. (2022). To Err is Human; To Reproduce Takes Time. *ACS Catal.* *12*, 3644–3650. 10.1021/acscatal.2c00967.

90. Neil M Schweitzer, ed., Rajamani Gounder, ed., and Robert M Rioux, ed. (2023). Addressing Rigor and Reproducibility in Thermal, Heterogeneous Catalysis. 10.5281/zenodo.8029159.
91. Schröder, E., Müller, G., and Arndt, K.-F. (2022). Polymer Characterization (Walter de Gruyter GmbH & Co KG).
92. Meunier, D.M., Wade, J.H., Janco, M., Cong, R., Gao, W., Li, Y., Mekap, D., and Wang, G. (2021). Recent Advances in Separation-Based Techniques for Synthetic Polymer Characterization. *Anal. Chem.* 93, 273–294. 10.1021/acs.analchem.0c04352.
93. Allcock, H.R., Lampe, F.W., Mark, J.E., and Allcock, H.R. (1981). Contemporary polymer chemistry (Prentice-Hall Englewood Cliffs, NJ).
94. Dietz, W.A. (1967). Response factors for gas chromatographic analyses. *J. Chromatogr. Sci.* 5, 68–71. 10.1093/chromsci/5.2.68.
95. Toraman, H.E., Dijkmans, T., Djokic, M.R., Van Geem, K.M., and Marin, G.B. (2014). Detailed compositional characterization of plastic waste pyrolysis oil by comprehensive two-dimensional gas-chromatography coupled to multiple detectors. *J. Chromatogr. A* 1359, 237–246. 10.1016/j.chroma.2014.07.017.
96. Itakura, M., Sato, K., Lusenкова, M.A., Matsuyama, S., Shimada, K., Saito, T., and Kinugasa, S. (2004). Molecular weight dependency of refractive index increment of polystyrene determined by uniform oligomers. *J. Appl. Polym. Sci.* 94, 1101–1106. 10.1002/app.21006.

97. Dumez, J.-N. (2018). Spatial encoding and spatial selection methods in high-resolution NMR spectroscopy. *Prog. Nucl. Magn. Reson. Spectrosc.* 109, 101–134. 10.1016/j.pnmrs.2018.08.001.
98. Zhou, Z., He, Y., Qiu, X., Redwine, D., Potter, J., Cong, R., and Miller, M. (2013). Optimum $\text{Cr}(\text{acac})_3$ Concentration for NMR Quantitative Analysis of Polyolefins. *Macromol. Symp.* 330, 115–122. 10.1002/masy.201300034.
99. Chamas, A., Qi, L., Mehta, H.S., Sears, J.A., Scott, S.L., Walter, E.D., and Hoyt, D.W. (2019). High temperature/pressure MAS-NMR for the study of dynamic processes in mixed phase systems. *Magn. Reson. Imaging* 56, 37–44. 10.1016/j.mri.2018.09.026.

Chapter 2. Polyethylene Upcycling to Long-Chain Alkylaromatics by Tandem Hydrogenolysis/Aromatization

Note: This chapter was adapted from sections of the following publication.

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Author Contributions: Performing experiments and data analysis.

2.1. Abstract

The current scale of plastics production and the accompanying waste disposal problems represent a largely untapped opportunity for chemical upcycling. Tandem catalytic conversion by platinum supported on γ -alumina converts various polyethylene grades in high yields (up to 80 weight percent) to low-molecular-weight liquid/wax products, in the absence of added solvent or molecular hydrogen, with little production of light gases. The major components are valuable long chain alkylaromatics and alkylnaphthalenes (average $\sim C_{30}$, dispersity $D = 1.1$). Coupling exothermic hydrogenolysis with endothermic aromatization renders the overall transformation thermodynamically accessible despite the moderate reaction temperature of 280 °C. This approach demonstrates how waste polyolefins can be a viable feedstock for the generation of molecular hydrocarbon products.

2.2. Introduction

Over the past 70 years, global production of synthetic, petroleum-based plastics has risen sharply, from less than 2 million tonnes in 1950 to 380 million tonnes in 2015.¹ Production is projected to double again within the next 20 years.² Plastics have become indispensable in many facets of modern life, enhancing the security of our food and health care systems, the performance of textiles, the versatility of consumer electronics, and the energy efficiency of transportation. About 40% of these plastics are destined for short-term use, and most (>90% in the United States) are not recycled.¹ The vast bulk of this plastic waste ends up in landfills or is incinerated. However, the embodied energy that can be recovered by combustion is far less than that used in the original manufacturing of plastic.³ Furthermore, a substantial fraction of the waste is mismanaged, ending up in rivers and oceans where its chemical inertness leads to extremely slow degradation and visible accumulation in the natural environment.^{4,5}

Efforts to develop closed-loop life cycles for synthetic plastics by relying on collection, separation, and mechanical recycling have had limited success. The inferior properties of the recycled materials, relative to virgin plastics, contribute to the economic challenges of the “downcycling” model.⁶ New types of polymers that degrade rapidly in the environment are being investigated,⁷ although such materials do not currently have either the physical properties or the cost structure to displace existing commodity plastics. Degradable plastics can also contaminate recycling streams and may encourage single-use product design. Depolymerization (also known as chemical or feedstock recycling) can recover the original monomer subunits, repolymerization of which yields materials with properties identical to those of the original plastic.⁸ However, this strategy requires prohibitive amounts of energy

for polyolefins such as polyethylene (PE) and polypropylene (PP). Controlled partial depolymerization could convert post-consumer waste plastics directly into more valuable chemicals (“upcycling”), although few such processes have yet been developed.

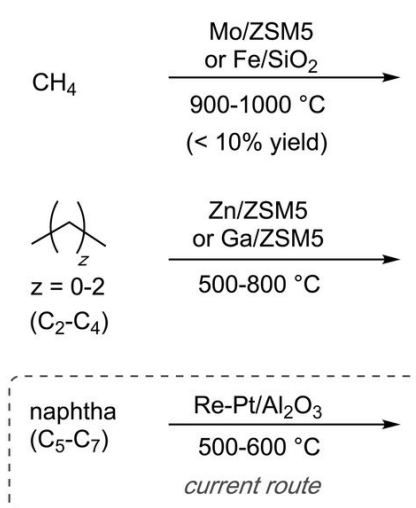
High- and low-density polyethylenes (HDPE and LDPE) currently represent the largest fraction (36% by mass) of all plastic waste.¹ Their depolymerization by pyrolysis at temperatures above 400°C, with or without a catalyst, generates complex, low-value mixtures of gas, liquid hydrocarbons, and char.^{9,10} Somewhat more selective disassembly can be achieved at lower temperatures via catalytic hydrogenolysis^{11,12} or tandem catalytic alkane metathesis,¹³ but the low-value alkane products are unlikely to recoup the costs of recovery, separation, and processing using large amounts of a co-reactant (H₂ or liquid alkanes, respectively).

Aromatics are more attractive target products from partial depolymerization. The conventional process for making aromatics is naphtha reforming. This energy-intensive process generates a mixture known as BTX (benzene-toluene-xylenes) at 500°C to 600°C.¹⁴ In a subsequent step with a large environmental footprint, BTX is alkylated to give linear alkylbenzenes (LABs, used for making surfactants). The most widely used processes require linear olefins (typically, C₁₀ to C₁₆) and liquid HF or AlCl₃-HCl as the acid catalyst.¹⁵ Manufacturing the BTX by aromatization of shale gas-derived light alkanes requires harsher reaction conditions (propane, 550°C to 700°C; ethane, 600°C to 800°C; methane, 900° to 1000°C),¹⁶ and the catalysts tend to deactivate rapidly. New zeolite-based catalysts can transform either methanol¹⁷ or syngas¹⁸ into BTX aromatics at lower temperatures, 300°C to 400°C. Biomass-based routes include oxidative coupling of ethanol to aromatic alcohols and

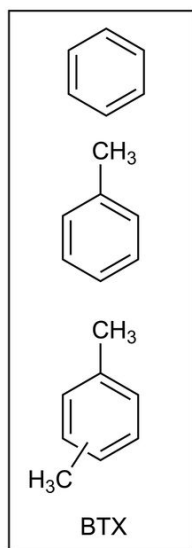
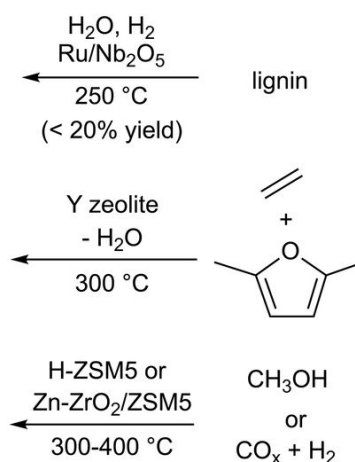
aldehydes,¹⁹ hydrogenolysis/hydrodeoxygenation of bio-oils or lignin to give propylbenzene,²⁰ and Diels-Alder reactions of carbohydrate-derived furanics to give *p*-xylene.²¹ However, slow rates, low yields, and high H₂ requirements make these processes expensive to operate, and none are practiced commercially. BTX is also formed in the catalytic pyrolysis of PE at 400°C to 600°C, although deactivation of the zeolite catalysts by coking is severe.²² The yields are moderate (up to 50 wt %), and large amounts of low-value gases (C₁ to C₅, > 50 wt %) are formed. Conventional and proposed routes to BTX and linear alkylaromatics are compared in **Figure 2.1**.

A Routes to benzene-toluene-xylenes (BTX) aromatics

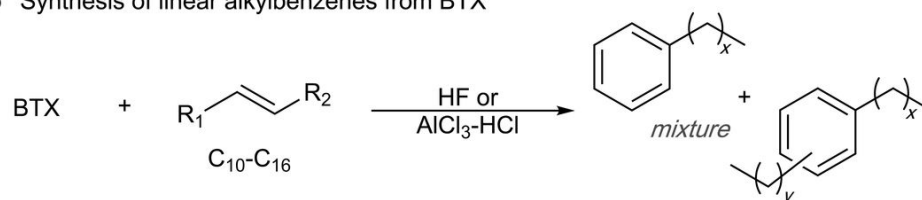
higher temperature routes



lower temperature routes



B Synthesis of linear alkylbenzenes from BTX



C One-pot synthesis of linear dialkylbenzenes from PE (this work)

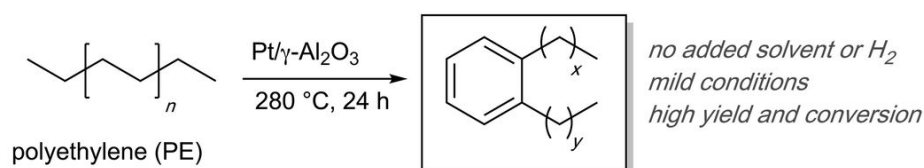


Figure 2.1. Routes to alkylbenzenes. (A to C) Current and proposed routes to BTX (A) and the current downstream transformation of BTX to linear alkylbenzenes (B) are compared to the one-pot tandem process from polyethylene (C) reported here.

2.3. Results and Discussion

2.3.1. Catalytic Conversion of Polyethylene to Alkylaromatics

Here, we report a one-pot, low-temperature catalytic method to convert various grades of PE directly to liquid alkylaromatics over a simple heterogeneous catalyst. In a proof-of-concept experiment, a low-molecular-weight PE (0.118 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.90$) was combined with Pt/ γ -Al₂O₃ (0.200 g, containing 1.5 wt % Pt dispersed as ~1-nm nanoparticles; **Figure A2.1**) in an unstirred mini-autoclave (internal volume 10 ml) without solvent or added H₂ (**Figure 2.2A**). After 24 hours at 280 (± 5)°C, the liquid/wax products (80% by mass) were recovered for characterization by dissolving in hot CHCl₃ (**Figure 2.2B**, experiment 1). According to gel permeation chromatography with refractive index detection (GPC-RI), most of the PE underwent a decrease in M_w by nearly a factor of 10, to 430 g mol⁻¹, as well as the expected²³ decrease in dispersity (to $D = 1.31$). On the basis of their orange color and the appearance of ¹H nuclear magnetic resonance (NMR) signals in the region 6.5 to 9.0 ppm, these hydrocarbons appear to have substantial aromatic content. The CHCl₃-insoluble solids include a small amount of organic residue (~5 wt %) in addition to the catalyst. The former includes unreacted polymer and large oligomers (including less soluble alkylaromatics), as judged by infrared and ¹H NMR spectroscopy (**Figure A2.2**). The missing mass (~15 wt %) is presumably volatile hydrocarbons and gases, which were not collected in this exploratory experiment. In a control experiment conducted without the catalyst under the same reaction conditions, the PE showed no appreciable decrease in M_w . A second control experiment using the same amount of γ -Al₂O₃ but without Pt resulted mostly in a CHCl₃-insoluble residue (~60 wt %) and a much lower yield of soluble hydrocarbon products (34 wt %), with a smaller decrease in molecular weight ($M_w = 1421 \text{ g mol}^{-1}$, $D = 1.85$) and negligible aromatic content (**Figure 2.2B**, experiment 0).

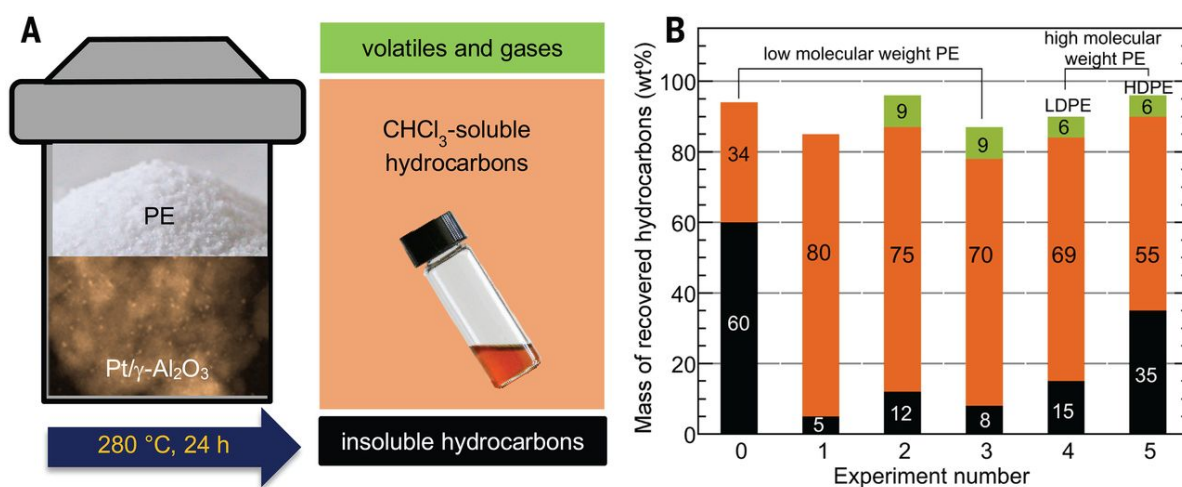


Figure 2.2. Solvent-free conversion of various types of polyethylene. (A) Schematic of reactor and product fractions, with photographs of the powdered polymer and liquid products, as well as a transmission electron micrograph of the catalyst. (B) Hydrocarbon distributions after 24 hours at 280°C. Reactions of a low-molecular-weight PE ($M_w = 3.52 \times 10^3 \text{ g mol}^{-1}$, $\bar{D} = 1.90$) in an unstirred mini-autoclave reactor: (0) catalyzed by γ -Al₂O₃ (no gas recovery); (1) catalyzed by Pt/ γ -Al₂O₃ (no gas recovery); (2) catalyzed by Pt/ γ -Al₂O₃ (with gas recovery). Reactions catalyzed by Pt/ γ -Al₂O₃ in a stirred autoclave reactor with gas recovery: (3) low-molecular-weight PE; (4) LDPE bag ($M_w = 9.45 \times 10^4 \text{ g mol}^{-1}$, $\bar{D} = 7.37$); (5) HDPE bottle cap ($M_w = 5.35 \times 10^4 \text{ g mol}^{-1}$, $\bar{D} = 3.61$).

To obtain a more complete mass balance and to characterize the volatile reaction products, the exploratory experiment was repeated in a mini-autoclave equipped with a gas port. The recovered gases represent a small fraction of the original polymer mass (9 wt %). They include H₂ (0.2 mg, quantified by GC-TCD) and light hydrocarbons (C₁ to C₈, 9.8 mg, quantified by

GC-FID) (**Figure A2.3** and **Figure A2.4**). The latter were primarily methane, ethane and propane, with minor amounts of *n*-hexane, cyclohexane, methylcyclopentane, benzene, and *n*-heptane. Additional volatile hydrocarbons (C₇ to C₁₁, 1.5 mg) were recovered by distillation from the autoclave at 150°C. Their major component was toluene (47 wt %). Together, the light hydrocarbons, the CHCl₃-soluble liquids/waxes (89 mg) and the insoluble organic residue (14 mg) represent an overall mass balance of 96% (**Figure 2.2B**, experiment 2).

When the reaction was conducted in a larger, stirred autoclave (internal volume 90 ml), most of the PE (70 wt %) was converted at 280°C to high-boiling liquids/waxes (**Figure 2.2B**, experiment 3). In this case, the waxes (24 wt%, $M_w = 723 \text{ g mol}^{-1}$, $D = 1.34$) separated spontaneously from the liquids (46 wt %, $M_w = 520 \text{ g mol}^{-1}$, $D = 1.12$) inside the reactor. GPC analysis of the liquid fraction using both RI and ultraviolet (UV) detection gave similar results (**Figure 2.3A**), demonstrating that the UV-active (i.e., aromatic) chromophores were evenly distributed across the molecular weight range. The ¹³C NMR spectrum contains signals in the aromatic region (120 to 150 ppm), most corresponding to unsubstituted ring carbons (**Figure 2.3B**). The ¹H NMR spectrum shows that most aromatic protons are associated with benzene rings (6.5 to 7.4 ppm), with fewer bonded to fused aromatic rings such as naphthalenes (7.4 to 9.0 ppm).²⁴ There is no evidence for olefins or dienes (4.5 to 6.5 ppm; **Figure A2.5**).

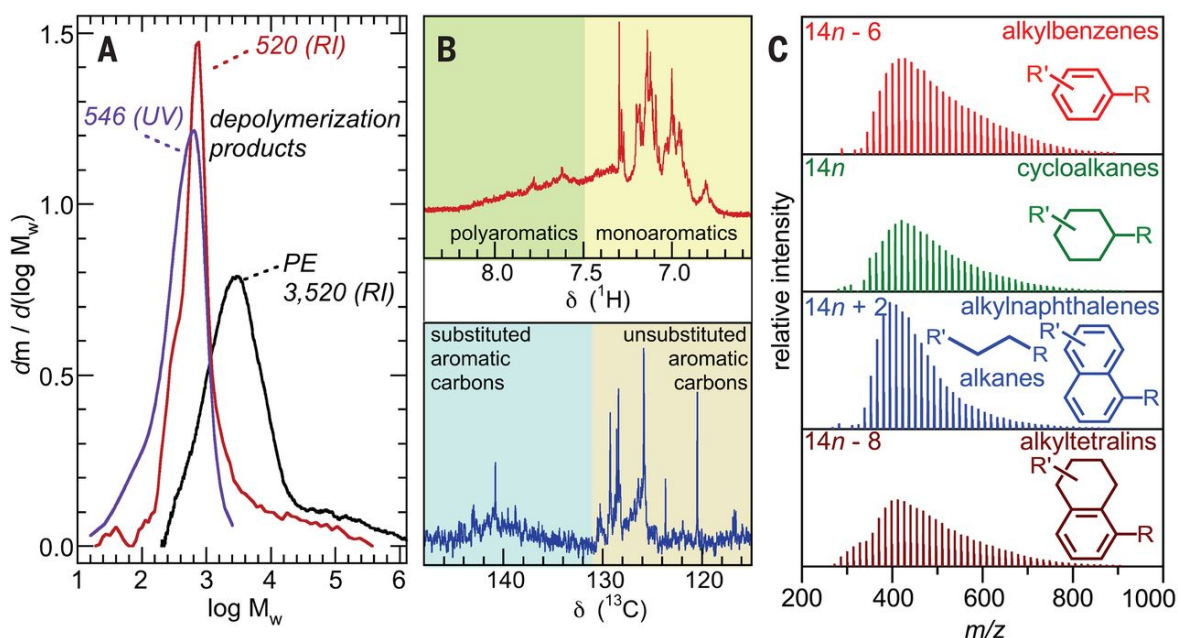


Figure 2.3. Analysis of the liquid hydrocarbon fraction from the solvent-free catalytic conversion of polyethylene. Sample had $M_w = 3.52 \times 10^3 \text{ g mol}^{-1}$ and was heated for 24 hours at 280°C (**Figure 2.2B**, experiment 3). (A) GPC analysis, conducted using both RI and UV detectors. (B) ^1H and ^{13}C NMR spectra, recorded in deuterated TCE. (C) FD-MS analysis.

The high yield of liquid alkylaromatics was particularly promising; such compounds find widespread application as surfactants, lubricants, refrigeration fluids, and insulating oils,²⁵ and their manufacture from waste polyethylene could displace fossil fuel-based routes. The ^1H NMR spectrum reveals more information about the alkyl substituents (**Figure A2.5**). Protons associated with an aliphatic carbon directly bonded to an aromatic ring (C_α) resonate in the region 2 to 4 ppm. The overall ratio $H_\alpha/H_{\text{aromatic}} = 1.1$ indicates that the major species are, on average, dialkylaromatics (**Figure A2.5**). This finding is consistent with a previous report in which dialkylbenzenes were the major products of catalytic aromatization of lighter

n-alkanes (C_6 to C_{12}),²⁶ and with their proposed mechanism of formation by dehydrocyclization of polyethylene (**Figure 2.4**). Combining this information with the overall fraction of aromatic protons (0.037) and the average carbon number (C_{34} for this experiment, based on the M_n value determined by GPC), we estimate the overall alkylaromatic selectivity in the liquid fraction to be 57 (± 5) mol %, of which ~ 40 mol % is monoaromatic (**Table A2.2**, experiment 3). Using the aromatic carbon fraction (0.10 according to ^{13}C NMR; **Figure A2.5B**) instead results in a similar estimate for the alkylaromatic selectivity, 52 (± 4) mol %. Furthermore, many of the alkyl substituents are unbranched at the C_α position, judging by the intense 1H signals at 2.35 to 2.85 ppm. The paraffinic $-CH_2/-CH_3$ ratio, 7.5, suggests that each alkyl substituent possesses, on average, < 1 branch point.

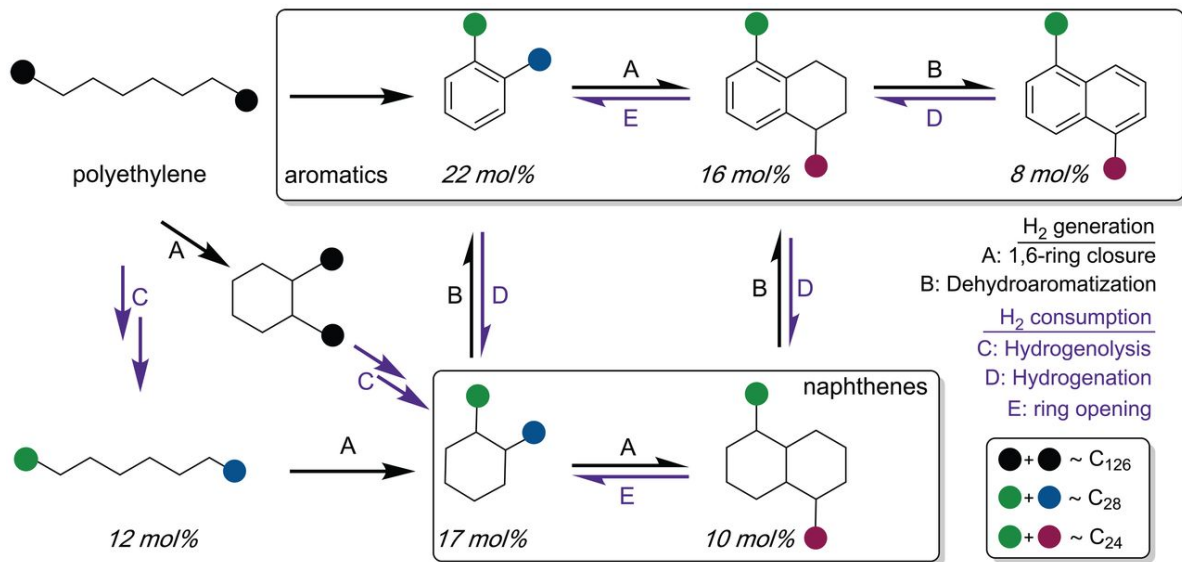


Figure 2.4. Overall PE conversion to alkylaromatics and alkylnaphthenes, and proposed mechanism of tandem polyethylene hydrogenolysis/aromatization via dehydrocyclization.

The yields of each product were estimated using a combination of ^1H NMR and FD-MS analysis (see supplementary materials and **Table A2.1** and **Table A2.3**).

Individual molecular components in the liquid fraction were identified using field desorption–mass spectrometry (FD-MS, **Figure A2.6**). Each mass series shows a log-normal distribution with a maximum intensity at $\sim\text{C}_{30}$. The most abundant products are the alkylbenzene series ($14n - 6$, ~ 22 mol %), as shown in **Figure 2.3C**. Saturated alkanes and alkylnaphthalenes share the same mass profile ($14n + 2$, 20 mol %) and are the next most abundant group, with smaller amounts of alkyltetralins ($14n - 8$, 16 mol %) and alkylnaphthenes (i.e., alkylcycloalkanes; $14n$, 17 mol %). Alkylnaphthalenes presumably arise by further dehydrocyclization of alkylbenzenes (**Figure 2.4**).²⁷ Minor aromatic products include polyaromatics such as alkylanthracenes and alkylphenanthrenes ($14n - 4$, 7 mol %) and their partially hydrogenated analogs ($14n - 10$, 8 mol %). According to FD-MS, the selectivity for monoaromatic products (including both alkylbenzenes and alkyltetralins) is ~ 40 mol %, consistent with the ^1H NMR analysis described above. The alkylnaphthene products, which have intrinsic value as solvents and hydrogen donors,²⁸ could be further dehydrogenated to alkylaromatics by active control of the partial pressure of H_2 in the reactor. The total yield of cyclic products (both alkylaromatics and alkylnaphthenes) in the liquid products is 88 mol% (**Table A2.4**).

2.3.2. Reaction Condition Optimization

When the reaction time was extended from 24 to 36 hours at 280°C, similar products were formed (**Table A2.2**, experiment S1), although the molecular weight distributions of both liquid and wax fractions shifted to slightly lower values (**Figure A2.7**) and the dispersity decreased further (to $\bar{D} = 1.06$). At the same time, the alkylaromatic selectivity increased (24 hours, 52 and 71 mol %, respectively, in the liquid and wax fractions; 36 hours, 70 and 88 mol %, respectively) (**Table A2.2**). Alkylaromatic yields were also strongly temperature-dependent. After 24 hours at a lower temperature (250°C), the CHCl₃-soluble hydrocarbons (13 wt %) showed a smaller extent of depolymerization ($M_w = 1.8 \times 10^3 \text{ g mol}^{-1}$, $\bar{D} = 2.11$) and negligible aromatic content; most PE was simply not converted. At a higher reaction temperature (330°C), the polymer was largely converted in 24 hours; however, the major products (77 wt %) were gases and volatile hydrocarbons. The yield of CHCl₃-soluble hydrocarbons was low (~10 wt %), although the overall yield of aromatics was higher ($H_{\text{aromatic}}/H_{\text{total}} = 0.38$), with more polyaromatics ($H_{\text{mono}}/H_{\text{poly}} = 0.25$). The optimum temperature for alkylbenzene formation is therefore $250^\circ\text{C} < T < 330^\circ\text{C}$.

2.3.3. Thermodynamics Assessment

We also assessed the thermodynamics of *n*-alkane aromatization. The temperature needed to achieve appreciable aromatic yields for this endothermic reaction (**Eq. 2.1**) decreases as the molecular weight increases.²⁹



Nonetheless, direct PE conversion to aromatics appears to require particularly mild conditions relative to the much higher operating temperatures generally required for making BTX from molecular *n*-alkanes (**Figure 2.1**). Thermodynamic values for converting linear PE chains to alkylaromatics at 280°C in 1 atm H₂, estimated using Benson group contributions for long chain *n*-alkanes,³⁰ are $\Delta H_1^\circ = 246$ kJ/mol and $\Delta G_1^\circ = 31$ kJ/mol. Thus, aromatization alone is indeed disfavored. However, the reaction occurs in tandem with hydrogenation of a suitable hydrogen acceptor. In solventless PE depolymerization, the PE chains themselves serve as an internal hydrogen sink (**Figure 2.4**). Using Benson group contributions again, the estimated thermodynamic values for C-C bond hydrogenolysis (**Eq. 2.2**) are $\Delta H_2^\circ = -49$ kJ/mol and $\Delta G_2^\circ = -74$ kJ/mol. Consequently, aromatization becomes favorable at 280°C ($\Delta G^\circ = 0$) when even 10% of the H₂ generated is consumed in PE hydrogenolysis.



On the basis of alkylaromatic yield, the aromatization in experiment 2 of **Figure 2.2B** generated 0.50 mmol H₂. More than 90% of this H₂ (0.47 mmol) was consumed in reducing the molecular weight of the polymer via hydrogenolysis, making the tandem process thermodynamically favorable. However, the residual H₂ found in the reactor headspace at the end of the reaction (0.11mmol) exceeds the expected value (0.03 mmol). Therefore, a significant amount of H₂ is generated in other reactions, such as PE dehydrocyclization to give cycloalkanes and tetralins. Both were observed by FD-MS (see above). Indeed, their yields are higher than the thermodynamic predictions, which favor aromatics. We observed that

some of these more saturated compounds condense outside the autoclave's heated zone where the catalyst is located, thereby preventing their further dehydrogenation.

To explore whether polyethylene is necessary to produce long-chain alkylaromatics by tandem catalytic hydrogenolysis/aromatization, we investigated the reaction of $n\text{-C}_{30}\text{H}_{62}$ under the same conditions (**Table A2.4**, experiments S2 and S3). Compared to PE, the $n\text{-C}_{30}\text{H}_{62}$ chains experience only half as much hydrogenolysis (consuming just 0.25 mmol H_2), as expected on the basis of the chain length dependence of hydrogenolysis kinetics.³¹ Molecules in the liquid products have an average chain length of C_{20} , with low alkylaromatic content (~ 10 mol %). Because hydrogenolysis and aromatization occur in tandem, they must occur together. Consequently, the formation of alkylaromatics is greatly enhanced by the use of polyethylene as a feedstock.

2.3.4. Kinetic Analysis

The time course of PE depolymerization was studied at 280°C (**Table A2.5**, experiments 1a to 1g). A short induction period, lasting about 1 hour, corresponds in large part to the time required for thermal equilibration of the reactor (~ 0.75 hours). After this time, the liquid hydrocarbon fraction increased (**Figure 2.5A**) as M_n decreased, eventually approaching a plateau at 315 g mol^{-1} after ~ 6 hours (**Figure 2.5B**). The dispersity $\bar{D}$ increased initially from 1.94 to 2.36, then decreased to stabilize at 1.31. The alkylaromatic yield also changed appreciably over the course of the reaction. After 3 hours, aromatic protons represented $<1\%$ of all protons, mainly associated with alkylbenzenes (**Figure 2.5, C and D**). At longer reaction times, the aromatic fraction and the yield of alkylnaphthalenes increased (**Table A2.5**).

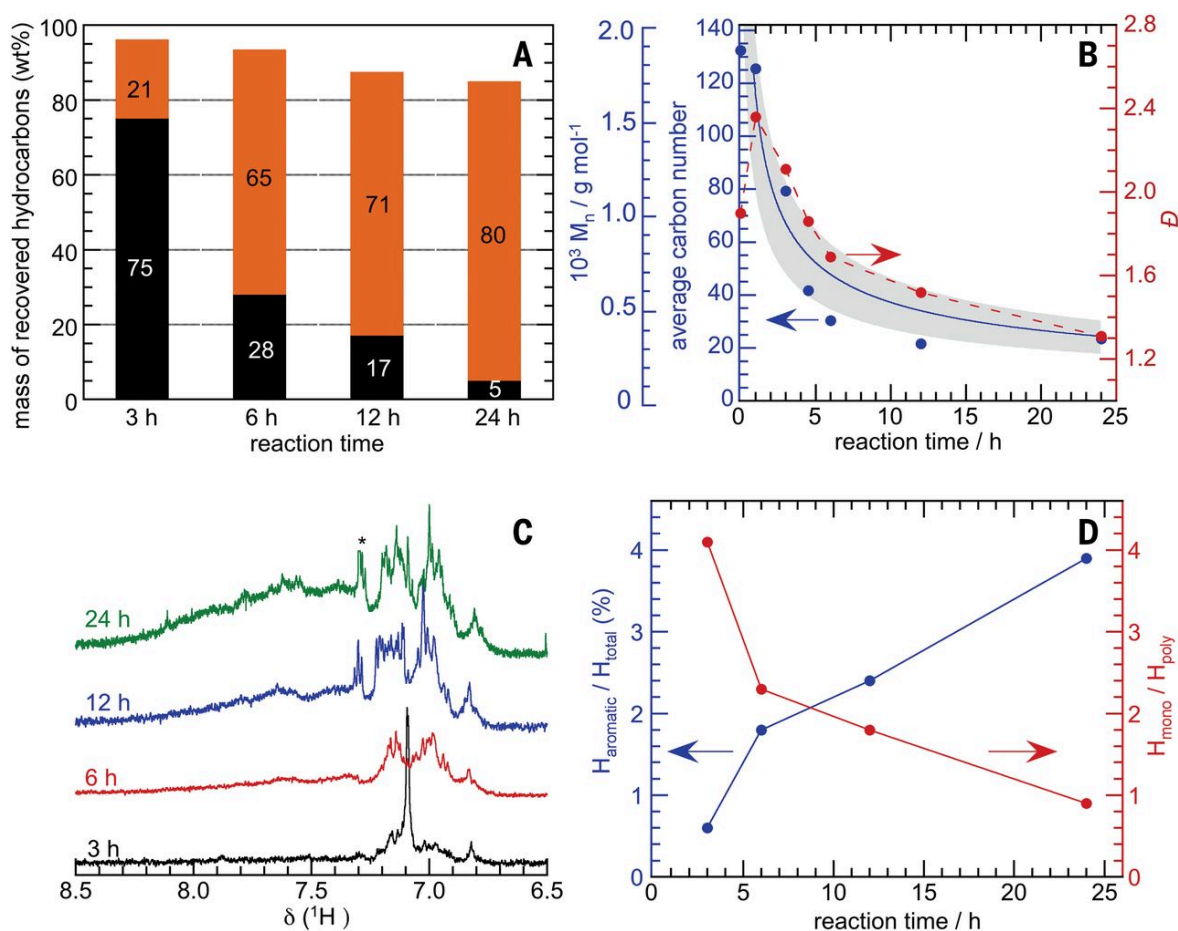


Figure 2.5. Time course of the solvent-free disassembly of polyethylene ($M_n = 1.85 \times 10^3 \text{ g mol}^{-1}$; $\bar{D} = 1.90$) catalyzed by Pt/ γ -Al₂O₃ in an unstirred mini-autoclave reactor at 280°C. (A) Evolution of major product fractions (orange, CHCl₃-soluble liquids/waxes; black, insoluble hydrocarbons). (B) Overall molecular weight (M_n , blue) and dispersity ($\bar{D}$, red) for all non-gas hydrocarbons. The red dashed line is present only to guide the eye. The curve fit (solid blue line) shows the refinement of **Eq. 2.3** to the M_n data. Initial conditions: total carbon $n_C = 8.4 \text{ mmol}$; number of polymer chains $N_0 = 68 \text{ mmol}$; total Pt $m_{\text{Pt}} = 3 \times 10^{-3} \text{ g}$; selectivity for aromatization versus hydrogenolysis, $s = 1/2$ (based on experimental observation). The shaded

region indicates the 95% confidence bands for the model fit. Each independent measurement, which may diverge from the fit because of measurement error, has a 95% confidence interval that represents the mean of many measurements. The set of confidence intervals at all reaction times represents the confidence bands in which the true fit, given the form in **Eq. 2.3**, lies. Because the fit and its confidence bands predict the mean of many measurements at a given reaction time, individual measurements can lie outside these bands. (C) Time course of the ^1H NMR spectra of the liquid/wax fraction in the aromatic region. The asterisk indicates a truncated residual solvent signal. (D) The fraction of aromatic protons and the ratio of mono- to polyaromatic protons.

Although there are far too many individual reactions and products to formulate a precise kinetic model, a simplified model captures the main features of the tandem reaction. We assume that the Pt surface is covered with molten PE and/or PE-derived hydrocarbons at all times, and that the hydrogenolysis turnover frequency is constant on sites not occupied by aromatic hydrocarbons. As the latter form, they adsorb more strongly than alkanes,³² occupying active sites and reducing the hydrogenolysis rate accordingly. We also assume that hydrogenolysis is random (i.e., all aliphatic C-C bonds are equally likely to be cleaved).³³ The sole adjustable parameter, k/K , is the ratio of the rate constant for hydrogenolysis (k) and the equilibrium constant for competitive adsorption of aromatics and aliphatic chains (K). **Eq 2.3** predicts the evolution of the average chain length as a function of the reaction time, initial total carbon amount n_{C} , and total platinum mass m_{Pt} .

$$\ln\left(1 - \frac{3}{M_n(t)} + \frac{3}{M_n(0)}\right) + \left(\frac{3}{M_n(t)} - \frac{3}{M_n(0)}\right) = -\frac{k}{K} \frac{m_{Pt}}{n_C} t \quad (2.3)$$

The curve fit of **Eq. 2.3** to an experimental dataset is shown in **Figure 2.5B**, starting with the data point at $t = 1$ hour (i.e., after the induction period caused by reactor heating). Assuming a preferential binding for aromatics of $K = 3.2 \times 10^6$,³² the hydrogenolysis rate constant k is estimated to be $6.4 \times 10^2 \text{ mol}_{C-C} \text{ bonds hour}^{-1} \text{ g}_{Pt}^{-1}$ at 280°C .

2.3.5. Catalyst Recyclability

The stability of the Pt/ γ - Al_2O_3 catalyst was investigated by conducting three consecutive 6-hour reactions (to ensure much less than full conversion), with regeneration of the recovered catalyst between each experiment (see Appendix I). The liquid/wax yield decreased by 15 wt % in the second run but stabilized in the third run (**Table A2.4**, experiments S4 to S6, and **Figure A2.8**). The activity decreases between the first and second runs was comparable to the decrease in the active Pt surface area measured by CO chemisorption, with no notable change between the second and third runs (**Table A2.4**, experiments S4 to S6). Thus, the intrinsic activity of the catalyst (turnover frequency) appears to be unchanged. The average carbon number of the liquid/wax product increased between the first and second 6-hour runs (as expected because of the lower extent of depolymerization), then stabilized in the third run. Transmission electron microscopy analysis of a catalyst used for 24 hours and regenerated by calcination showed that the Pt nanoparticles increased in size slightly, from 0.8 to 1.2 nm (**Figure A2.1C and D**).

2.3.6. Multiple Polyethylene Grades and Reaction Scale-up

To investigate how a tandem catalytic process could be deployed to convert waste polyethylene without large energy input, we also performed solvent-free depolymerization of two different commercial grades of PE: an LDPE plastic bag ($M_w = 9.45 \times 10^4 \text{ g mol}^{-1}$, $D = 7.37$) and an HDPE water-bottle cap ($M_w = 5.35 \times 10^4 \text{ g mol}^{-1}$, $D = 3.61$). These higher-molecular weight polymers behaved similarly to the low molecular-weight polyethylene, giving liquid/ wax products with an average carbon number of $\sim C_{30}$. After 24 hours at 280°C , the overall liquid yields were 69 and 55 wt % for LDPE and HDPE, respectively (**Figure 2.2**, experiments 4 and 5), with alkylaromatic selectivities of ~ 44 and 50 mol % (**Table A2.4**, experiments 4 and 5). Thus, the extent of depolymerization is slightly lower in the same reaction time. For these higher-molecular-weight polyethylenes, the batch process generates its own highly viscous solvent as depolymerization proceeds. Recycling some of the alkylaromatic liquids to serve as solvent for the next batch may accelerate the reaction by facilitating mass and heat transport. The similar results for three very different plastics (including two commercial grade samples of LDPE and HDPE) suggest that density, degree of branching, and common processing impurities are not major issues.

2.4. Conclusions and Outlook

Shorter residence times should also improve the selectivity for monoaromatic hydrocarbons relative to naphthalenes, etc., and suppress the already low gas yields even further. Alkylbenzene selectivity may be further improved by active control of the partial pressure of H_2 , which must be high enough to promote PE hydrogenolysis but low enough to

suppress aromatic hydrogenation. Catalyst improvements in these directions will be necessary to make the tandem reaction compatible with continuous processing and, ultimately, economically viable. The alkylbenzenes with their linear side chains could be sulfonated to produce biodegradable surfactants, which are interesting as higher value chemical products. This type of commodity polymer upcycling can result in displacement of fossil carbon-based feedstocks, while simultaneously incentivizing better management of plastic waste and recovering considerable material value that can be recirculated into the global economy.

2.5. Experimental Procedures

2.5.1. Catalyst Synthesis and Characterization

γ -Alumina was calcined in flowing air at 500 °C for 4 h, followed by evacuation (10^{-4} Torr) at 450 °C for 12 h. Volatile trimethyl(cyclopentadienyl)platinum (32 ± 1 mg) was deposited onto the dry alumina (1.000 ± 0.020 g) by vacuum sublimation (ca. 10^{-4} Torr) at room temperature.^{33,34} The reactor was shaken vigorously during the procedure to promote uniform deposition, then was evacuated at room temperature for 1 h to remove physisorbed $\text{PtCp}(\text{CH}_3)_3$. The resulting solid was reduced in flowing H_2 (4.0% in Ar, 30 mL/min) as the temperature was ramped to 250 °C at a rate of 2 °C/min. The reactor was held at this temperature for 2 h, then cooled to room temperature and evacuated for 15 min. The reduced catalyst was stored in an Ar-filled glovebox until use to avoid re-oxidation in air.

TEM images of the catalyst were obtained on either a FEI Titan 80-300 kV S/TEM or ThermoFisher Talos F200X. Pt particle sizes were measured from the high angle annular dark field (HAADF) images. The fresh catalyst contains particles with an average size of $(0.9 \pm$

0.2) nm (**Figure A2.1a,b**). After the catalytic disassembly of PE at 280 °C for 24 h, the average size increased slightly, to (1.2 ± 0.3) nm (**Figure A2.1c,d**).

Metal analyses were performed by Inductively-Coupled Plasma (ICP) – Optical Emission Spectrometry (ICP-OES) on a Thermo iCAP 6300. A calibration curve was constructed using standard Pt solutions, prepared using a commercial Pt standard with a mixture of aqua regia in HPLC-grade water (4% v:v). Pt was extracted from solid catalyst samples at 75 °C in aqua regia under magnetic stirring for 30 min, based on a slight modification of a previously described procedure.³⁵ The resulting suspensions were allowed to stand at room temperature for 24 h, then filtered. The solid residue was washed three times with HPLC-grade H₂O. The combined filtrates were diluted with aqua regia (4% v:v in water) and analyzed by ICP-OES, using the spectral lines at 214.423 and 203.646 nm. The fresh catalyst contains 1.5 wt% Pt.

The accessible Pt surface area, dispersion and particle size of fresh and recycled Pt catalysts were also determined by CO chemisorption, using a Micrometrics Autochem ii 2920. A U-shaped quartz reactor was packed with a plug of quartz wool which supported a catalyst bed of ca. 35 mg. A thermocouple was attached to the outside of the reactor, at the level of the middle of the bed. The catalyst was first activated by heating in H₂/Ar (10 vol%) to 200 °C at a ramp rate of 5 °C min⁻¹, and held at 200 °C for 2 h before cooling to room temperature under flowing He. Next, the catalyst was subjected to 20 pulses of CO (9.890 vol% in He). Each pulse had a volume of 124 microliter at 1 atm. The amount of CO not adsorbed in each pulse was measured using a TCD detector.

2.5.2. Catalytic Conversion of Polyethylene

Initial screening reactions and time-resolved experiments were conducted in unstirred stainless-steel mini-autoclaves made from Swagelok junctions,³⁶ each with an internal volume of ca. 10 mL. In a typical procedure, the reduced catalyst (1.5 wt% Pt/ γ -Al₂O₃, 0.200 g) and a sample of the appropriate PE material (0.118 g) were loaded into an autoclave reactor inside an Ar-filled glove-box. The reactor was sealed, removed from the glove-box and placed in a temperature-controlled muffle furnace (Thermo Scientific Lindberg/Blue M BF51848C) that was pre-heated to the desired temperature. When the furnace door was opened to insert the autoclave, the temperature decreased by 20-30 °C, but returned to the desired temperature within ca. 5 min. Reaction timing started when the temperature stabilized. During the 24 h reaction time, the furnace temperature fluctuated by ± 5 °C. After the specified reaction time, the reactor was removed from the oven and cooled rapidly in a jet of compressed air to quench the reaction.

At the end of the reaction, the reactor was opened inside a fume hood and the gases were vented. The remaining material was transferred onto a fine glass frit (4.0-5.5 μ m), washed with hot (50 °C) chloroform, and filtered to remove insolubles. Soluble hydrocarbons were recovered by evaporating the chloroform under reduced pressure (0.1 Torr) overnight. The insoluble material, including the catalyst and hydrocarbons insoluble in hot chloroform, was recovered from the frit. After removing the chloroform residue by evacuating under reduced pressure (0.1 Torr) overnight, the insoluble material was weighed. The yield of insoluble hydrocarbons was calculated as the difference between the total mass of recovered solid and the initial mass of the catalyst. Since volatiles were not recovered in these experiments, their

yield was calculated as the difference between the initial mass of PE and that of the recovered soluble and insoluble hydrocarbons.

To characterize volatile reaction products, a mini-autoclave was modified with a gas outlet made from a Swagelok hose connector sealed with a hexagon socket head screw cap containing a Cu O-ring. The total internal volume of the reactor and the gas outlet, 13 mL, was measured by filling with water. The mini-autoclave and a Schlenk flask capped with a white rubber septum were connected via Tygon tubing to a glass vacuum line equipped with a pressure gauge and a port for gas sampling. The Schlenk flask and the lines were evacuated under reduced pressure (10^{-4} Torr), then isolated from the pumping system. The gases in the autoclave were expanded into the line by loosening the screw cap, and the pressure was measured. The volatiles yield was estimated using the total volume of the gas line and the Schlenk flask as measured by gas expansion (152 mL), and the ideal gas law. An aliquot of gas (400 μ L) was removed via the sampling port for analysis of H_2 by GC-TCD, using a gas-tight syringe. The Ar present in the autoclave at the start of the reaction (1 atm) was used as the internal standard. Propene, which is not a reaction product, was injected into the Schlenk tube as an internal standard for hydrocarbon analysis by GC-FID. An aliquot (0.2 mL) was then removed for analysis. The total GC yields of H_2 and light hydrocarbons are consistent with the total yield of gases based on pressure measurement, with a precision of $\pm 10\%$.

To analyze volatile hydrocarbons that may have been lost during solvent removal from the chloroform-soluble fraction, the reactor contents were transferred with the aid of chloroform (5 mL) into a Schlenk flask. The contents were distilled at 150 $^{\circ}$ C, while condensing volatile products and chloroform in a receiving flask cooled in a dry ice/acetone

bath. The clear, colorless distillate was transferred to a 10 mL volumetric flask, 2 mg mesitylene was added as an internal standard, and the flask was filled to the 10 mL mark with chloroform. The solution was analyzed on an Agilent 6890N Network Gas Chromatograph equipped with a DB-5 column and an FID detector, using response factors measured for toluene and light *n*-alkanes (C₇-C₁₁) relative to mesitylene. The total mass of recovered volatile products from distillation is small (ca. 1.5 mg, measured by GC-FID), with toluene being the major product. Some reactions were conducted in a larger autoclave reactor (Parr Series 5000 Multiple Reactor System, internal volume ca. 100 mL, stainless steel). The contents were stirred at 678 rpm, using a magnetic stir bar encapsulated in Pyrex. Timing of the reaction began when the internal temperature reached the set temperature, 250 °C; reported reaction times do not include the time (ca. 30 min) needed to heat the reactor from room temperature. Since the internal thermocouple is located above the solids in the reactor, it reads the temperature of the gas phase rather than the solid/liquid phase. The temperature of the autoclave wall was also measured externally with a thermometer and stabilized at (280 ± 5) °C during the reaction time. The autoclave was cooled to room temperature prior to opening, by immersing the bottom of the vessel in 25 °C water for 15 min. Gases were collected as described above. When the autoclave lid was removed, an oily liquid was observed to have adhered on the lid and separated from the catalyst at the bottom of the vessel. It was recovered by dissolving in hot chloroform, then evaporating the solvent under reduced pressure overnight. The solid products were transferred onto a fine glass frit, then washed with hot chloroform. The solvent was removed from the filtrate by evaporation overnight at 0.1 Torr. The insoluble material remaining on the frit, including the catalyst and insoluble

hydrocarbons, was recovered and weighed. The mass of insoluble hydrocarbons was calculated by subtracting the initial mass of the catalyst. Some hydrocarbons were not recovered during workup, due to the difficulty in washing the dead volumes in the connectors and valves of the autoclave.

2.5.3. Catalytic Conversion of *n*-C₃₀H₆₂

A mixture of 0.120 g *n*-C₃₀H₆₂ and 0.200 g Pt/ γ -Al₂O₃ was heated at (280 $\pm$ 5) °C under Ar for 24 h in mini-autoclaves. After the reaction, the gas products were analyzed by GC-TCD and GC-FID as described above. The remaining material was extracted with CHCl₃ at room temperature, separated from the insoluble catalyst as a yellow liquid, then, mesitylene (2.0 mg) was added as an internal standard. The solution was analyzed on an Agilent 6890N gas chromatograph equipped with a DB-5 column and an FID detector.

Peak assignments were made by comparing retention times to a standard mixture of *n*-alkanes (C₇ - C₄₀), standard mesitylene, as well as by matching to peaks identified by GC-MS with the aid of a mass spectral library (NIST 107). Among the liquid products, the major species are *n*-alkanes (C₇ - C₃₀). The minor products are mostly branched alkanes, with smaller contributions from cycloalkanes and alkylbenzenes. The presence of multiple isomers with overlapping peaks hindered more complete analysis. Nevertheless, hydrocarbons that elute together have the same carbon number and very similar response factors (within 3%). Therefore, based on the mass of mesitylene, the peak areas and response factors for each species, the absolute amount of each species could be obtained. Since there is a negligible amount of insoluble hydrocarbon in the solid.

2.6. References

1. Geyer, R., Jambeck, J.R., and Law, K.L. (2017). Production, use, and fate of all plastics ever made. *Sci. Adv.* 3, e1700782. 10.1126/sciadv.1700782.
2. Lebreton, L., and Andrady, A. (2019). Future scenarios of global plastic waste generation and disposal. *Palgrave Commun.* 5, 1–11. 10.1057/s41599-018-0212-7.
3. Eriksson, O., and Finnveden, G. (2009). Plastic waste as a fuel - CO₂-neutral or not? *Energy Environ. Sci.* 2, 907–914. 10.1039/b908135f.
4. Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., and Law, K.L. (2015). Plastic waste inputs from land into the ocean. *Science* 347, 768–771. 10.1126/science.1260352.
5. Chamas, A., Moon, H., Zheng, J., Qiu, Y., Tabassum, T., Jang, J.H., Abu-Omar, M., Scott, S.L., and Suh, S. (2020). Degradation Rates of Plastics in the Environment. *ACS Sustain. Chem. Eng.* 8, 3494–3511. 10.1021/acssuschemeng.9b06635.
6. Rahimi, A., and García, J.M. (2017). Chemical recycling of waste plastics for new materials production. *Nat. Rev. Chem.* 1, 1–11. 10.1038/s41570-017-0046.
7. Zhu, Y., Romain, C., and Williams, C.K. (2016). Sustainable polymers from renewable resources. *Nature* 540, 354–362. 10.1038/nature21001.
8. Vollmer, I., Jenks, M.J.F., Roelands, M.C.P., White, R.J., van Harmelen, T., de Wild, P., van der Laan, G.P., Meirer, F., Keurentjes, J.T.F., and Weckhuysen, B.M. (2020). Beyond Mechanical Recycling: Giving New Life to Plastic Waste. *Angew. Chem. Int. Ed.* 59, 15402–15423. 10.1002/anie.201915651.

9. Ignatyev, I.A., Thielemans, W., and Vander Beke, B. (2014). Recycling of Polymers: A Review. *ChemSusChem* 7, 1579–1593. 10.1002/cssc.201300898.
10. Anuar Sharuddin, S.D., Abnisa, F., Wan Daud, W.M.A., and Aroua, M.K. (2016). A review on pyrolysis of plastic wastes. *Energy Convers. Manag.* 115, 308–326. 10.1016/j.enconman.2016.02.037.
11. Dufaud, V., and Basset, J.-M. (1998). Catalytic Hydrogenolysis at Low Temperature and Pressure of Polyethylene and Polypropylene to Diesels or Lower Alkanes by a Zirconium Hydride Supported on Silica-Alumina: A Step Toward Polyolefin Degradation by the Microscopic Reverse of Ziegler–Natta Polymerization. *Angew. Chem. Int. Ed.* 37, 806–810. 10.1002/(SICI)1521-3773(19980403)37:6<806::AID-ANIE806>3.0.CO;2-6.
12. Celik, G., Kennedy, R.M., Hackler, R.A., Ferrandon, M., Tennakoon, A., Patnaik, S., LaPointe, A.M., Ammal, S.C., Heyden, A., Perras, F.A., et al. (2019). Upcycling Single-Use Polyethylene into High-Quality Liquid Products. *ACS Cent. Sci.* 5, 1795–1803. 10.1021/acscentsci.9b00722.
13. Jia, X., Qin, C., Friedberger, T., Guan, Z., and Huang, Z. (2016). Efficient and selective degradation of polyethylenes into liquid fuels and waxes under mild conditions. *Sci. Adv.* 2, e1501591. 10.1126/sciadv.1501591.
14. Rahimpour, M.R., Jafari, M., and Iranshahi, D. (2013). Progress in catalytic naphtha reforming process: A review. *Appl. Energy* 109, 79–93. 10.1016/j.apenergy.2013.03.080.
15. Perego, C., and Ingallina, P. (2002). Recent advances in the industrial alkylation of aromatics: new catalysts and new processes. *Catal. Today* 73, 3–22. 10.1016/S0920-5861(01)00511-9.

16. Kanitkar, S.R., and Spivey, J.J. (2018). Light alkane aromatization: efficient use of natural gas. *Nat. Gas Process. Midstream Downstr.*, 379–401.
17. Yarulina, I., Chowdhury, A.D., Meirer, F., Weckhuysen, B.M., and Gascon, J. (2018). Recent trends and fundamental insights in the methanol-to-hydrocarbons process. *Nat. Catal.* 1, 398–411. 10.1038/s41929-018-0078-5.
18. Cheng, K., Zhou, W., Kang, J., He, S., Shi, S., Zhang, Q., Pan, Y., Wen, W., and Wang, Y. (2017). Bifunctional Catalysts for One-Step Conversion of Syngas into Aromatics with Excellent Selectivity and Stability. *Chem* 3, 334–347. 10.1016/j.chempr.2017.05.007.
19. Wang, Q.-N., Weng, X.-F., Zhou, B.-C., Lv, S.-P., Miao, S., Zhang, D., Han, Y., Scott, S.L., Schüth, F., and Lu, A.-H. (2019). Direct, Selective Production of Aromatic Alcohols from Ethanol Using a Tailored Bifunctional Cobalt–Hydroxyapatite Catalyst. *ACS Catal.* 9, 7204–7216. 10.1021/acscatal.9b02566.
20. Maneffa, A., Priecel, P., and Lopez-Sanchez, J.A. (2016). Biomass-Derived Renewable Aromatics: Selective Routes and Outlook for p-Xylene Commercialisation. *ChemSusChem* 9, 2736–2748. 10.1002/cssc.201600605.
21. Williams, C.L., Chang, C.-C., Do, P., Nikbin, N., Caratzoulas, S., Vlachos, D.G., Lobo, R.F., Fan, W., and Dauenhauer, P.J. (2012). Cycloaddition of Biomass-Derived Furans for Catalytic Production of Renewable p-Xylene. *ACS Catal.* 2, 935–939. 10.1021/cs300011a.
22. Lopez, G., Artetxe, M., Amutio, M., Bilbao, J., and Olazar, M. (2017). Thermochemical routes for the valorization of waste polyolefinic plastics to produce fuels and chemicals. A review. *Renew. Sustain. Energy Rev.* 73, 346–368. <https://doi.org/10.1016/j.rser.2017.01.142>.

23. Inaba, A., and Kashiwagi, T. (1986). A calculation of thermal degradation initiated by random scission. 1. Steady-state radical concentration. *Macromolecules* 19, 2412–2419. 10.1021/ma00163a014.
24. Behera, B., Ray, S.S., and Singh, I.D. (2007). Chapter 12 NMR studies of FCC feeds, catalysts and coke. In *Studies in Surface Science and Catalysis Fluid Catalytic Cracking VII Materials, Methods and Process Innovations.*, M. L. Ocelli, ed. (Elsevier), pp. 163–200. 10.1016/S0167-2991(07)80195-9.
25. Luo, S., Ho, S.C., and Wu, M.M. (2020). Alkylated Aromatics. *Synth. Miner. Oils Bio-Based Lubr. Chem. Technol.*, 161.
26. Ahuja, R., Punji, B., Findlater, M., Supplee, C., Schinski, W., Brookhart, M., and Goldman, A.S. (2011). Catalytic dehydroaromatization of *n*-alkanes by pincer-ligated iridium complexes. *Nat. Chem.* 3, 167–171. 10.1038/nchem.946.
27. Mostad, H.B., Riis, T.U., and Ellestad, O.H. (1990). Catalytic cracking of naphthenes and naphtheno-aromatics in fixed bed micro reactors. *Appl. Catal.* 63, 345–364. 10.1016/S0166-9834(00)81724-8.
28. Zhu, Q.-L., and Xu, Q. (2015). Liquid organic and inorganic chemical hydrides for high-capacity hydrogen storage. *Energy Environ. Sci.* 8, 478–512. 10.1039/C4EE03690E.
29. Pradhan, S., Lloyd, R., Bartley, J.K., Bethell, D., Golunski, S., Jenkins, R.L., and Hutchings, G.J. (2012). Multi-functionality of Ga/ZSM-5 catalysts during anaerobic and aerobic aromatisation of *n*-decane. *Chem. Sci.* 3, 2958. 10.1039/c2sc20683h.
30. Linstrom, P. (1998). NIST chemistry webbook, NIST standard reference database number 69. *J Phys Chem Ref Data Monogr.* 9, 1–1951.

31. Flaherty, D.W., and Iglesia, E. (2013). Transition-State Enthalpy and Entropy Effects on Reactivity and Selectivity in Hydrogenolysis of *n*-Alkanes. *J. Am. Chem. Soc.* *135*, 18586–18599. 10.1021/ja4093743.
32. Carter, J.L., Cusumano, J.A., and Sinfelt, J.H. (1971). Hydrogenolysis of *n*-heptane over unsupported metals. *J. Catal.* *20*, 223–229. 10.1016/0021-9517(71)90083-2.
33. Gozum, J.E., Pollina, D.M., Jensen, J.A., and Girolami, G.S. (1988). “Tailored” organometallics as precursors for the chemical vapor deposition of high-purity palladium and platinum thin films. *J. Am. Chem. Soc.* *110*, 2688–2689. 10.1021/ja00216a073.
34. JR, V.G., and Goto, T. (2003). Chemical vapor deposition of iridium, platinum, rhodium and palladium. *Mater. Trans.* *44*, 1717–1728. 10.2320/matertrans.44.1717.
35. Marinho, R.S., Silva, C.N. da, Afonso, J.C., and Cunha, J.W.S.D. da (2011). Recovery of platinum, tin and indium from spent catalysts in chloride medium using strong basic anion exchange resins. *J. Hazard. Mater.* *192*, 1155–1160. 10.1016/j.jhazmat.2011.06.021.
36. Macala, G.S., Matson, T.D., Johnson, C.L., Lewis, R.S., Iretskii, A.V., and Ford, P.C. (2009). Hydrogen Transfer from Supercritical Methanol over a Solid Base Catalyst: A Model for Lignin Depolymerization. *ChemSusChem* *2*, 215–217. 10.1002/cssc.200900033.

2.7. Appendix I

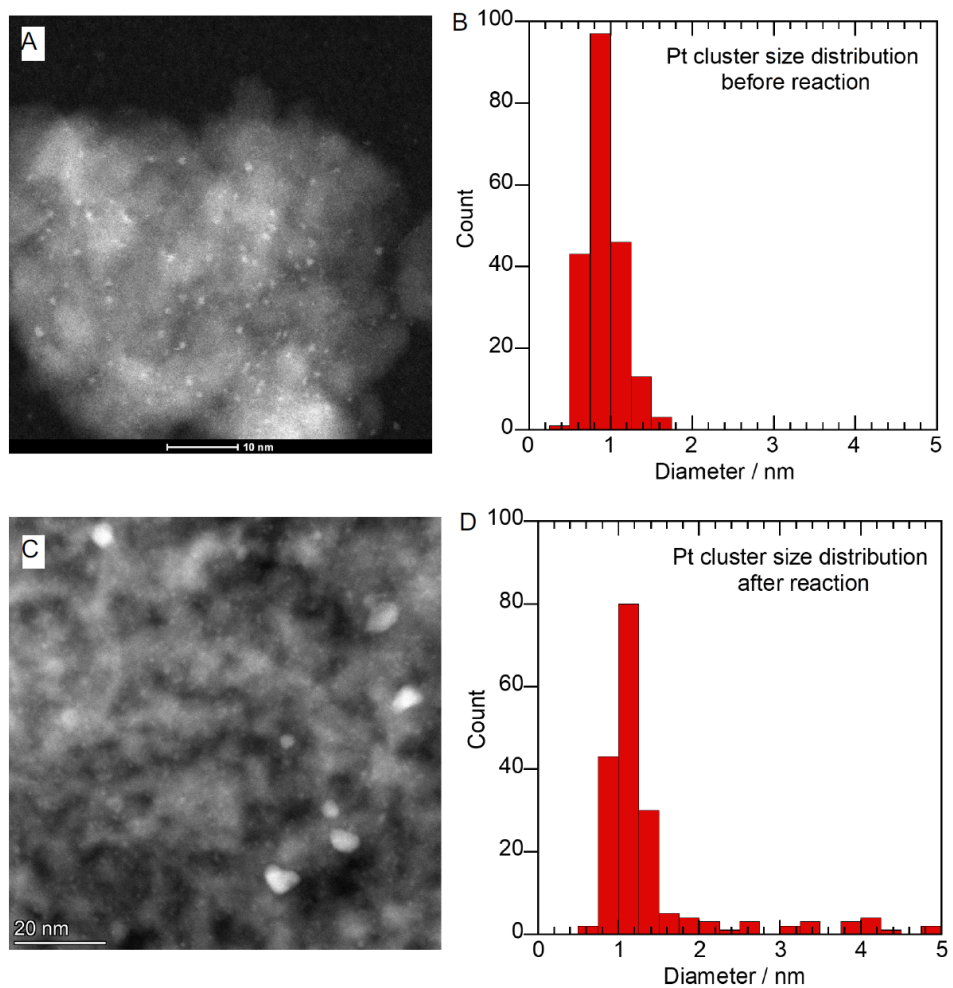


Figure A2.1. (A-B) HAADF-STEM images of fresh Pt/ γ -Al₂O₃, and (C-D) histograms showing Pt cluster size distribution.

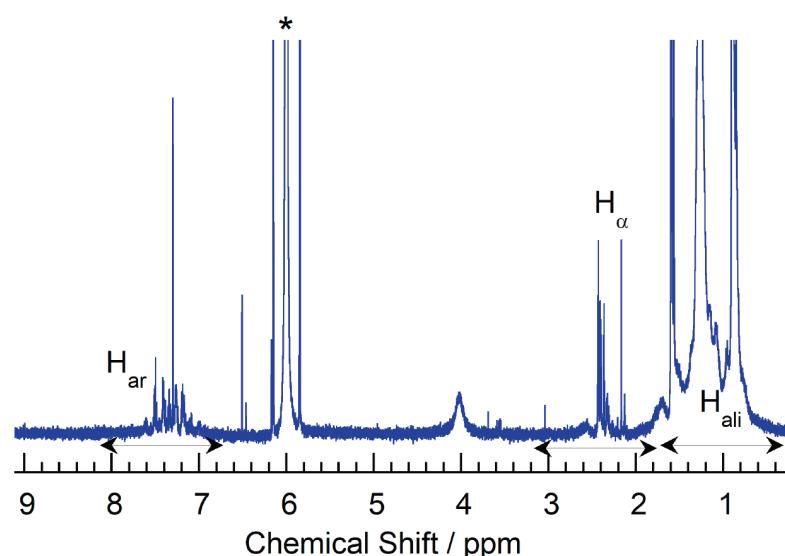


Figure A2.2. ^1H NMR spectrum (recorded at room temperature) of the soluble component recovered from the solid residue after stirring in $\text{TCE-}d_2$ at $150\text{ }^\circ\text{C}$ for 21 h. PE ($M_w = 3.52 \times 10^3\text{ g mol}^{-1}$, $M_n = 1.85 \times 10^3\text{ g mol}^{-1}$, $\bar{D} = 1.9$, average C_{132}) was heated with Pt/ $\gamma\text{-Al}_2\text{O}_3$ (1.5 wt% Pt) in a mini-autoclave at $280\text{ }^\circ\text{C}$ for 24 h. * indicates residual protons in the solvent ($\text{TCE-}d_2$).

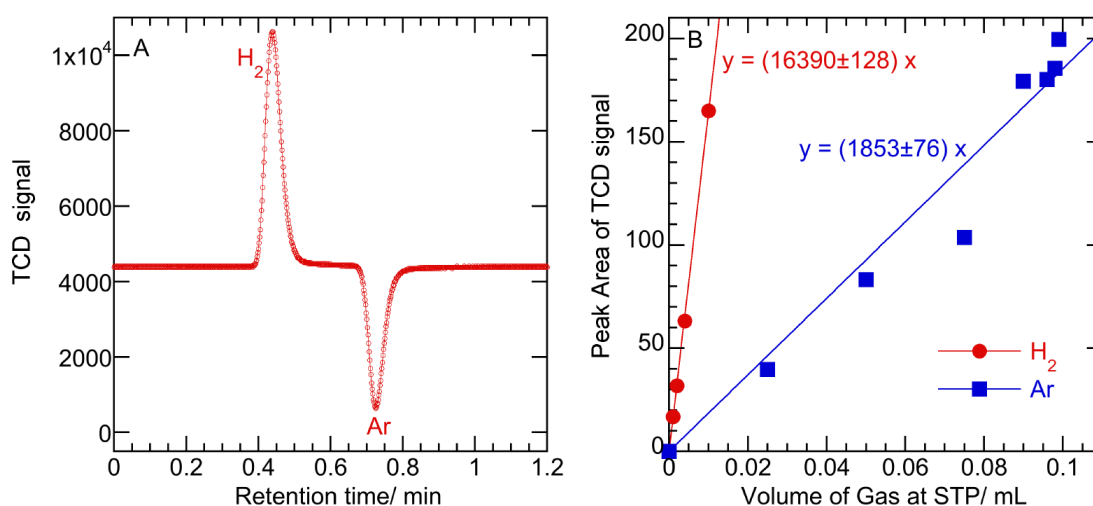


Figure A2.3. (A) GC-TCD of gases collected after the catalytic disassembly of PE ($M_w = 3.52 \times 10^3 \text{ g mol}^{-1}$), by heating with 1.5 wt% Pt/ γ - Al_2O_3 for 24 h at 280 °C in a 13 mL mini-autoclave, with Ar (12.8 mL, 1 atm) present as internal standard; (B) TCD calibration curve for H_2 and Ar. The molar ratio of H_2 to Ar was determined from the peak areas and response factors.

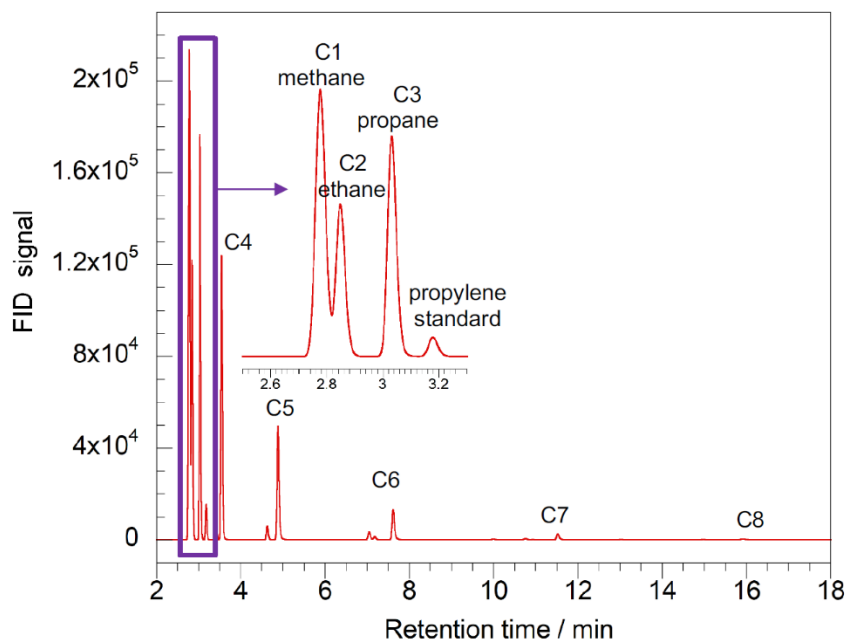


Figure A2.4. GC-FID of gases collected after catalytic disassembly of PE ($M_w = 3.52 \times 10^3 \text{ g mol}^{-1}$), by heating with 1.5 wt% Pt/ γ - Al_2O_3 for 24 h at 280 °C in a 13 mL mini-autoclave. Propene was added as an internal standard. Relative carbon response factors were assumed to be 1.0.

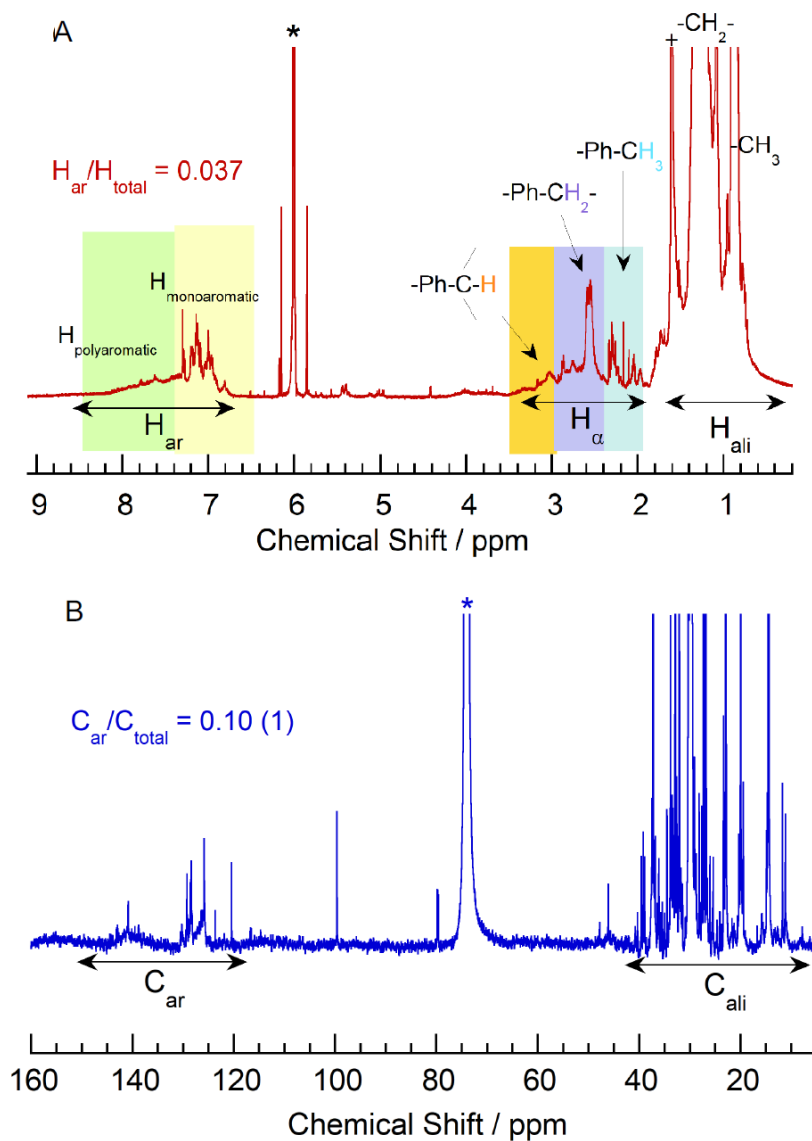


Figure A2.5. NMR spectra of the chloroform-soluble wax product obtained from the solvent-free depolymerization of PE ($M_n = 1.85 \times 10^3 \text{ g mol}^{-1}$, $\bar{D} = 1.9$, average C_{132}) in a Parr autoclave reactor, after 24 h at 280 °C: (A) ^1H NMR spectrum; and (B) ^{13}C NMR spectrum. * indicates the solvent ($\text{TCE-}d_2$).

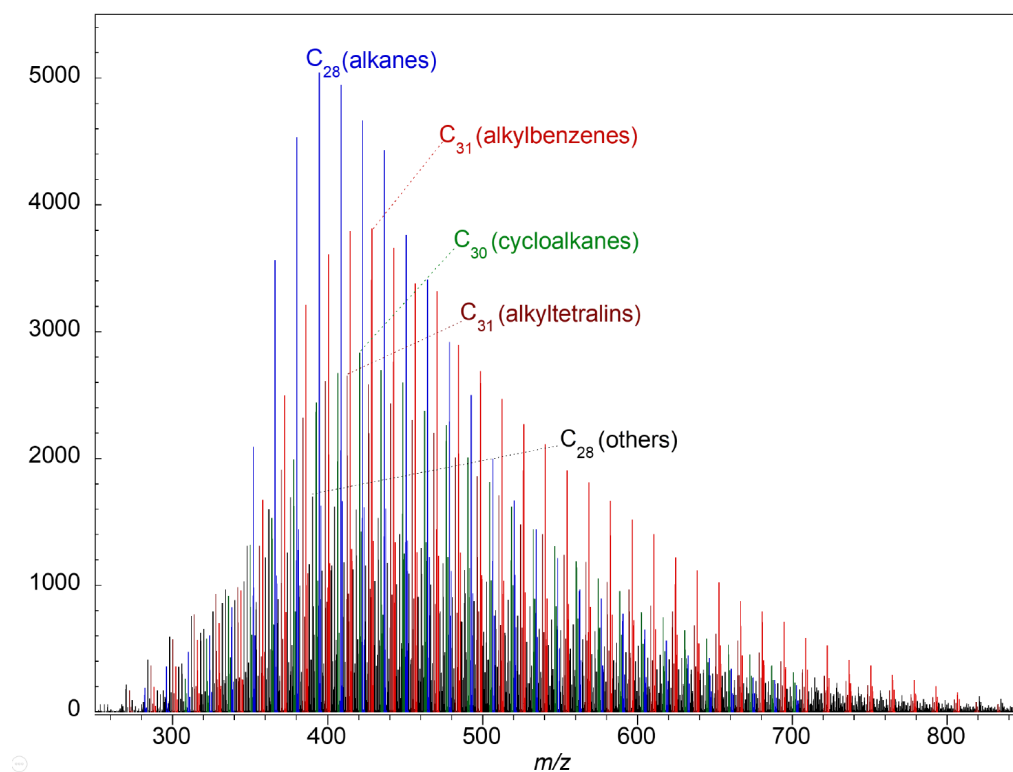


Figure A2.6. Full-range FD-MS analysis of lighter hydrocarbons from the solvent-free conversion of PE ($M_w = 3.52 \times 10^3 \text{ g mol}^{-1}$, $M_n = 1.85 \times 10^3 \text{ g mol}^{-1}$, $\bar{D} = 1.9$, average C_{132}), catalyzed by 1.5 wt% Pt/ $\gamma\text{-Al}_2\text{O}_3$ at 280 °C in Parr reactor for 24 h. The carbon number labels indicate the highest peak intensity within each color-coded mass series. The black series includes dicyclopaffins ($14n-2$), alkylanthracenes ($14n-4$) and benzodicyclopaffins ($14n-10$).

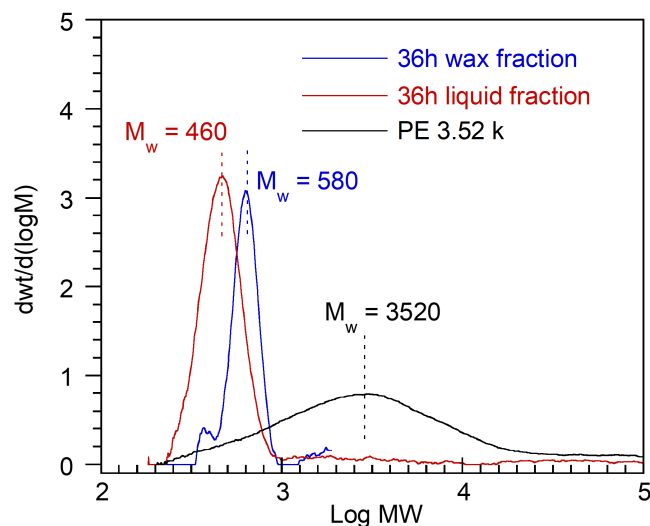


Figure A2.7. GPC and molecular weight distribution of lighter and heavier fractions of liquid/wax products from the catalytic disassembly of PE ($M_w = 3.52 \times 10^3 \text{ g mol}^{-1}$, $\bar{D} = 1.9$, average C_{132}), after heating with 1.5 wt% Pt/ γ - Al_2O_3 for 36 h at 280 °C in Parr reactor.

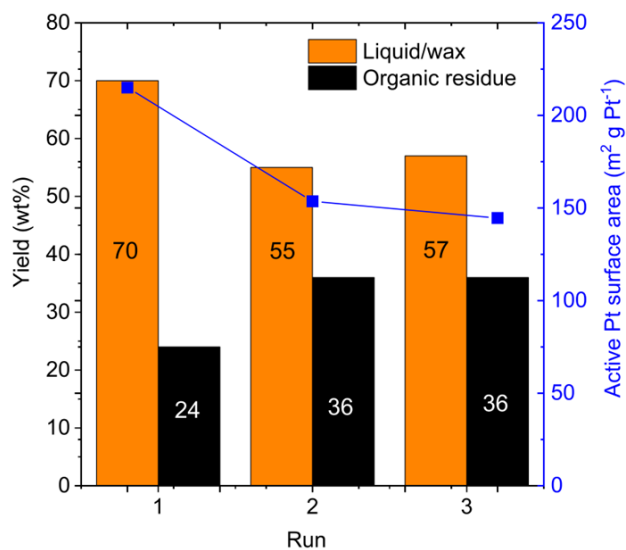


Figure A2.8. Comparison of yields of liquid/wax products and organic residue, as well as the active Pt surface area ($\text{m}^2 \text{ g Pt}^{-1}$) of fresh and recycled catalyst measured by CO chemisorption

prior to reaction, in three consecutive catalytic reactions of PE catalyzed by Pt/ γ -Al₂O₃ (**Table A2.4**, experiments S4-6). The yield of liquid/wax and organic residue of first and second run are average from two duplicate reactions.

Table A2.1. Mass series of hydrocarbon products observed by FD-MS

m/z	Alternate m/z	Most probable assignment	Alternate assignments
14n		cycloalkanes	diphenylparaffins, naphthocycloparaffins
14n + 2	14n-12	alkanes, alkylnaphthalenes	
14n + 4	14n-10	benzodicycloparaffins	
14n + 6	14n-8	benzocycloparaffins	
14n + 8	14n-6	alkylbenzenes	
14n + 10	14n-4	alkylanthracenes/phenanthrenes	tricycloparaffins
14n + 12	14n-2	dicycloparaffins	alkylphenalenes, alkylfluorenes

Table A2.2. GPC and ^1H NMR characterization of liquid/wax hydrocarbons recovered from the tandem conversion of various PEs *

Exp.	Reactor		Products								Total S _{Ar}	
	PE	Volume										
	<i>M_n</i>		Yield	<i>M_n</i>	<i>D</i>	$\frac{H_{Ar}}{H_{total}}$	$\frac{H_{mono}}{H_{poly}}$	<i>S</i> _{Ar} [‡]	$\frac{C_{Ar}}{C_{total}}$	<i>S</i> _{Ar} [§]	mol%	
	g mol ⁻¹	mL	%	g mol ⁻¹				mol%		mol%		
0 [¶]	1.85 x10 ³	10	34	768	1.9	-	-	-				
1	(<i>D</i> = 1.9)	10	80	328	1.3	0.039	0.9	40(3)				
2		13	75	414	1.2	0.040	1.1	52(4)				
3		90	46	466	1.1	0.037	1.6	57(5)	0.10	52(4)		
			24	538	1.3	0.047	1.0	77(6)	0.11	61(5)	64(5)	
S1		90	42	431	1.1	0.054	2.3	75(5)	0.13	64(5)		
			13	551	1.1	0.058	1.0	92(7)	0.16	91(7)	81(6)	
4	12.8 x10 ³	90	39	366	1.1	0.031	1.8	39(3)	0.09	37(3)		
	(<i>D</i> = 7.4)		30	355	1.1	0.045	1.1	50(4)	0.10	39(4)	44(4)	
5	14.8 x10 ³	90	20	347	1.1	0.041	1.8	46(4)				
	(<i>D</i> = 3.6)		35	353	1.3	0.047	1.0	52(4)			50(4)	

* Reaction conditions: 118 mg reactant, 200 mg catalyst (Pt/ γ - Al_2O_3 , 1.5 wt%), 280 °C, 24 h (except Exp S1 for 36 h). Two entries are presented for the same experiment, the liquid/wax hydrocarbon products were collected and analyzed separately. [‡] Selectivity to alkylaromatics (S_{Ar}) calculated based on analysis of ^1H NMR spectrum. [§] Selectivity to alkylaromatics (S_{Ar}), calculated based on analysis of

¹³C NMR spectrum. Uncertainties are propagated from the uncertainty in the average carbon number.

[†] Reaction with γ -Al₂O₃ support only.

Table A2.3. FD-MS selectivities for various mass series in the liquid hydrocarbons recovered from tandem PE conversion *

Mass series	Major assignment	Method 1 [†]		Method 2 [‡]	
		area	%	area	%
14n	cycloparaffins	63270	17	5282	19
14n+2	alkanes, alkylnaphthalenes	77706	20	5914	21
14n+4	benzodicycloparaffins	31089	8	2200	8
14n+6	benzocycloparaffins	60489	16	3714	14
14n+8	alkylbenzenes	85390	22	5229	19
14n+10	alkylanthracenes, etc.	27776	7	2117	8
14n+12	dicycloparaffins	37993	10	3047	11
Total		383713	100	27504	100
monoaromatics			46		41
Polyaromatics [§]			15		14
paraffins			39		45

* Exp. 3 (see main text). [†] Based on peak heights. [‡] Based on peak areas. [§] The ratio ¹H_{mono}/¹H_{poly} = 1.6

was used to calculate the fractional contribution of alkylnaphthalenes in the (14n+2) mass species.

Table A2.4. GPC and ^1H NMR characterization of liquid/wax hydrocarbons recovered from the tandem conversion of triacontane and PE*

Exp.	Reactant	Reactor	Products							Active Pt surface
		volume	Yield	M_n	$\bar{D}$	C_{avg}	$\frac{H_{\text{Ar}}}{H_{\text{total}}}$	$\frac{H_{\text{mono}}}{H_{\text{poly}}}$	S_{Ar}	area
		mL	%	g mol^{-1}		$\dagger$			$\ddagger$	$\text{m}^2 \text{ g}_{\text{Pt}}^{-1}$
				1					%	
S2	$\text{C}_{30}\text{H}_{62}$	10	70	-	-	17 $\ddagger\ddagger$	0.012	2.2	9	--
S3		13	72	-	-	20 $\ddagger\ddagger$	0.016	2.1	14	--
S4	PE	10 $\S$	70(2)	328	1.9	23	0.017	2.0	18	215.2
			$\P$							
S5		10 $\#$	55(2)	628	2.2	45	0.013	3.4	27	153.6
			$\P$							
S6		10 $\ast\ast$	57	694	2.6	50	0.008	2.8	18	144.6
S7		90 $\dagger\dagger$	4	234	1.1	17	0.017	1.1	14	--
			46	373	1.3	27	0.021	1.8	27	

* Reaction conditions: 118 mg reactant (triacontane or PE, $M_n = 1.85 \times 10^3 \text{ g mol}^{-1}$, $\bar{D} = 1.90$), 200 mg reduced catalyst (Pt/ γ - Al_2O_3 , 1.5 wt% Pt), 280 °C for 24 h except where noted. $\dagger$ Calculated as $M_n/14$.

$\ddagger$ Selectivity for alkylaromatics (S_{Ar}), calculated based on analysis of ^1H NMR spectrum. $\S$ Calculated based on CO chemisorption. $\#$ Two parallel reactions in two 10 mL mini-autoclaves at 280 °C for 6 h using fresh catalyst. $\P$ The yield of liquid/wax in Exps. S4 and S5 are the average of two duplicate reactions, with the variance in parentheses. $\ast\ast$ Two parallel reactions in two 10 mL mini-autoclaves at

280 °C for 6 h using once-recycled catalyst. ** Reaction in 10 mL mini-autoclave at 280 °C for 6 h using twice-recycled catalyst. †† Reaction with 1.1 g PE reactant and 1.8 g catalyst at 280 °C. Liquid/wax hydrocarbon products were collected and analyzed separately. †† Calculated based on GC-FID analysis.

Table A2.5. GPC and ¹H NMR of liquid/wax hydrocarbons recovered from tandem PE conversion, as a function of reaction time*

Exp.	Time	Products						
		Yield	M_w	M_n	$\bar{D}$	$C_{avg}^{\dagger}$	$\frac{H_{Ar}}{H_{total}}$	$\frac{H_{mono}}{H_{poly}}$
	h	%	g mol ⁻¹	g mol ⁻¹				
1a	1.0 [‡]	-	4156	1758	2.36	126	-	-
1b	3.0 [‡]	-	2350	1110	2.11	79	-	-
1c	3.0	21	1177	789	1.49	56	0.004	3.8
1d	4.5 [‡]	-	1084	584	1.86	42	-	-
1e	6.0	66	716	424	1.69	30	0.018	2.0
1f	12.0	70	460	302	1.52	22	0.024	1.8
1g [§]	24.0	80	430	328	1.31	23	0.039	0.9

* Reaction conditions: 118 mg PE ($M_n = 1.85 \times 10^3$ g mol⁻¹, $\bar{D} = 1.90$), 200 mg catalyst (Pt/ γ -Al₂O₃, 1.5 wt% Pt), 280 °C, 10 mL mini-autoclave. Each experiment was performed independently (not as continuous sampling from one experiment). [†] Calculated as $M_n/14$. [‡] GPC analysis was performed on the crude reaction mixture. [§] This experiment is the same as Exp. 1 in **Figure 2.2B** and **Table A2.2**.

Chapter 3. Bifunctional Tandem Catalytic Upcycling of Polyethylene to Surfactant-Range Alkylaromatics

Note: This chapter was adapted from the following publication.

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3.1. Abstract

Catalytic conversion of waste polyolefins to value-added alkylaromatics could contribute to carbon recycling. Compared to tandem hydrogenolysis/aromatization of polyethylene (PE) catalyzed by Pt/ γ -Al₂O₃ at 280°C, both a five-fold enhancement in the rate of C-C bond scission and a doubling of the molar yield of alkylaromatics were realized using a more acidic Pt/F-Al₂O₃ catalyst instead. Bifunctional (metal/acid) catalysts also generate alkylaromatic products with lower average carbon numbers (ca. C₂₀), similar to conventional anionic surfactants. Since physical mixtures of weakly acidic Pt/ γ -Al₂O₃ or non-acidic Pt/SiO₂ with strongly Brønsted acidic Cl-Al₂O₃ or F-Al₂O₃ are also effective, the tandem reaction does not require nano-scale intimacy between metal and acid active sites. Kinetic studies using triacontane (*norm*-C₃₀H₆₂) as a model for PE show that the Pt-catalyzed dehydrogenation/hydrogenation reactions are quasi-equilibrated, while the acid-catalyzed C-C bond scission and skeletal transformations (isomerization and cyclization) determine the overall rates of depolymerization and aromatic formation.

3.2. Introduction

Polyolefins (POs) are widely used as materials for packaging, construction, transportation, electronics and in many other applications because of their excellent strength-to-weight ratio, wear resistance, chemical inertness, and low cost. More than 9 billion metric tons of plastics have been manufactured since 1950,¹ with global annual plastic production reaching ca. 370 million tons in 2019. Just two POs: polyethylene (PE) and polypropylene (PP), comprise about half of all plastics production.¹ Plastic manufacturing is projected to triple by 2050, by when it could consume as much as 20% of global petroleum production.²

A major use of POs is in single-use packaging, and they represent a major fraction of plastic waste. Despite the desire to scale back single-use plastics, the volume actually expanded during the recent COVID-19 pandemic, due to increased demand for personal protective equipment and expanded use of disposable and take-away packaging,³ resulting in an additional 8 million tons of pandemic-associated plastic waste as of August, 2021.⁴ Worldwide, the fate of most plastic waste is either landfilling (~40%) or incineration (~25%). These disposal choices produce carbon emissions,⁵ environmental pollution, and emergent human/ecosystem health concerns.^{6,7} Mismanagement of a significant fraction (~19%) of plastic waste leads to uncontrolled litter,⁸ although the magnitude of the problem varies widely across different geographic regions. Overall, only 9% of waste plastics are currently destined for mechanical recycling.⁸ It results in, at best, materials with similar intrinsic value, but more often with lower value because of contamination issues, and because the mechanical shear degrades the physicochemical properties of the polymers.

Chemical conversion of used plastics to higher value products is not widely practiced today, but could expand the recyclable fraction of waste plastics and create new valuable materials (open-loop upcycling).^{9,10} Unfortunately, POs are typically recalcitrant to chemical recycling due to their lack of chemical functionality and low solubility. Until recently, these processes focused on producing low-value gasoline- and/or diesel-range hydrocarbons for combustion as transportation fuels,¹¹ or use as hydrocarbon-based lubricants.^{12–18} The most accessible chemical conversion technology today is pyrolysis, which is typically performed at temperatures over 400°C and leads to pyrolysis oils that can be further cracked to generate light alkenes that are raw materials for virgin POs. Catalysts can reduce the required reaction temperatures (catalytic cracking),¹⁹ however, the products are still largely unselective mixtures of light alkanes, naphthenes, and aromatic hydrocarbons and are accompanied by low-value coke, which poisons catalyst active sites.^{20,21} Coke formation can be suppressed by adding H₂, directing the product slate towards alkanes.^{22,12} Lower temperature approaches that couple (transfer) dehydrogenation with alkene isomerization and metathesis can generate light alkanes and alkenes directly and, in some cases, selectively.^{23–25} Several approaches to the partial chemical depolymerization of PE are illustrated in **Figure 3.1**.

Long-chain alkylaromatics are high-value chemicals with commercial applications as solvents, refrigeration fluids, and precursors to anionic surfactants.²⁶ In our recent report, a recyclable Pt/ γ -Al₂O₃ catalyst converted various types of PE to aromatic hydrocarbons with average carbon number C_{~30}.²⁷ The alkylaromatics are thermodynamically accessible from PE at moderate temperatures (ca. at 280°C) in the absence of external H₂ because of the coupling of endothermic dehydroaromatization with exothermic C-C bond hydrogenolysis. Since the

polymer is both H₂ source and sink, the accessible aromatic yields are higher than when the feedstock is a low-molecular weight alkane. However, depolymerization catalyzed by Pt/ γ -Al₂O₃ proceeds slowly, and the alkyl side-chains are longer than desired for direct use in anionic surfactants (which typically require total carbon numbers C₁₆₋₂₂, corresponding to the so-called “surfactant range”).²⁸

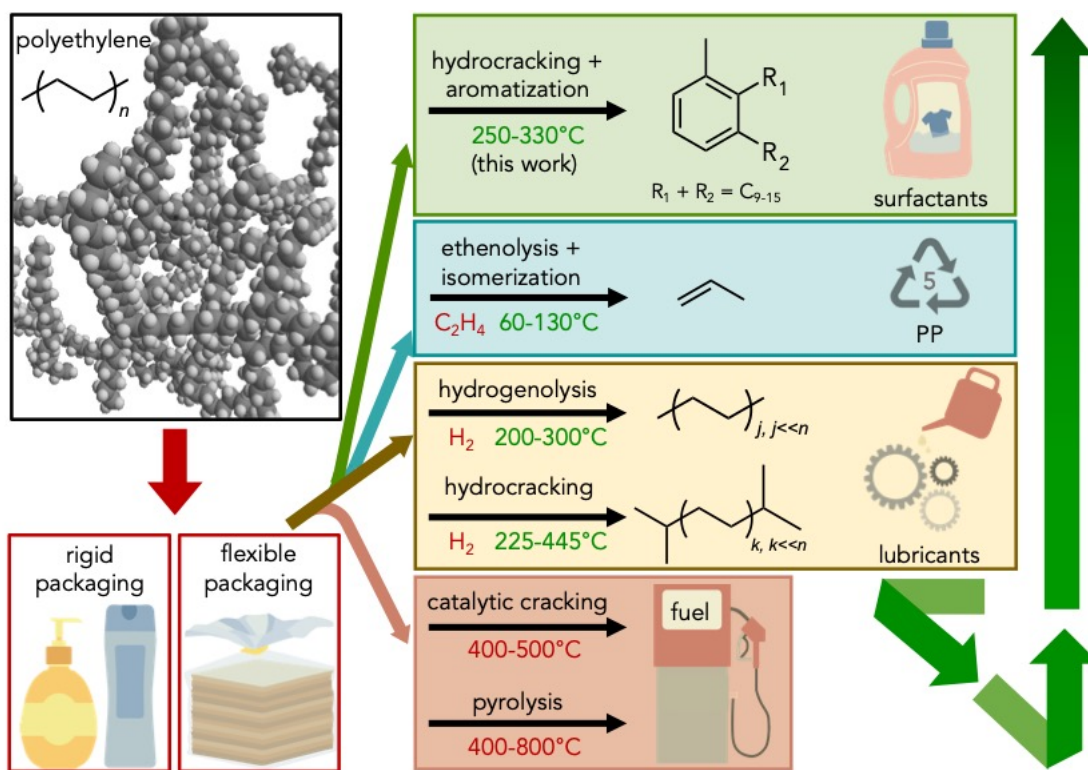


Figure 3.1. Some of the chemical approaches to polyethylene (PE) upcycling, by partial depolymerization to value-added products.

Halogenated aluminas have long been used in large-scale catalytic reforming.^{29,30} A typical reforming catalyst consists of Pt nanoparticles supported on γ -Al₂O₃ modified with 1-

2 wt % Cl,^{30,31} where the Cl serves to enhance the surface acidity.³² Inspired by this bifunctional design, we reformulated our original PE depolymerization catalyst to accelerate the tandem reaction, and to target surfactant-range alkylaromatics. Pt nanoparticles were supported on a variety of acidic solids to investigate the effect of acidity on the rate of C-C bond cleavage and the selectivity to alkylaromatic products.

3.3. Results and Discussion

3.3.1. Effect of Support Acidity on PE Depolymerization

To increase catalyst acidity, a series of catalysts was prepared by supporting Pt on various aluminas (unmodified, or modified with either Cl or F). All materials had similar Pt loadings (ca. 1.5 wt %) and dispersions (70-87 %), **Table 3.1**. Depolymerization of low-molecular-weight PE was conducted in a stirred autoclave at $(280 \pm 5)^{\circ}\text{C}$, without added H_2 or solvent. The reaction time (8 h) was limited to ensure comparison of the outcomes at less than full conversion. Each catalyst converted the PE to a mixture of light hydrocarbon gases, an orange liquid, and residual carbon present as a black solid mixed with the catalyst.

Table 3.1. Acidic Pt catalysts and the properties of their liquid hydrocarbon products from PE depolymerization ^a

Catalyst	Pt ^b		X (Cl or F)	Liquid hydrocarbon products ^c				
	Loading	<i>D</i>	Loading	Yield	Aromatics Yield	$\bar{t}$ ^h	$\bar{D}$ ⁱ	
	(wt %)	(%)	(wt %) ^d	(wt %) ^e	(μ mol) ^f	(wt %) ^g		
Pt/ γ -Al ₂ O ₃	1.5	87	-	44	59	36	52	2.2

Pt/Cl-Al ₂ O ₃	1.5	82	1.4	70	92 ^j	27 ^j	25 ^j	1.2 ^j
Pt/F-Al ₂ O ₃	1.6	70	0.8	64	131	36	24	1.1
Pt/F-Al ₂ O ₃ ^k	1.6	70	0.8	59	124	35	23	1.1
Pt/ γ -Al ₂ O ₃	1.5	87		61	146	29	17	1.1
+ F-Al ₂ O ₃ ^l			1.3					

^a Reaction conditions: PE (0.120 g, $M_w = 3.5 \times 10^3$ g mol⁻¹, $\bar{D} = 1.9$), total catalyst mass 0.200 g (except where noted), Ar, (280 ± 5)°C, 8 h.

^b Pt loading measured by ICP-OES. Pt dispersion (D) measured by CO chemisorption, assuming CO/Pt_{surf} = 1.³³

^c Soluble in hot CH₂Cl₂.

^d Measured by ion chromatography.

^e Excluding the lighter hydrocarbons (C₇-C₁₁) eliminated during solvent removal (**Figure A3.20**).

^f Calculated from $\bar{r}$ and the ¹H NMR integration in the aromatic region (see **Section 3.8.2.7** and **eq A3.30** and **A3.31** in the Appendix II).

^g The mass yield of aromatics is estimated as liquid yield (wt %) × S_{arom} (wt %), where S_{arom} (wt %) ≈ S_{arom} (mol %, estimated using **eqs A3.25-A3.27**). The justification for these assumptions is presented in **Section 3.8.2.7** of the Appendix II.

^h Average carbon number, calculated as $M_n/14$ based on GPC-RI analysis of the liquid after solvent removal (**Table A3.6**).

ⁱ Dispersity ($\bar{D} = M_w/M_n$) after solvent removal, as measured by GPC-RI.

^j Exceptionally in this experiment, a bimodal molecular weight distribution was observed, due to skeletal isomerization of the polymer and its resulting increased solubility. Results are given for the lower M_n peak of the bimodal distribution, corresponding to a mass fraction of 45 wt% (**Figure**

A3.23B). For the higher M_n peak, corresponding to a mass fraction of 55 wt%, $\bar{t} = 67$, $D = 2.6$. The value of $\bar{t}$ overall (weighted average of both peaks) is 39.

^k Reaction conducted with a higher molecular weight PE (0.120 g, $M_w = 2.6 \times 10^4$ g mol⁻¹, $D = 3.9$).

^l Physical mixture of Pt/ γ -Al₂O₃ (0.200 g) and F-Al₂O₃ (0.100 g).

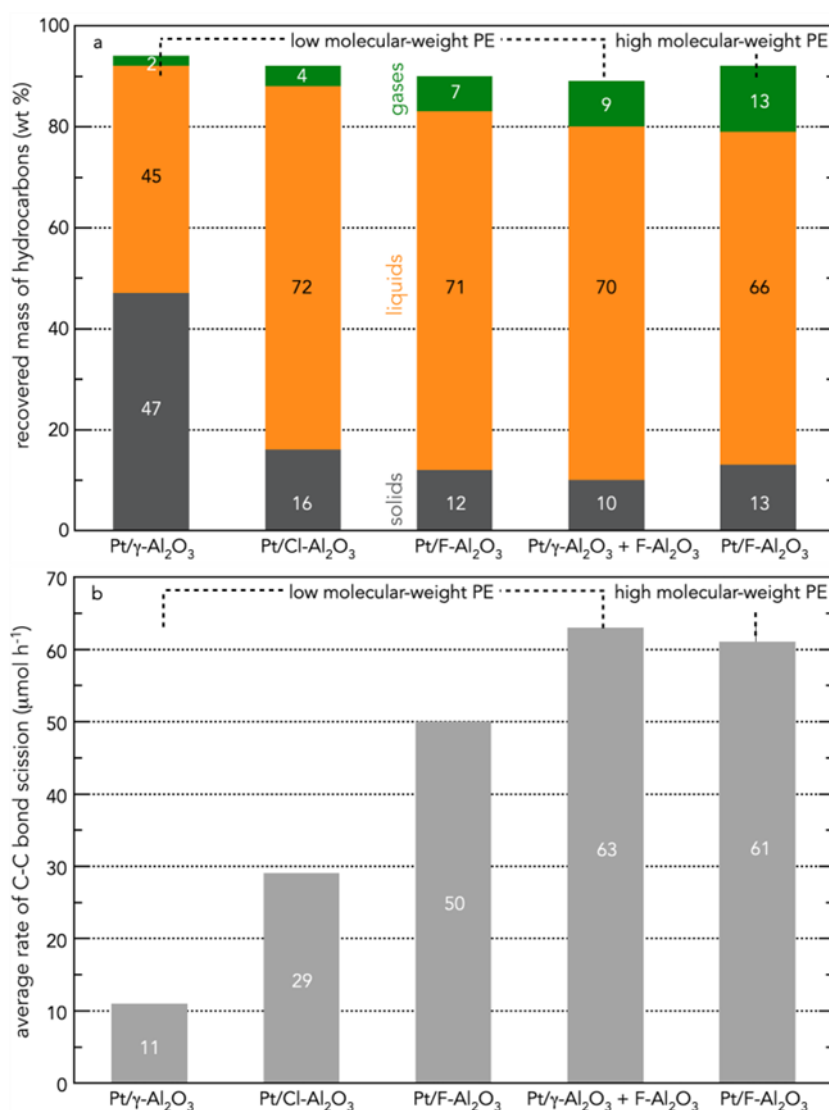


Figure 3.2. Effect of catalyst acidity on the hydrocarbon product distribution and the rate of PE chain cleavage.

Reaction conditions: low molecular-weight PE (0.120 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) or high molecular-weight PE (0.120 g, $M_w = 2.6 \times 10^4 \text{ g mol}^{-1}$, $D = 3.9$), Pt catalyst (0.200 g, see compositions in **Table 3.1**) under Ar, 8 h, 280°C. In the experiment with the mixture of catalysts, Pt/ γ -Al₂O₃ was combined with F-Al₂O₃ (0.100 g, see compositions in **Table 3.1**).

(a) Mass fractions of hydrocarbons recovered from the batch reactor: green, gases; orange, liquids soluble in hot CH₂Cl₂; black, organic residues insoluble in hot CH₂Cl₂. Each result is the average of duplicate experiments. Data are shown in **Table A3.5**.

(b) The average, zeroth-order rate of C-C bond scission (as defined in **eq 3.1** below), estimated from GC-FID and GPC data. For details, see **Rate of carbon-carbon bond scission** in the Appendix II.

The overall hydrocarbon distributions in the reaction products are shown in **Figure 3.2A**. According to analysis by gas chromatography with flame ionization detection (GC-FID), the gases in the reactor headspace are predominantly alkanes (methane, ethane, propane, etc.; **Figure A3.17**). Interestingly, the halogenated catalysts produced less methane relative to higher alkanes and relative to Pt/ γ -Al₂O₃. The more acidic Pt/Cl-Al₂O₃ and Pt/F-Al₂O₃ also converted more PE to liquid hydrocarbons resulting in a lower yield of insoluble carbon (as judged by thermogravimetric analysis; **Figure A3.40**). The liquid hydrocarbons, recovered by extraction into hot CH₂Cl₂, were initially analyzed by GC-FID. Prior to solvent removal, lighter alkanes (hexanes, heptanes, octanes, etc.) were present (**Figure A3.20**). After solvent removal, the remaining heavier hydrocarbons were analyzed by gel permeation chromatography (GPC), proton nuclear magnetic resonance spectroscopy (¹H NMR), and ion chromatography (the latter detected no residual halogens; **Table A3.7**). The average carbon number in the liquid fraction was C₅₂ for Pt/ γ -Al₂O₃, C₂₅ for Pt/Cl-Al₂O₃, and C₂₄ for Pt/F-

Al₂O₃. The molecular dispersity $\bar{D}$ of the liquid products decreased from 2.2 for Pt/ γ -Al₂O₃ to 1.2 and 1.1 for Pt/Cl-Al₂O₃ and Pt/F-Al₂O₃, respectively (**Tables 3.1** and **A3.6**). This trend in $\bar{D}$ correlates, as expected, with the increased degree of depolymerization.

To explore the effect of higher melt viscosity on the depolymerization rate, a polymer sample with a molecular weight closer to a typical commercial PE grade ($M_w = 2.6 \times 10^4$ g mol⁻¹) was heated with Pt/F-Al₂O₃ for 8 h at 280°C. The gas and liquid yields are similar, at 13 wt % and 66 wt %, respectively (**Figure 3.2A**), and the recovered liquid has a similar average carbon number (C_{23}) and dispersity, $\bar{D} = 1.1$ (**Table 3.1** and **Table A3.6**). Therefore, PE molecular weight does not appear to be a major limiting factor for the efficiency of tandem depolymerization. The insensitivity of the liquid product distribution to PE molecular weight is consistent with a constant rate of C–C bond scission in the same initial mass of polymer (see section **Evolution of number-averaged molecular weight** of the Appendix II).

3.3.2. Characterization of Alkylaromatic Products

The liquid products show aromatic ¹H NMR signals (H_{arom}) from 6.5 to 9.0 ppm (**Figure A3.31**). This range of chemical shifts as well as the orange color suggest that in addition to alkylbenzenes, alkylnaphthalenes and larger fused-ring structures are present (predominantly alkylphenanthrenes, according to **Figures A3.31, A3.34** and **A3.39**).^{34,35} The amounts of each type of aromatic product were estimated by integration (see section **Analysis of aromatic yield and substitution patterns**, and eqs **A3.22-27, A3.30-31** in the Appendix II). Both halogen-containing Pt catalysts generated more alkylaromatics in the desired surfactant range (C_{16} - C_{22})²⁸ compared to Pt/ γ -Al₂O₃. Yields of alkylbenzenes in the liquid fraction were similar

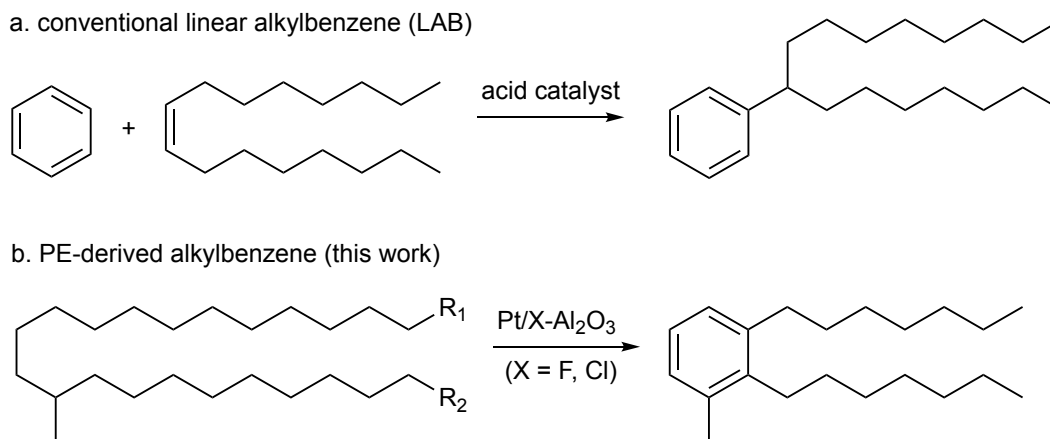
for Pt/Cl-Al₂O₃ and Pt/F-Al₂O₃ (n_{benz} = 38 and 45 μmol , respectively), and comparable to that for Pt/ γ -Al₂O₃ (48 μmol). However, Pt/Cl-Al₂O₃ and Pt/F-Al₂O₃ gave higher yields of the larger alkylaromatics ($n_{\text{phen}} + n_{\text{naph}}$ = 54 and 86 μmol , respectively) compared to Pt/ γ -Al₂O₃ (11 μmol , **Table A3.12**).

Some information about the nature of the alkyl substituents on the aromatic rings can be deduced from the ¹H NMR spectra. Protons on the carbons (C_α) directly bonded to an aromatic ring give signals at 2.0-3.5 ppm. These signals can be subdivided into $H_{\alpha,\text{methyl}}$ (2.00 - 2.50 ppm), $H_{\alpha,\text{methylene}}$ (2.50 - 3.10 ppm) and $H_{\alpha,\text{methine}}$ (3.10 - 3.50 ppm) regions.^{36,37} For all three catalysts, the average alkyl substituent is $C_\alpha\text{H}_2\text{R}$. Combining this information with the H_α/H_{arom} values gives the average number of alkyl substituents (**Table A3.12**, **Figure A3.32**). For Pt/ γ -Al₂O₃, H_α/H_{arom} = 1.1 implies that the aromatics are predominantly dialkyl-substituted. For Pt/Cl-Al₂O₃ and Pt/F-Al₂O₃, higher ratios of 1.5 and 1.6, respectively, imply that the aromatics are trialkyl-substituted. About two-thirds of these alkyl substituents are unbranched at C_α , while the remaining one-third is evenly split between branched alkyls and methyl groups. Presumably, acid-catalyzed skeletal isomerization creates methyl-branched *iso*-alkanes, whose aromatization generates methyldialkylaromatics as well as α -branched (i.e., $C_\alpha\text{HR}_2$) substituents, as well as (see **Scheme 3.3** below).

Scheme 3.1 compares the typical structure of the PE-derived alkylbenzene with that of the linear alkylbenzenes used to make conventional anionic surfactants. Some branching on the longer alkyl chains can be present, and may be beneficial for surfactant properties.³⁸ However, the extent of branching must be carefully controlled to preserve biodegradability. We note

that in general, methyl substituents on the benzene ring are not expected to impede biodegradation, while quaternary carbons attached to the ring confer poor biodegradability.^{39–}

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Scheme 3.1. Comparison of preparation and typical structures for long-chain linear alkylbenzenes (LABs). (A) LAB synthesized by conventional acid-catalyzed benzene alkylation,²⁸ and (B) LAB derived from catalytic PE depolymerization (this work).

3.3.3. Catalyst Reusability

Alumina halogenation is reported to stabilize small Pt nanoparticles found in commercial hydrocracking catalysts.⁴² To explore re-use of Pt/F-Al₂O₃, three consecutive 8-h reactions of PE were conducted, with calcination of the recovered catalyst in O₂ at 500°C followed by re-reduction in H₂ at 280°C between each reaction (see section **Catalyst recycling** in the Appendix II). The liquid yield decreased slightly, from 71 wt % with the fresh catalyst to 65 wt % with the once-recycled catalyst, then stabilized at 64 wt% for the twice recycled catalyst (**Figure A3.42**). The modest (11%) decrease in active Pt surface area (**Table A3.2**) is consistent with a minor amount of sintering, as previously reported for Pt/ γ -Al₂O₃.²⁷ The

liquid hydrocarbon products have a similar average molecular weight and aromatic yield in the initial and subsequent reactions (**Tables A3.12 and A3.13**).

3.3.4. Quantifying the Rate of PE Depolymerization

We define the depolymerization rate as the average rate of C-C bond scission (r_{C-C}), **eq 3.1**. It corresponds to the rate of formation of new hydrocarbon chains, dN/dt , where $N(0)$ and $N(t)$ represent the total number of chains present at time 0 and time t , respectively (see section **Rate of carbon-carbon bond scission** in the Appendix II).

$$r_{C-C} = dN/dt \approx \Delta N(t)/t = [N(t) - N(0)]/t \quad (3.1)$$

A constant (i.e., zeroth-order) rate of chain cleavage implies that the acid sites be occupied at all times. Since each bond scission event generates one additional chain, $DN(t)$ is both the cumulative number of such events, and the number of new chains. The rate is much higher for the bifunctional catalysts, rising from 11 $\mu\text{mol h}^{-1}$ for Pt/ $\mu\text{-Al}_2\text{O}_3$ to 29 $\mu\text{mol h}^{-1}$ for Pt/Cl- Al_2O_3 and 50 $\mu\text{mol h}^{-1}$ for Pt/F- Al_2O_3 . Thus catalyst acidity accelerates PE depolymerization up to 5-fold, relative to Pt/ $\mu\text{-Al}_2\text{O}_3$, **Figure 3.2B**. The average rate of C-C bond scission for the higher M_w PE, 61 $\mu\text{mol h}^{-1}$ is comparable to that for the lower M_w PE.

The effect of halogenation on both chain scission activity and aromatic selectivity confirms the importance of acid sites in the tandem reaction. To probe the role of proximity between the metal and acid sites, we also conducted PE depolymerization with a physical mixture of Pt/ $\gamma\text{-Al}_2\text{O}_3$ (0.200 g, 1.5 wt %Pt) and F- Al_2O_3 (0.100 g, 1.3 wt% F). The total Pt

and F contents in this mixture are very similar to those of Pt/FAl₂O₃ (0.200 g, 1.6 wt % Pt, 0.8 wt % F). The physical mixture of catalysts generated yields of gas and liquid hydrocarbon products comparable with those made using the catalyst with co-located active sites. Indeed, for the physical catalyst mixture, the resulting alkylaromatic content is even higher (121 μ mol) and the average carbon number in the liquid (C₁₇) is even lower than for Pt/F-Al₂O₃ (**Figure A3.22; Table 3.1**).

3.3.5. Optimization of Support Acidity for Chain Cleavage

To explore the optimum acidity for PE depolymerization, a series of non-halogenated catalysts with constant Pt loading and similar Pt dispersions was prepared (**Table 3.2**). Among the catalyst supports investigated here, mesoporous SiO₂ has no acidity, while microporous HZSM-5 is a strong Brønsted acid. Mesoporous SiO₂-Al₂O₃ possesses both stronger Brønsted and Lewis acidity than γ -Al₂O₃, although it is less acidic than HZSM-5. To analyze the effects of acidity on the rates of alkane chain scission, skeletal isomerization, and aromatization and to facilitate complete product characterization, each was used to catalyze the reaction of a linear PE model compound, triacontane (i.e., *norm*-C₃₀H₆₂). Its low molecular weight relative to PE results in gas and liquid phase products that are more readily characterized and ensuring good mass balances (85–96 wt %, **Table A3.10**).

Table 3.2. Characterization of non-halogenated Pt catalysts

Catalyst	Pt nanoparticles ^a	Acid sites (μ mol g ⁻¹) ^b
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	Loading (wt %)	Dispersion (%)	Lewis	Brønsted
Pt/SiO ₂	1.0	44	-	-
Pt/ γ -Al ₂ O ₃	1.0	68	98(4)	~0
Pt/SiO ₂ -Al ₂ O ₃ ^c	1.0	43	136(5)	41(2)
Pt/HZSM-5	1.0	41	77(3)	63(3)

^a Loading measured by ICP-OES. Dispersion measured by CO chemisorption, assuming CO/Pt_{surf} = 1.³³

^b Estimated from the pyridine remaining adsorbed after desorption at 150°C and 10⁻² Torr (**Figure A3.10**), via the peak areas at 1545 cm⁻¹ (BAS) and 1455 cm⁻¹ (LAS). Uncertainties (in parentheses) are propagated from uncertainties in the extinction coefficients (**Figure A3.8B**).

^c SiO₂-Al₂O₃ (7.6 wt % Al) is an amorphous mixed oxide.

Figure 3.3 illustrates the striking effect of catalyst support acidity on the hydrocarbon product distribution. Pt/SiO₂ shows negligible activity toward triacontane at 280°C. At the same temperature, Pt/ γ -Al₂O₃ converts triacontane to a Schulz-Flory-like distribution of liquid hydrocarbons (C₆₋₃₀, 81 wt %). The liquid products are dominated by linear paraffins, with a minor contribution from alkylaromatics (whose formation nevertheless supplies the H₂ needed for hydrogenolysis), **Table A3.10**.

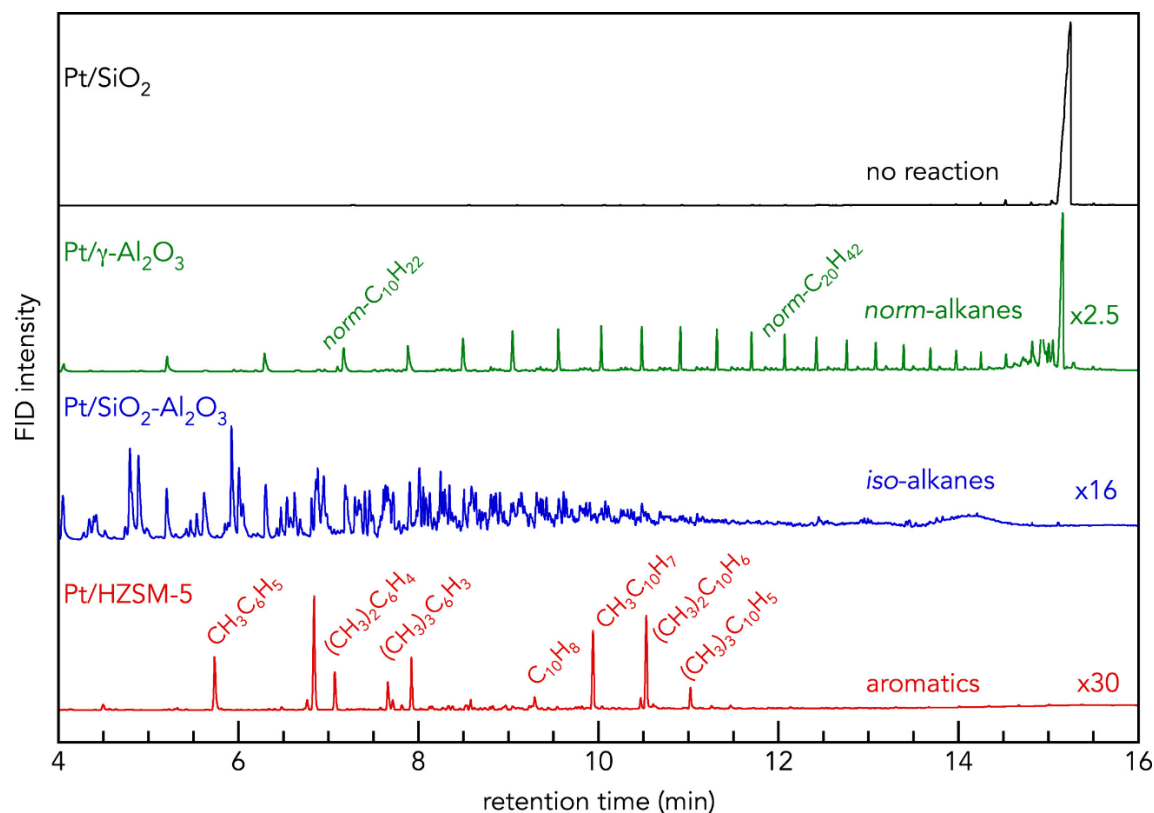


Figure 3.3. GC-FID analyses of liquid hydrocarbons recovered from the partial depolymerization of triacontane ($norm\text{-}C_{30}H_{62}$), catalyzed by Pt nanoparticles supported on various oxides.

Reaction conditions: $norm\text{-}C_{30}H_{62}$ (0.120 g), catalyst (0.200 g, 1.0 wt % Pt), Ar, 24 h, 280°C. Aromatic products identified for the reaction catalyzed by Pt/HZSM-5 include toluene, xylenes, naphthalene, and methylnaphthalenes.

Pt/SiO₂-Al₂O₃ possesses both strong Brønsted and Lewis acidity and is much more reactive towards triacontane than Pt/γ-Al₂O₃. After 24 h, there are effectively no hydrocarbons with C_{>16} remaining. The product distribution includes a higher fraction of light hydrocarbons (C_{≤6}, 18 wt %), compared to 4 wt % for Pt/g-Al₂O₃. Furthermore, each carbon number includes

a large number of skeletal isomers, and includes both saturated hydrocarbons and aromatics, **Table A3.10**. The even higher Brønsted acidity of Pt/HZSM-5 results in a majority of light hydrocarbon gases ($C_{\leq 6}$, 74 wt %); the liquid range is only a small fraction of the hydrocarbon products (8 wt %), and consists mostly of small aromatics (**Figures 3.3 and A3.28-3.29, Table A3.10**).

The average rate of C-C bond cleavage in triacontane therefore follows the acidity of the oxide supports, $SiO_2 < \gamma-Al_2O_3 < SiO_2-Al_2O_3 < HZSM-5$. This finding strongly suggests that Pt sites operate cooperatively with acid sites to achieve PE depolymerization at 280°C. However, both highly acidic catalysts (Pt/SiO₂-Al₂O₃ and Pt/HZSM-5) make predominantly light gases and insoluble heavier hydrocarbons (**Table A3.10**), instead of the more valuable lubricant-range hydrocarbons and long-chain alkylaromatics. Consequently, there is an optimum catalyst acidity to achieve selectivity to the desired molecular weight range at acceptable rates. The moderate acidities of $\gamma-Al_2O_3$ and its halogenated derivatives appear to be most suitable for this kind of PE upcycling.

3.3.6. Quantifying the Acidity of Halogenated Aluminas

Mild halogenation of $\gamma-Al_2O_3$ has little influence on its surface area or porosity (**Figure A3.6; Table A3.3**). However, partial replacement of the surface hydroxyl groups by halides (**Figure A3.7**)³⁰ results in changes to the number, type, and Brønsted acid strength of the remaining hydroxyl groups, as well as changes in the Lewis acidity of surface Al sites owing to the inductive effects of the halide ligands. The Lewis acidity of the various aluminas was quantified by infrared (IR) spectroscopy of adsorbed pyridine (**Figure A3.11**). Bands at ca.

1,625, 1,575, and 1,455 cm^{-1} correspond to pyridine coordinated to Lewis acid sites (LASs).⁴³ The total LAS number on each type of alumina was estimated as the amount of pyridine remaining after desorption of weakly-bound material by evacuation at 150°C. The numbers are similar for $\gamma\text{-Al}_2\text{O}_3$ and $\text{F-Al}_2\text{O}_3$, while $\text{Cl-Al}_2\text{O}_3$ contains ca. 50% more LAS (**Table 3.3**). Next, the number of strong LASs was determined after pyridine desorption at 350°C (**Figure A3.11**). The number of strong LASs is similar for $\text{Cl-Al}_2\text{O}_3$ and $\text{F-Al}_2\text{O}_3$ and is much higher than that for $\gamma\text{-Al}_2\text{O}_3$ (**Table 3.3**).

Table 3.3. Effect of halogenation on alumina acidity

Support	Lewis acid sites (LAS, $\mu\text{mol g}^{-1}$) ^a			Brønsted acid sites (BAS, $\mu\text{mol g}^{-1}$) ^b		
	Weak	Strong	Total	Weak	Strong	Total
$\gamma\text{-Al}_2\text{O}_3$	71(3)	33(1)	104(4)	14(1)	9(1)	23(1)
$\text{Cl-Al}_2\text{O}_3$	94(4)	63(2)	157(6)	6(1)	14(1)	21(1)
$\text{F-Al}_2\text{O}_3$	63(2)	51(2)	114(4)	0	34(2)	34(2)

^a From the IR peak area for adsorbed pyridine at 1455 cm^{-1} , after desorption at 10^{-2} Torr and 150°C (total LAS), or 350°C (strong LAS). The number of weak LAS was estimated by difference. Uncertainties (in parentheses) are propagated from the calibration in **Figure A3.8B**.

^b From the IR peak areas for adsorbed 2,6-dimethylpyridine at 1605 cm^{-1} (hydrogen-bonded sites, DMP-H, representing weak BAS), and 1650 and 1630 cm^{-1} (DMPH^+ , representing strong BAS), after desorption at 10^{-2} Torr and 150°C. The total number of BAS is the sum. Uncertainties (in parentheses) are propagated from the calibration in **Figure A3.9B**.

Pyridine-modified F-Al₂O₃ also shows characteristic peaks for pyridinium ions (1,635 and 1,545 cm⁻¹).⁴⁴ Their absence on γ -Al₂O₃ and Cl-Al₂O₃ means these supports possess weaker Brønsted acid sites (BAS) (**Figure A3.11**). However, pyridine itself is a relatively weak base (pK_b = 8.8).⁴⁵ Use of the stronger base 2,6-dimethylpyridine (DMP, pK_b = 7.4)⁴⁵ can reveal the presence of these weaker BASs. IR spectra recorded after desorption at 150°C show bands corresponding to various types of adsorbed DMP (**Figure A3.12**).⁴⁶ All three aluminas have peaks for DMPH⁺ at (1,650 ± 5) and (1,630 ± 5) cm⁻¹. Their abundance increases in the order as follows: γ -Al₂O₃ < Cl-Al₂O₃ << F-Al₂O₃ (**Table 3.3**). In addition, the bands are slightly redshifted on F-Al₂O₃ compared with γ -Al₂O₃ and Cl-Al₂O₃, indicating that F-Al₂O₃ has stronger BAS.⁴⁶ Weak BASs give rise to hydrogen-bonded DMP (DMP-H, 1,605 ± 5) cm⁻¹. These sites decrease in abundance in the order γ -Al₂O₃ > Cl-Al₂O₃ > F-Al₂O₃ (**Table 3.3**). The addition of Pt (ca. 1.5 wt %) had no significant effect on the acidities of γ - and F-aluminas, nor did catalyst use and regeneration alter the support acidity (**Table A3.4**).

3.3.7. Effect of Catalyst Acidity on the Extent of Hydrocarbon Chain Cleavage

Initially, catalyst acidity was varied by combining Pt/ γ -Al₂O₃ with an equivalent mass of halide-modified alumina (either more Lewis acidic Cl-Al₂O₃ or more Brønsted acidic F-Al₂O₃). The reaction of triacontane was conducted at 280°C. In the absence of an acidic alumina, the starting material was mostly unreacted after 12 h (81 wt % remaining; **Figure 3.4**; **Table A3.8**). Addition of either halogenated alumina enhanced the extent of C–C bond scission significantly, and most triacontane (≥ 88 wt %) was converted to lighter hydrocarbons in the same time period. Halogenation caused the value of r_{C-C} (as defined in **Equation 3.1**)

to increase by an order of magnitude, from 3 $\mu\text{mol h}^{-1}$ for Pt/ $\gamma\text{-Al}_2\text{O}_3$ alone to 16 and 34 $\mu\text{mol h}^{-1}$ in combination with Cl- Al_2O_3 and F- Al_2O_3 , respectively (**Figure 3.4**).

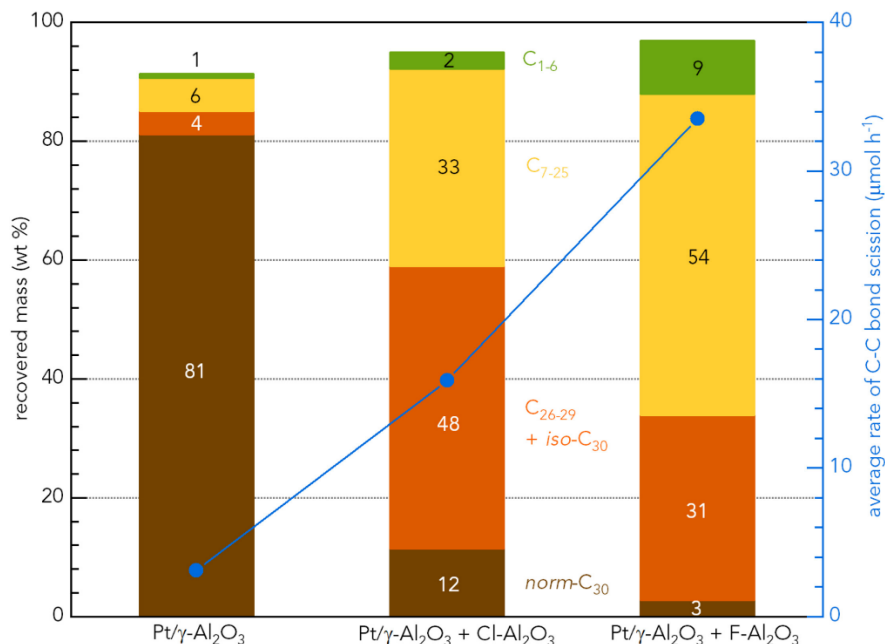


Figure 3.4. Hydrocarbon product distribution (bars) and average rate of C–C bond scission (blue circles) in the catalytic conversion of *norm*- $\text{C}_{30}\text{H}_{62}$

Reaction conditions: Pt/ $\gamma\text{-Al}_2\text{O}_3$ (0.100 g, 1.5 wt % Pt), acidic alumina (0.100 g, Cl- Al_2O_3 : 1.8 wt% Cl, or F- Al_2O_3 : 1.3 wt % F), *norm*- $\text{C}_{30}\text{H}_{62}$ (0.120 g), 12 h, 280°C. Green, C_{1–6}; yellow, C_{7–25}; orange, C_{26–29} and *iso*-C₃₀; brown, unreacted triacontane. The rate of C–C bond scission is defined in

Equation 3.1 (see section **Rate of carbon–carbon bond scission** in the Appendix II for details).

3.3.8. Apparent Turnover Frequencies

The rate law for polymer chain cleavage was also assessed using triacontane as a model reactant. To investigate the contributions of LASs and BASs to the rate of C–C bond scission, the mass of solid acid was varied, while the mass of Pt/ $\gamma\text{-Al}_2\text{O}_3$ was held constant. In each

experiment, the metal-acid balance ($n_{\text{Pt}}/n_{\text{BAS}}$) was high enough to ensure operation at the plateau in the acid-normalized rate (**Figure A3.43**), such that Pt-controlled reaction steps are not rate determining.^{47,48} The results are shown in **Table 3.4**.

Table 3.4. Comparison of catalytic activities and yields for mono- vs. bifunctional catalyst systems, in the tandem conversion of triacontane (*norm*-C₃₀H₆₂)

Pt catalyst ^a	Mass of acid catalyst		Rate ^b ($\mu\text{mol h}^{-1}$)	Yield (mol %)		
	F-Al ₂ O ₃	Cl-Al ₂ O ₃		<i>norm</i> -	<i>iso</i> -	aromatics ^c
	(mg)	(mg)		alkanes ^c	alkanes ^d	
Pt/ γ -Al ₂ O ₃	-	-	3.0(0.2)	102(1)	4(1)	5.9(2.6)
	5	-	8.3	87	38	11.1
	25	-	13.8(0.4)	83(1)	61 (4)	13.8(3.6)
	50	-	23.1(2.4)	52(2)	124(9)	22.9(1.8)
	100	-	33.7(2.1)	66(14)	149(24)	28.2(2.3)
	-	25	7.7(1.6)	80(19)	42(13)	10.5(1.1)
	-	50	9.6(0.4)	79(2)	48(4)	14.8(1.3)
	-	100	15.7(1.8)	52(21)	96(15)	18.2(4.4)
Pt/SiO ₂	-	-	0.9	102	2	1.8
	100	-	34.1	42	164	30.5
none	100	-	11.9(0.4)	100(6)	52(7)	-
	-	100	3.3(0.3)	96(2)	17(2)	-

^a Reaction conditions: *norm*-C₃₀H₆₂ (0.120 g), Pt catalyst (0.100 g, 1.5 wt % Pt) alone or physically mixed with various amounts of either F-Al₂O₃ (1.3 wt % F), or Cl-Al₂O₃ (1.8 wt % Cl), 12 h at 280°C. Uncertainties (in parentheses) represent the standard deviation of duplicate experiments.

^b Zeroth-order rate of C-C bond scission, **Equation 3.1** (see section **Rate of carbon-carbon bond scission** in the Appendix II for details).

^c Yield of *norm*-alkanes, relative to the initial charge of *norm*-C₃₀H₆₂ (see section **Analysis of *norm*- and *iso*-alkane yields** in the Appendix II for details).

^d Yield of *iso*-alkanes in the range C₄₋₃₀, relative to the initial charge of *norm*-C₃₀H₆₂. For details, see section **Analysis of *norm*- and *iso*-alkane yields** in the Appendix II.

^e Yield of alkylaromatics (alkylbenzenes, -naphthalenes, and -phenanthrenes) in the liquid products, relative to the initial charge of *norm*-C₃₀H₆₂ (see section **Analysis of aromatic yields and substitution patterns** in the Appendix II for details).

The rates correlate poorly with the number of LASs (weak, strong, or total), **Figure A3.44**. They also correlate poorly with the numbers of weak and total BASs, **Figure A3.45**. However, they do correlate approximately linearly with the number of strong BASs (**Figure 3.5A**, filled points). This finding is consistent with other reports stating that Brønsted acidity controls the rate of hydrocracking for both light hydrocarbons⁴⁹ and POs.¹⁴ In the hydroconversion of cetane (*norm*-C₁₆H₃₄), a fairly linear relationship between the rate of hydrocracking and the amount of ultrastable zeolite Y (USY) was found.⁵⁰ Although pyridine adsorption revealed no strong Brønsted acidity for γ-Al₂O₃ (**Figure A3.10**), the use of more basic DMP confirmed a small number of strong BASs (**Figure A3.13**; **Table A3.4**) whose abundance adequately accounts for the low rate of C–C bond cleavage over Pt/γ-Al₂O₃ (**Figure 3.5A**; **Table 3.4**).

Therefore, this material is also a bifunctional catalyst. In contrast, Pt/SiO₂ has no strong BAS and shows a very low activity toward *norm*-C₃₀H₆₂ under the reaction conditions.

The slopes in **Figure 3.5A** are apparent turnover frequencies (TOFs). In the absence of Pt, the halogenated aluminas alone give apparent TOF values that are ca. 3-fold lower than those for the bifunctional catalysts. In addition, their selectivities are very different. Thus, the major products of acid-catalyzed cracking are light (C₄₋₆) alkanes and alkenes, with negligible yields of intermediate-chain-length hydrocarbons (C₇₋₂₉, **Table A3.8**). Similar product distributions were reported for acid-catalyzed cracking of long-chain alkanes at higher temperatures.⁴⁹ In contrast, physical mixtures of Pt/ γ -Al₂O₃ with halogenated aluminas gave average carbon numbers of C_{~15} in the liquid hydrocarbon fraction after 12 h (**Table A3.10**). The apparent TOF for C–C bond scission by catalyst mixtures containing F is slightly higher on average than for catalyst mixtures containing Cl (**Figures 3.5A** and **A3.43**), reflecting the higher average acid strength of the sites in the F-containing materials.³² However, while the acid strengths of the strong BASs on different supports vary, **Figure 3.5** shows that the main difference between these catalysts is the number, not the nature, of the active sites. Otherwise, separate linear correlations would be observed for each support, which is clearly not the case. Similar analyses for the rates of bifunctional skeletal isomerization and aromatization lead to apparent TOFs for the three major reaction types that decrease in the following order: isomerization > C–C bond scission > aromatization (see section **Apparent turnover frequencies (TOFs)** in the Appendix II).

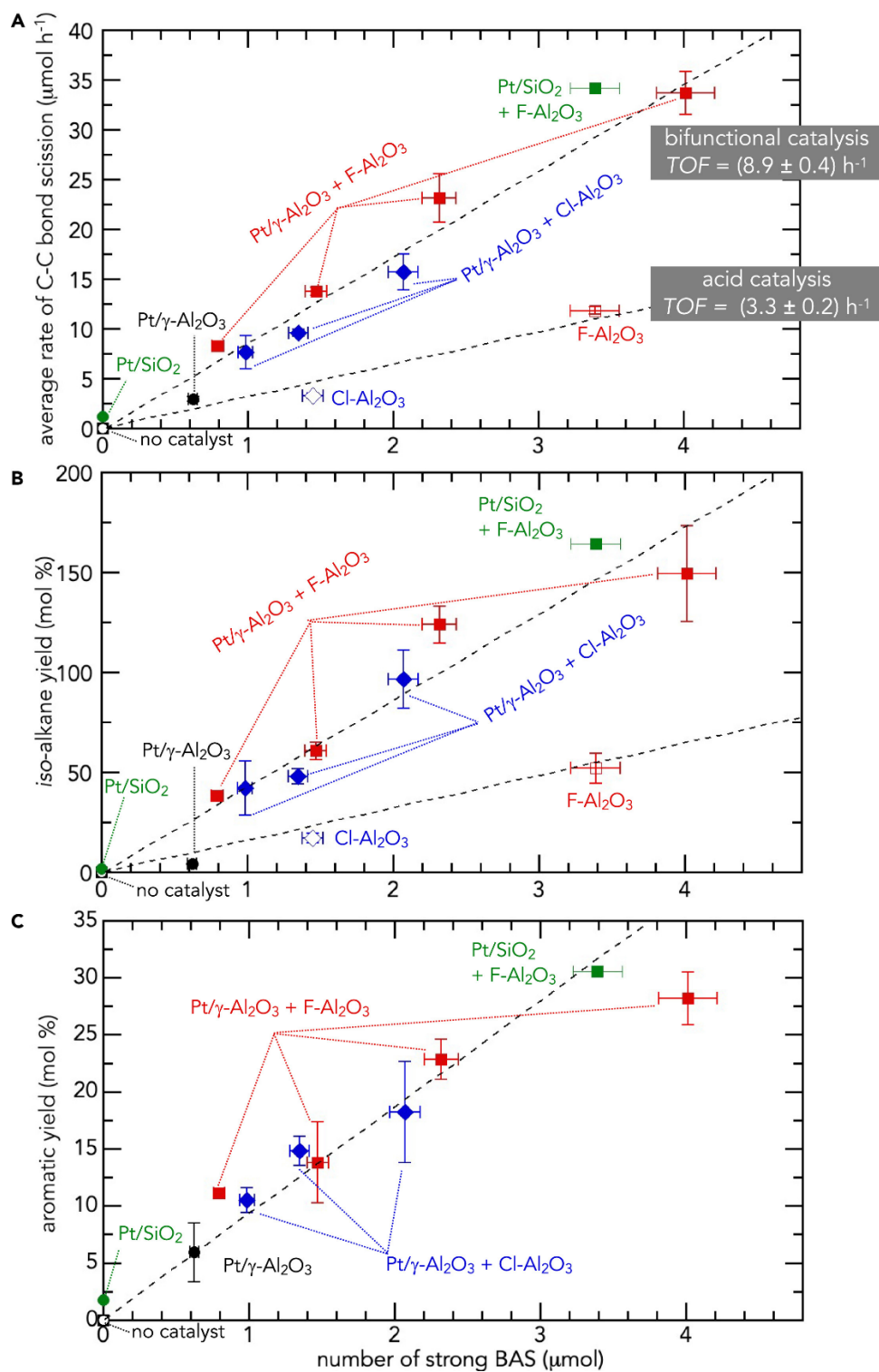


Figure 3.5. The number of strong Brønsted acid sites controls the kinetics of triacontane conversion. (A) The average rate of C–C bond scission, (B) the *iso*-alkane yield, and (C) the aromatic yield.

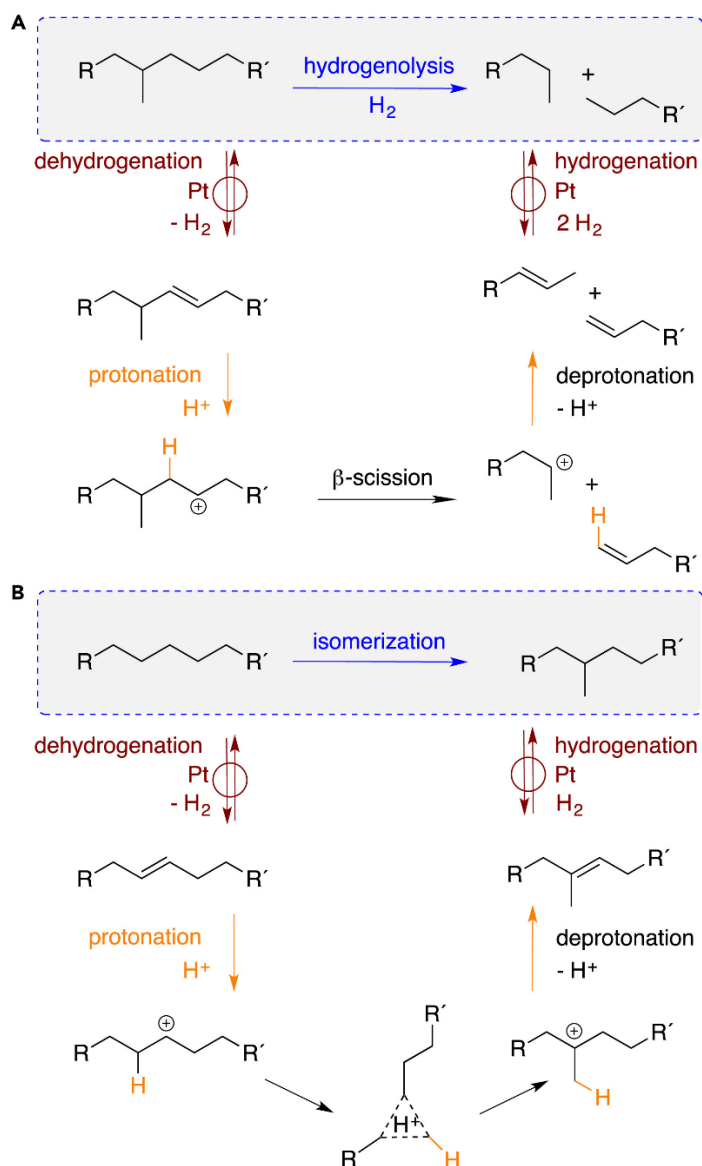
Reaction conditions in **Table 3.4**. Abscissa error bars represent the standard deviation in the measurement of the sum of the number of strong BASs contributed by each catalyst support (**Table 3.3**). Ordinate error bars represent standard deviations of duplicate reaction experiments.

3.3.9. Bifunctional Mechanism for Tandem PE Depolymerization

Both the acid-promoted rate enhancements and the changes in selectivity upon catalyst halogenation are consistent with the bifunctional chain cleavage mechanism proposed in **Scheme 3.2A**, where quasi-equilibrated Pt-catalyzed dehydrogenation precedes rate-determining Brønsted acid-catalyzed chain scission of the resulting alkenes.⁴⁹ Protonation by a strong BAS leads to chain cleavage near a branch point owing to the greater stability of the resulting secondary carbocation. After deprotonation, the resulting alkenes are rehydrogenated at metal sites.

BASs are also known to catalyze skeletal isomerization of linear hydrocarbons.^{49,51,52} The extent of isomerization was gauged from the *iso*-alkane yield in the hydrocarbons ranging from C_{4–30}, **Table 3.4**. The yield of *iso*-alkanes increases monotonically with the number of strong BASs (**Figures 3.5B** and **A3.25**) for both monofunctional (acid only) and bifunctional (metal/acid) catalyst systems. This correlation suggests a second role for BASs in C–C bond cleavage, because branch formation will increase the rate of β -scission.⁴⁹ The bifunctional catalysts generate ca. 3-fold higher *iso*-alkane yields compared to the corresponding

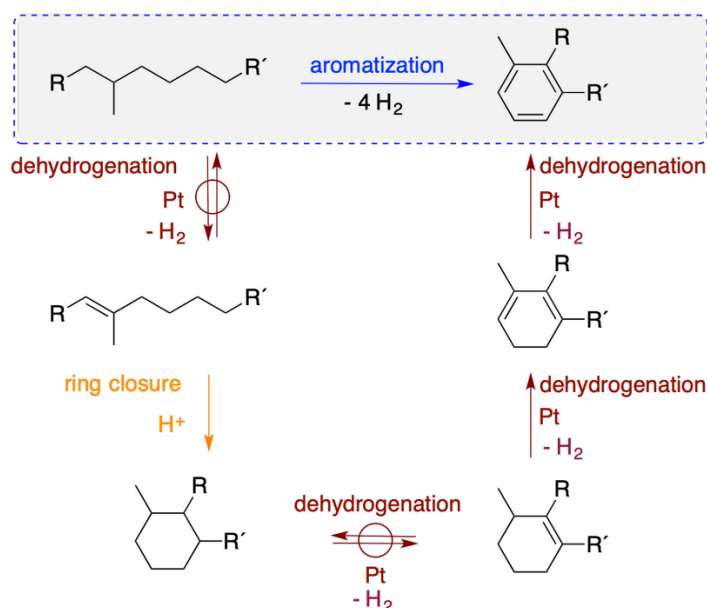
monofunctional acid catalysts. Note that the yields (and the TOFs derived from them) represent minimum values because each *iso*-alkane may be the result of more than one isomerization, and the alkylaromatic products can also contain branches. A bifunctional mechanism for skeletal isomerization of *norm*-alkanes is proposed in **Scheme 3.2B**. Initial dehydrogenation and protonation lead to a secondary carbenium ion, which rearranges via a protonated cyclopropane intermediate to a tertiary carbenium ion.³¹ Finally, deprotonation and rehydrogenation generate a branched alkane.



Scheme 3.2. Proposed bifunctional mechanisms for C-C bond scission and alkane isomerization

Mechanisms for (A) H_2 -induced chain cleavage adjacent to pre-existing branch points via metal acid-catalyzed steps (overall, C–C bond hydrogenolysis), and (B) skeletal rearrangement to generate new branch points (overall, alkane isomerization). In each case, the net reactions are highlighted in the gray boxes.

The alkylaromatics yield from triacontane increases monotonically with the number of strong BASs in the bifunctional catalyst systems (**Figures 3.5C** and **A3.37**; **Tables 3.4** and **A3.11**). While the higher H/C ratio of triacontane generates fewer alkylaromatics relative to PE for the same number of C–C bond scission events, the trends in alkylaromatic yields are the same. Control experiments using X-Al₂O₃ (X = Cl, F) alone, without Pt, gave almost no aromatic products, confirming that Pt is required. The amount of free H₂ present at the end of each experiment corresponds well to the difference between the amount formed by aromatization (source) and consumed by C–C bond scission (sink), indicating that these processes represent the major forms of hydrogen redistribution (see section **Hydrogen balance** in the Appendix II). The proposed bifunctional mechanism for forming aromatics involves Pt-catalyzed dehydrogenation followed by acid catalyzed alkene cyclization,^{53,54} **Scheme 3.3**. Cyclization may occur to cyclohexanes directly, or to cyclopentanes followed by ring expansion. Pt can then catalyze further dehydrogenation to yield alkylaromatic products.



Scheme 3.3. Proposed bifunctional mechanism for the aromatization of polyethylene fragments

Cyclization of a tri-substituted alkene is followed by cyclohexane dehydrogenation to give methyldialkyl-substituted aromatics. The net reaction is highlighted in the gray box.

To identify the active sites for alkene cyclization, 1-octadecene was heated with either Pt/SiO₂ or a Pt-free alumina (unmodified, or modified with either Cl or F) for 4 h at 280°C. In the presence of Pt/SiO₂, γ -Al₂O₃, or Cl-Al₂O₃, a ¹H NMR peak at 5.40 ppm in the hydrocarbon products indicated isomerization to internal alkenes (**Figure A3.15**). The absence of aromatics was confirmed by the lack of signals between 6.5 and 9.0 ppm. In contrast, the reaction catalyzed by F-Al₂O₃ yielded aromatics in addition to internal alkenes, implying that cyclization occurs more readily over its strong BAS. Aromatics were also observed in the reaction catalyzed by Cl-Al₂O₃ when the reaction time was prolonged to 12 h. Therefore, Cl-Al₂O₃ can catalyze alkene cyclization, but does so more slowly than F-Al₂O₃.

The higher catalytic activity of F-Al₂O₃ compared with Cl-Al₂O₃ in forming aromatics is attributed to the higher BAS strength due to fluorination.³² Thus, it appears that alkene cyclization/aromatization follows a bifunctional mechanism.

3.3.10. Active Site Proximity in Bifunctional Tandem PE Upcycling

The effect of physical proximity between the metal and acid sites in bifunctional hydrocracking catalysts has been the subject of much investigation and discussion.⁵⁵ Acid sites must intercept unsaturated hydrocarbon intermediates before they are rehydrogenated, while metal sites must rehydrogenate the isomerized intermediates before they undergo acid-catalyzed oligomerization. Weisz proposed a maximum distance requirement between metal and acid sites (the so called intimacy criterion) so that hydrocracking activity is not impeded by slow diffusion of unsaturated intermediates.⁵⁶ Although some studies have shown that such nanoscale proximity enhances catalyst performance,^{57,58} others report no effect of separation (from nm to mm scales).⁵⁹ In a few cases, intimacy appears to be disadvantageous.^{60,61} The lack of a benefit for nanoscale proximity in tandem PE aromatization is evident in the similar behaviors of Pt/X-Al₂O₃ and physical mixtures of Pt/ γ -Al₂O₃ and X-Al₂O₃. The latter are actually slightly faster at generating liquid phase hydrocarbons (**Figure 3.2A**), although the difference is small. Because alumina consists of micron-sized particles, metal-acid distances in the micron range must allow for effective cooperation in the tandem conversion of PE. The absence of a proximity effect is consistent with the BASs being fully occupied by alkenes and therefore with pseudo-zeroth-order behavior with respect to the hydrocarbon concentration.

The mass action form of the rate law for PE depolymerization is therefore zeroth-order in Pt, first-order in strong BASs, and zeroth-order in saturated C–C bonds, summarized as follows:

$$r_{\text{C-C}} = k n_{\text{Pt}}^0 n_{\text{BAS}}^1 n_{\text{C-C}}^0 \quad (3.2)$$

These findings suggested that non-acidic Pt/SiO₂ could be an effective component of a bifunctional catalyst if combined with an acidic alumina. Indeed, when Pt/SiO₂ (0.100 g) was mixed with F-Al₂O₃ (0.100 g, 1.3 wt% F), the value of $r_{\text{C-C}}$ in the tandem conversion of triacontane increased dramatically from 1 to 34 $\mu\text{mol h}^{-1}$, and the aromatic yield increased from 2 to 30 mol % (**Table 3.4**). Although each component is individually a poor catalyst, in combination they became the most effective catalytic system tested here (**Figure 3.5**). The validated prediction illustrates the power of mechanistic and kinetic understanding in rational catalyst design.

3.4. Conclusion

This study illuminates the complementary roles of metal and acid sites in the tandem conversion of PE to long-chain alkylaromatics. At 280°C, Pt/Cl-Al₂O₃ and Pt/F-Al₂O₃ are more effective catalysts than Pt/ γ -Al₂O₃, giving much higher average rates of C–C bond cleavage, skeletal isomerization, and alkylaromatic formation from triacontane. The rates of each type of transformation correlate linearly with the number of strong BASs. Pt sites are principally responsible for alkane hydrogenation/dehydrogenation, while strong BASs protonate alkenes to give carbenium ions that undergo C–C bond cleavage and isomerization,

as well as cyclization. Nanoscale proximity between Pt and BAS is not required to convert alkanes to alkylaromatics. Thus, a physical mixture of Pt/ γ -Al₂O₃ and F-Al₂O₃ shows similar activity to Pt/F-Al₂O₃, and addition of F-Al₂O₃ to Pt/SiO₂ makes for a highly effective bifunctional tandem catalyst.

Effective bifunctional catalysts maximize both activity and selectivity. Although increased acidity results in faster PE conversion and a higher fraction of alkylaromatics in the molecular weight range desired for use as surfactants and lubricants (C₁₆₋₂₂), strongly acidic catalysts also produce more low-value gases, polyaromatics, and coke during PE upcycling. Future development of this process to obtain valuable alkylaromatics from waste PE will need to further minimize their formation, as well as address the impact of inorganic fillers, organic additives, and other polymers, which are typically present in post-consumer plastic waste. Furthermore, the surfactant properties of the PE-derived alkylaromatics upon sulfonation, as well as their biodegradability, remain to be explored.

3.5. Simplified Experimental Procedures

3.5.1. Catalyst Synthesis

Cl-Al₂O₃ was synthesized by passing a stream of CCl₄ vapor through a bed of γ -Al₂O₃ at 300°C. F-Al₂O₃ was synthesized by incipient wetness impregnation of γ -Al₂O₃ with an aqueous solution of NH₄F, followed by calcination at 550°C. Various synthesis methods were required to ensure fairly constant Pt dispersion. Pt/ γ -Al₂O₃ (1.5 wt % Pt) and Pt/F-Al₂O₃ (1.6 wt % Pt) were synthesized by chemical vapor deposition of CpPtMe₃, followed by reduction in H₂ at 280°C. Pt/Cl-Al₂O₃ (1.5 wt % Pt) was synthesized by co-impregnation of

[Pt(NH₃)₄](NO₃) and HCl onto γ -Al₂O₃ followed by calcination and reduction in H₂ (both at 500°C). Pt/SiO₂ (1.5 wt % Pt) was synthesized by incipient wetness impregnation of [Pt(NH₃)₄](NO₃)₂ followed by calcination and reduction in H₂ (both at 350°C). Pt/SiO₂, Pt/ γ -Al₂O₃, Pt/SiO₂-Al₂O₃, and Pt/HZSM-5 (all 1.0 wt % Pt) were synthesized by impregnation of H₂PtCl₆·6H₂O, followed by calcination at 500°C and reduction in H₂ at 350°C.

3.5.2. Catalytic Conversion of Polyethylene

PE and a H₂-reduced Pt catalyst, with or without added acid catalyst, were loaded into a stainless steel autoclave inside an Ar-filled glove-box. The contents were magnetically stirred at 280°C $\pm$ 5°C for the desired reaction time, then the reaction was quenched by immersing the reactor in a room-temperature water bath. Volatile hydrocarbon products sampled from the reactor headspace were characterized by GC-FID, using propene added as an internal standard via gas-tight syringe. Liquid hydrocarbon products were extracted from the reactor using CH₂Cl₂ (10 mL) and filtered. The filtrate was analyzed by GC-FID to quantify C_{6–13} hydrocarbons. After solvent removal under reduced pressure (0.1 Torr, 1 h), a portion of the liquid (2 mg) was dissolved in 1,1,2,2-tetrachloroethane-*d*₂ for ¹H NMR analysis. Another portion (6–7 mg) was dissolved in CHCl₃ containing 0.25 vol % triethylamine (1.5 mL) for GPC analysis. Insoluble material remaining on the frit, including the catalyst and insoluble hydrocarbons, was recovered and weighed.

3.6. References

1. Geyer, R., Jambeck, J.R., and Law, K.L. (2017). Production, use, and fate of all plastics ever made. *Sci. Adv.* 3, e1700782. 10.1126/sciadv.1700782.
2. World Economic Forum (2016). The new plastics economy: Rethinking the future of plastic. <https://www.weforum.org/reports/the-new-plastics-economy-rethinking-the-future-of-plastics/>.
3. Sills, J., and Adyel, T.M. (2020). Accumulation of plastic waste during COVID-19. *Science* 369, 1314–1315. 10.1126/science.abd9925.
4. Peng, Y., Wu, P., Schartup, A.T., and Zhang, Y. (2021). Plastic waste release caused by COVID-19 and its fate in the global ocean. *Proc. Natl. Acad. Sci.* 118, e2111530118. 10.1073/pnas.2111530118.
5. Eriksson, O., and Finnveden, G. (2009). Plastic waste as a fuel - CO₂-neutral or not? *Energy Environ. Sci.* 2, 907–914. 10.1039/b908135f.
6. Rochman, C.M., Browne, M.A., Halpern, B.S., Hentschel, B.T., Hoh, E., Karapanagioti, H.K., Rios-Mendoza, L.M., Takada, H., Teh, S., and Thompson, R.C. (2013). Classify plastic waste as hazardous. *Nature* 494, 169–171. 10.1038/494169a.
7. Bouwmeester, H., Hollman, P.C.H., and Peters, R.J.B. (2015). Potential health impact of environmentally released micro- and nanoplastics in the human food production chain: experiences from nanotoxicology. *Environ. Sci. Technol.* 49, 8932–8947. 10.1021/acs.est.5b01090.
8. Hundertmark, T., Mayer, M., McNally, C., Simons, T.J., and Witte, C. (2018). How plastics-waste recycling could transform the chemical industry (McKinsey & Company).

- <https://www.mckinsey.com/~/media/McKinsey/Industries/Chemicals/Our%20Insights/How%20plastics%20waste%20recycling%20could%20transform%20the%20chemical%20industry/How-plastics-waste-recycling-could-transform.pdf>
9. Garcia, J.M., and Robertson, M.L. (2017). The future of plastics recycling. *Science* 358, 870–872. 10.1126/science.aag0324.
 10. Nicholson, S.R., Rorrer, J.E., Singh, A., Konev, M.O., Rorrer, N.A., Carpenter, A.C., Jacobsen, A.J., Román-Leshkov, Y., and Beckham, G.T. (2022). The critical role of process analysis in chemical recycling and upcycling of waste plastics. *Annu. Rev. Chem. Biomol. Eng.* 13, 301–324. 10.1146/annurev-chembioeng-100521-085846.
 11. Kunwar, B., Cheng, H.N., Chandrashekar, S.R., and Sharma, B.K. (2016). Plastics to fuel: a review. *Renew. Sustain. Energy Rev.* 54, 421–428. 10.1016/j.rser.2015.10.015.
 12. Jia, C., Xie, S., Zhang, W., Intan, N.N., Sampath, J., Pfaendtner, J., and Lin, H. (2021). Deconstruction of high-density polyethylene into liquid hydrocarbon fuels and lubricants by hydrogenolysis over Ru catalyst. *Chem Catal.* 1, 437–455. 10.1016/j.checat.2021.04.002.
 13. Tennakoon, A., Wu, X., Paterson, A.L., Patnaik, S., Pei, Y., LaPointe, A.M., Ammal, S.C., Hackler, R.A., Heyden, A., Slowing, I.I., et al. (2020). Catalytic upcycling of high-density polyethylene via a processive mechanism. *Nat. Catal.* 3, 893–901. 10.1038/s41929-020-00519-4.
 14. Liu, S., Kots, P.A., Vance, B.C., Danielson, A., and Vlachos, D.G. (2021). Plastic waste to fuels by hydrocracking at mild conditions. *Sci. Adv.* 7, eabf8283. 10.1126/sciadv.abf8283.

15. Vance, B.C., Kots, P.A., Wang, C., Hinton, Z.R., Quinn, C.M., Epps, T.H., Korley, L.T.J., and Vlachos, D.G. (2021). Single pot catalyst strategy to branched products via adhesive isomerization and hydrocracking of polyethylene over platinum tungstated zirconia. *Appl. Catal. B Environ.* 299, 120483. 10.1016/j.apcatb.2021.120483.
16. Celik, G., Kennedy, R.M., Hackler, R.A., Ferrandon, M., Tennakoon, A., Patnaik, S., LaPointe, A.M., Ammal, S.C., Heyden, A., Perras, F.A., et al. (2019). Upcycling single-use polyethylene into high-quality liquid products. *ACS Cent. Sci.* 5, 1795–1803. 10.1021/acscentsci.9b00722.
17. Rorrer, J.E., Troyano-Valls, C., Beckham, G.T., and Román-Leshkov, Y. (2021). Hydrogenolysis of polypropylene and mixed polyolefin plastic waste over Ru/C to produce liquid alkanes. *ACS Sustain. Chem. Eng.* 9, 11661–11666. 10.1021/acssuschemeng.1c03786.
18. Rorrer, J.E., Beckham, G.T., and Román-Leshkov, Y. (2021). Conversion of polyolefin waste to liquid alkanes with Ru-based catalysts under mild conditions. *JACS Au* 1, 8–12. 10.1021/jacsau.0c00041.
19. Serrano, D.P., Aguado, J., and Escola, J.M. (2012). Developing advanced catalysts for the conversion of polyolefinic waste plastics into fuels and chemicals. *ACS Catal.* 2, 1924–1941. 10.1021/cs3003403.
20. Buekens, A. (2006). Introduction to Feedstock Recycling of Plastics. In *Feedstock Recycling and Pyrolysis of Waste Plastics* (John Wiley & Sons, Ltd), pp. 1–41. <https://doi.org/10.1002/0470021543.ch1>.

21. Buekens, A.G., and Huang, H. (1998). Catalytic plastics cracking for recovery of gasoline-range hydrocarbons from municipal plastic wastes. *Resour. Conserv. Recycl.* 23, 163–181. 10.1016/S0921-3449(98)00025-1.
22. Munir, D., Irfan, M.F., and Usman, M.R. (2018). Hydrocracking of virgin and waste plastics: A detailed review. *Renew. Sustain. Energy Rev.* 90, 490–515. 10.1016/j.rser.2018.03.034.
23. Jia, X., Qin, C., Friedberger, T., Guan, Z., and Huang, Z. (2016). Efficient and selective degradation of polyethylenes into liquid fuels and waxes under mild conditions. *Sci. Adv.* 2, e1501591. 10.1126/sciadv.1501591.
24. Wang, N.M., Strong, G., DaSilva, V., Gao, L., Huacuja, R., Konstantinov, I.A., Rosen, M.S., Nett, A.J., Ewart, S., Geyer, R., et al. (2022). Chemical recycling of polyethylene by tandem catalytic conversion to propylene. *J. Am. Chem. Soc.* 10.1021/jacs.2c07781.
25. Conk, R.J., Hanna, S., Shi, J.X., Yang, J., Ciccio, N.R., Qi, L., Bloomer, B.J., Heuvel, S., Wills, T., Su, J., et al. (2022). Catalytic deconstruction of waste polyethylene with ethylene to form propylene. *Science* 377, 1561–1566. 10.1126/science.add1088.
26. Rudnick, L.R. (2020). *Synthetics, Mineral Oils, and Bio-Based Lubricants: Chemistry and Technology* (CRC Press).
27. Zhang, F., Zeng, M., Yappert, R.D., Sun, J., Lee, Y.-H., LaPointe, A.M., Peters, B., Abu-Omar, M.M., and Scott, S.L. (2020). Polyethylene upcycling to long-chain alkylaromatics by tandem hydrogenolysis/aromatization. *Science* 370, 437–441. 10.1126/science.abc5441.

28. Holmberg, K. (2019). Surfactants. In Ullmann's Encyclopedia of Industrial Chemistry (John Wiley & Sons, Ltd), pp. 1–56. 10.1002/14356007.a25_747.pub2.
29. le Goff, P.-Y., Kostka, W., and Ross, J. (2017). Catalytic Reforming. In Springer Handbook of Petroleum Technology, C. S. Hsu and P. R. Robinson, eds. (Springer International Publishing), pp. 589–616. 10.1007/978-3-319-49347-3_18.
30. Digne, M., Raybaud, P., Sautet, P., Guillaume, D., and Toulhoat, H. (2008). Atomic scale insights on chlorinated γ -alumina surfaces. *J. Am. Chem. Soc.* *130*, 11030–11039. 10.1021/ja8019593.
31. Marcilly, C. (2006). Acido-basic catalysis: application to refining and petrochemistry (Editions Technip).
32. Berteau, P., Kellens, M.A. and Delmon, B. (1991). Acid-Base Properties of Modified Aluminas. *J Chem Soc Faraday Trans.* *87*, 1425–1431. 10.1039/FT9918701425.
33. Martin, N.M., Nilsson, J., Skoglundh, M., Adams, E.C., Wang, X., Velin, P., Smedler, G., Raj, A., Thompsett, D., Brongersma, H.H., et al. (2016). Characterization of surface structure and oxidation/reduction behavior of Pd–Pt/Al₂O₃ model catalysts. *J. Phys. Chem. C* *120*, 28009–28020. 10.1021/acs.jpcc.6b09223.
34. Ernst, L., and Schulz, P. (1992). ¹³C and ¹H NMR chemical shift assignments of 1- and 2-alkylnaphthalenes (R = Me, Et, *i*-Pr, *t*-Bu) and determination of substituent effects on ¹³C and ¹H chemical shifts. *Magn. Reson. Chem.* *30*, 73–76. 10.1002/mrc.1260300114.
35. Bartle, K.D., and Smith, J.A.S. (1967). High-resolution nuclear magnetic resonance spectra of phenanthrenes—I Phenanthrene and some alkyl derivatives. *Spectrochim. Acta Part Mol. Spectrosc.* *23*, 1689–1714. 10.1016/0584-8539(67)80053-9.

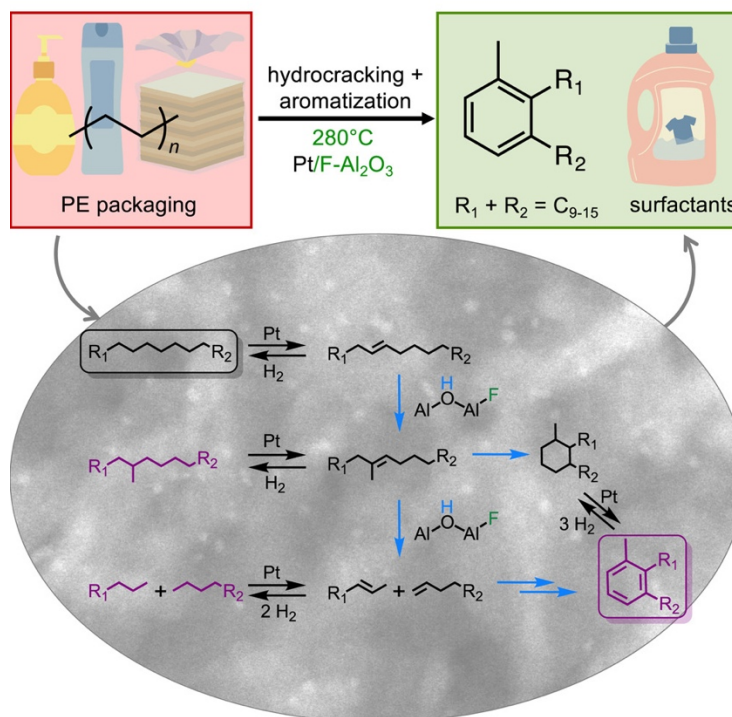
36. Madhushaw, R.J., Lo, C.-Y., Hwang, C.-W., Su, M.-D., Shen, H.-C., Pal, S., Shaikh, I.R., and Liu, R.-S. (2004). Ruthenium-catalyzed cycloisomerization of o-(ethynyl)phenylalkenes to diene derivatives via skeletal rearrangement. *J. Am. Chem. Soc.* *126*, 15560–15565. 10.1021/ja045516n.
37. Li, C., Chen, T., Li, B., Xiao, G., and Tang, W. (2015). Efficient synthesis of sterically hindered arenes bearing acyclic secondary alkyl groups by Suzuki–Miyaura cross-couplings. *Angew. Chem. Int. Ed.* *54*, 3792–3796. 10.1002/anie.201411518.
38. Danzik, M. (1990). Steam enhanced oil recovery method using dialkyl aromatic sulfonates. U.S. Patent No. 4,967,837. 6 Nov. 1990.
39. Hashim, M.A., Kulandai, J., and Hassan, R.S. (1992). Biodegradability of branched alkylbenzene sulphonates. *J. Chem. Technol. Biotechnol.* *54*, 207–214. 10.1002/jctb.280540302.
40. DeFrank, J.J., and Ribbons, D.W. (1977). p-cymene pathway in *Pseudomonas putida*: initial reactions. *J. Bacteriol.* *129*, 1356–1364. 10.1128/jb.129.3.1356-1364.1977.
41. Mahajan, M.C., Phale, P.S., and Vaidyanathan, C.S. (1994). Evidence for the involvement of multiple pathways in the biodegradation of 1- and 2-methylnaphthalene by *Pseudomonas putida* CSV86. *Arch. Microbiol.* *161*, 425–433. 10.1007/BF00288954.
42. Avenier, P., Bazer-Bachi, D., Bazer-Bachi, F., Chizallet, C., Deleau, F., Diehl, F., Gornay, J., Lemaire, É., Moizan-Basle, V., Plais, C., et al. (2016). Catalytic reforming: methodology and process development for a constant optimisation and performance enhancement. *Oil Gas Sci. Technol. - Rev. IFP Energ. Nouv.* *71*. 10.2516/ogst/2015040.

43. Zhang, F., Szeto, K.C., Taoufik, M., Delevoye, L., Gauvin, R.M., and Scott, S.L. (2018). Enhanced metathesis activity and stability of methyltrioxorhenium on a mostly amorphous alumina: role of the local grafting environment. *J. Am. Chem. Soc.* *140*, 13854–13868. 10.1021/jacs.8b08630.
44. Chakraborty, B., and Viswanathan, B. (1999). Surface acidity of MCM-41 by in situ IR studies of pyridine adsorption. *Catal. Today* *49*, 253–260. 10.1016/S0920-5861(98)00431-3.
45. Healy, M.H., Wieserman, L.F., Arnett, E.M., and Wefers, K. (1989). Infrared spectroscopy and microcalorimetric investigations of d-q and k aluminas using basic probe molecules: acetonitrile, pyridine, 2,6-lutidine, and *n*-butylamine. *Langmuir* *5*, 114–123. 10.1021/la00085a021.
46. Oliviero, L., Vimont, A., Lavalley, J.-C., Romero Sarria, F., Gaillard, M., and Maugé, F. (2005). 2,6-Dimethylpyridine as a probe of the strength of Brønsted acid sites: study on zeolites. Application to alumina. *Phys Chem Chem Phys* *7*, 1861–1869. 10.1039/B500689A.
47. Lyu, Y., Yu, Z., Yang, Y., Wang, X., Zhao, X., Liu, X., and Yan, Z. (2019). Metal-acid balance in the in-situ solid synthesized Ni/SAPO-11 catalyst for *n*-hexane hydroisomerization. *Fuel* *243*, 398–405. 10.1016/j.fuel.2019.01.013.
48. Guisnet, M. (2013). “Ideal” bifunctional catalysis over Pt-acid zeolites. *Catal. Today* *218–219*, 123–134. 10.1016/j.cattod.2013.04.028.
49. Weitkamp, J. (2012). Catalytic hydrocracking—mechanisms and versatility of the Process. *ChemCatChem* *4*, 292–306. <https://doi.org/10.1002/cctc.201100315>.

50. Pirngruber, G.D., Maury, S., Daudin, A., Alspektor, P.Y., Bouchy, C., and Guillon, E. (2020). Balance between (de)hydrogenation and acid sites: comparison between sulfide-based and Pt-based bifunctional hydrocracking catalysts. *Ind. Eng. Chem. Res.* *59*, 12686–12695. 10.1021/acs.iecr.0c01680.
51. Calemme, V., Peratello, S., and Perego, C. (2000). Hydroisomerization and hydrocracking of long chain *n*-alkanes on Pt/amorphous SiO₂–Al₂O₃ catalyst. *Appl. Catal. Gen.* *190*, 207–218. 10.1016/S0926-860X(99)00292-6.
52. Alvarez, F., Ribeiro, F.R., Perot, G., Thomazeau, C., and Guisnet, M. (1996). Hydroisomerization and hydrocracking of alkanes. *J. Catal.* *162*, 179–189. 10.1006/jcat.1996.0275.
53. Hoffkes, H. (1982). Reactions of hexene on silica-aluminas and aluminas with special regard to cyclization reactions. *J. Catal.* *77*, 257–262. 10.1016/0021-9517(82)90166-X.
54. Ma, H., Chen, Y., Wei, Z., Wang, S., Qin, Z., Dong, M., Li, J., Wang, J., and Fan, W. (2018). Reaction mechanism for direct cyclization of linear C₅, C₆, and C₇ alkenes over H-ITQ-13 zeolite investigated using density functional theory. *ChemPhysChem* *19*, 496–503. 10.1002/cphc.201701020.
55. Samad, J.E., Blanchard, J., Sayag, C., Louis, C., and Regalbuto, J.R. (2016). The controlled synthesis of metal-acid bifunctional catalysts: The effect of metal:acid ratio and metal-acid proximity in Pt silica-alumina catalysts for *n*-heptane isomerization. *J. Catal.* *342*, 203–212. 10.1016/j.jcat.2016.08.004.

56. Weisz, P.B., and Swegler, E.W. (1957). Stepwise reaction on separate catalytic centers: isomerization of saturated hydrocarbons. *Science* *126*, 31–32. 10.1126/science.126.3262.31.
57. Weisz, P.B. (1962). Polyfunctional Heterogeneous Catalysis. In *Advances in Catalysis*, D. D. Eley, P. W. Selwood, P. B. Weisz, A. A. Balandin, J. H. De Boer, P. J. Debye, P. H. Emmett, J. Horiuti, W. Jost, G. Natta, et al., eds. (Academic Press), pp. 137–190. 10.1016/S0360-0564(08)60287-4.
58. Batalha, N., Pinard, L., Bouchy, C., Guillon, E., and Guisnet, M. (2013). *n*-Hexadecane hydroisomerization over Pt-HBEA catalysts. Quantification and effect of the intimacy between metal and protonic sites. *J. Catal.* *307*, 122–131. 10.1016/j.jcat.2013.07.014.
59. Gutierrez-Acebo, E., Leroux, C., Chizallet, C., Schuurman, Y., and Bouchy, C. (2018). Metal/acid bifunctional catalysis and intimacy criterion for ethylcyclohexane hydroconversion: when proximity does not matter. *ACS Catal.* *8*, 6035–6046. 10.1021/acscatal.8b00633.
60. Zecevic, J., Vanbutsele, G., de Jong, K.P., and Martens, J.A. (2015). Nanoscale intimacy in bifunctional catalysts for selective conversion of hydrocarbons. *Nature* *528*, 245–248. 10.1038/nature16173.
61. Cheng, K., Wal, L.I., Yoshida, H., Oenema, J., Harmel, J., Zhang, Z., Sunley, G., Zečević, J., and Jong, K.P. (2020). Impact of the spatial organization of bifunctional metal–zeolite catalysts on the hydroisomerization of light alkanes. *Angew. Chem.* *132*, 3620–3628. 10.1002/ange.201915080.

3.7. Table of Content Graph



3.8. Appendix II

3.8.1. Materials

Trimethyl(cyclopentadienyl)platinum (CpPtMe_3 , 99%) and $\gamma\text{-Al}_2\text{O}_3$ (Lot 35231600, B.E.T. surface area $186 \text{ m}^2 \text{ g}^{-1}$, pore volume $0.50 \text{ cm}^3 \text{ g}^{-1}$) were purchased from Strem. Chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), tetraammineplatinum(II) nitrate ($[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$, 50.0+/% Pt basis), ammonium fluoride ($\geq 98.0\%$), pyridine (anhydrous, 99.8%), 2,6-dimethylpyridine (DMP, 99%), triacontane (*norm*- $\text{C}_{30}\text{H}_{62}$, 98%), *n*-octadecane (*norm*- $\text{C}_{18}\text{H}_{38}$, 99%), 1-octadecene ($\geq 95.0\%$), carbon tetrachloride (99.9%), a standard Pt solution containing $(976 \pm 2) \text{ mg Pt/kg}$ in 5% w/w HCl, di-*tert*-butylhydroxytoluene ($> 99\%$), chromium(III) acetylacetonate ($\text{Cr}(\text{acac})_3$, 99.99%), and polyethylene of two different

molecular weights (Lots SKU 427772 and SKU 427799), and a standard mixture of saturated alkanes (C7 - C40, certified reference material, 1000 µg/mL each component in hexane) were all purchased from Sigma-Aldrich. HPLC-grade water, HPLC-grade hexanes, HPLC-grade triethylamine, HPLC-grade 1,2,4-trichlorobenzene, and carbon disulfide ($\geq 99.9\%$) were purchased from Fisher Chemicals. 1,1,2,2-Tetrachloroethane- d_2 (TCE- d_2 , ≥ 99.5 at% D) was purchased from Cambridge Isotope Laboratories. Chloroform (HPLC grade, OmniSolv®, CX1054-6), nitric acid (68.0-70.0 wt%), and hydrochloric acid (36.5-38.0 wt%) were obtained from EMD Millipore Corp.

Silica (Sylopol 952, B.E.T. surface area $249 \text{ m}^2 \text{ g}^{-1}$, $33 \text{ }\mu\text{m}$ particle size, pore volume 1.61 mL g^{-1}), silica–alumina (Davicat 3113, 7.6 wt % Al, B.E.T. surface area $573 \text{ m}^2 \text{ g}^{-1}$, pore volume $0.76 \text{ cm}^3 \text{ g}^{-1}$), HZSM-5 (FCC catalyst formulation, Lot 2010228, 33.8 wt% Al_2O_3) were obtained from Grace-Davison.

H_2 (5.048 vol% in Ar, Airgas Certified Standard) was purified by passing through 13X molecular sieves and BTS catalyst (Sigma Aldrich) before its use for Pt reduction. Propene (99.8%) was obtained from PRAXAir. Argon (UHP) was purchased from Airgas. H_2 (4.976 vol% in He, Airgas Certified Standard) and O_2 (99.999%, Airgas) were used to regenerate catalysts post-reaction. Carbon monoxide (9.890 vol% in He, Airgas Certified Standard) was used in pulsed CO chemisorption.

3.8.2. Detailed Experimental Procedures

3.8.2.1. Catalyst Synthesis

3.8.2.1.1. Preparation of Catalyst Supports

Unmodified supports (SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, $\text{SiO}_2\text{-Al}_2\text{O}_3$, and HZSM-5). Prior to Pt deposition, each unmodified support (1.50 g) was calcined in air in a temperature-controlled muffle furnace (Thermo Scientific Lindberg/Blue M BF51848C) at 500°C for 4 h.

Chlorinated alumina ($\text{Cl-Al}_2\text{O}_3$). Calcined $\gamma\text{-Al}_2\text{O}_3$ (1.50 g) was dehydrated at ca. 10^{-2} Torr and 400°C for 8 h. After cooling to room temperature, CCl_4 -saturated Ar (5 mL min^{-1}) was flowed through the bed as the temperature was ramped to 300°C at a rate of 2°C min^{-1} , then held at that temperature for 1 h. The resulting material (denoted $\text{Cl-Al}_2\text{O}_3$) was evacuated at ca. 10^{-2} Torr and 400°C for 8 h to remove weakly-bound surface species.¹ The Cl loading was determined by flask combustion/ion chromatography (Atlantic Microlab, Inc., Norcross, GA) to be 1.8 wt%.

Fluorinated alumina ($\text{F-Al}_2\text{O}_3$). Calcined $\gamma\text{-Al}_2\text{O}_3$ (1.50 g) was combined with an aqueous solution (0.6 mL, roughly corresponding to the pore volume) of NH_4F (either 43.8 or 87.6 mg). The mixture was dried in air in an oven at 80°C for 2 h, followed by ramping the temperature to 550°C at a rate of 2°C min^{-1} and holding for 5 h. The resulting materials were evacuated at ca. 10^{-2} Torr and 400°C for 8 h to remove weakly-bound surface species. F loadings were determined by flask combustion/ion chromatography (Atlantic Microlab, Inc., Norcross, GA) to be 0.8 and 1.3 wt %.²

3.8.2.1.2. Synthesis of Supported Pt Catalysts

All supported Pt catalysts containing 1.0 wt% Pt were prepared by incipient wetness impregnation. Each support (1.50 g) was mixed with the appropriate pore volume of an aqueous solution containing $\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O}$ (39.9 mg), followed by drying in air in an oven at

80°C for 2 h. The solid was calcined in static air by heating to 500°C at a rate of 2°C min⁻¹ in a muffle furnace. After 3 h, the material was reduced in flowing H₂ (5.0 vol% in Ar, 30 mL min⁻¹) as the temperature was ramped at 2°C min⁻¹ to 350°C, where it was held for 2 h. The reactor was cooled to room temperature in flowing H₂, then evacuated at ca. 10⁻² Torr for 30 min.

As a control for comparison to prior work,³ Pt/ γ -Al₂O₃ containing 1.5 wt% Pt was synthesized by chemical vapor deposition. Calcined γ -Al₂O₃ (1.20 g) was evacuated at ca. 10⁻² Torr and 400°C for 12 h. CpPtMe₃ (35 mg) was deposited onto the dry γ -Al₂O₃ at room temperature, followed by reduction by heating in flowing H₂ (5.0 vol% in Ar) from room temperature at a ramp rate of 2°C min⁻¹ to 280°C, then holding at this temperature for 2 h. The reactor was cooled to room temperature in flowing H₂, then evacuated for 30 min.

Pt/SiO₂ containing 1.5 wt% Pt was synthesized by incipient wetness impregnation. Calcined SiO₂ (1.50 g) was mixed with an aqueous solution (1.5 mL) containing [Pt(NH₃)₄](NO₃)₂ (45.0 mg), followed by drying in static air in an oven at 80°C for 2 h then calcination by heating at a rate of 2°C min⁻¹ and holding at 350°C for 3 h to decompose the Pt complex.⁴ The resulting material was reduced by heating at a rate of 2°C min⁻¹ in flowing H₂ (5.0 vol% in Ar) to 350°C, then holding at that temperature for 2 h. Finally, the reactor was cooled to room temperature in flowing H₂, then evacuated at ca. 10⁻² Torr for 30 min.

Pt/Cl-Al₂O₃ containing 1.5 wt% Pt and 1.4 wt% Cl was synthesized by incipient wetness impregnation, following a previously described method.⁵ Calcined γ -Al₂O₃ (1.50 g) was mixed with an aqueous solution (0.6 mL) containing [Pt(NH₃)₄](NO₃)₂ (45.0 mg) and HCl (130.0 mg), followed by drying in air in an oven at 80°C for 2 h then calcination

in air by heating to 500°C at a rate of 2°C min⁻¹ and holding for 3 h. After cooling to RT, the material was reduced by heating to 500°C at a rate of 2°C/min in flowing H₂ (5.0 vol% in Ar), then holding at that temperature for 2 h. Finally, the sample was evacuated at ca. 10⁻² Torr and room temperature for 30 min.

Pt/F-Al₂O₃ containing 1.6 wt% Pt was synthesized by chemical vapor deposition of CpPtMe₃ (35 mg) onto F-Al₂O₃ (1.3 g, 0.8 wt% F), followed by reduction by heating to 280°C at a rate of 2°C min⁻¹ in flowing H₂ (5.0 vol% in Ar), then holding for 2 h.³ This method was found to give better dispersed Pt NPs compared with simultaneous incipient wetness impregnation of [Pt(NH₃)₄](NO₃)₂ and NH₄F.

All freshly-reduced catalysts were protected from air exposure by storage in an Ar-filled glovebox prior to further characterization or use.

3.8.2.2. Characterization of Pt Catalysts

3.8.2.2.1. Pt Analysis

Pt analysis was performed using Inductively-Coupled Plasma (ICP) – Optical Emission Spectrometry (ICP-OES), on a Thermo iCAP 6300. The calibration curve in **Figure A3.1** was constructed using a standard Pt solution, prepared by diluting the commercial Pt standard with homemade aqua regia (5 vol%) in HPLC-grade water. In general, Pt was extracted from catalyst samples following a literature procedure,⁶ involving stirring in aqua regia at 75°C for 30 min. To ensure complete digestion of Pt, the extraction method was modified by allowing the suspensions to stand at room temperature for an additional 12 h. The suspensions were then filtered through a syringe filter (pore size 0.2 μm). The solid

residues were washed three times with HPLC-grade H₂O. The filtrate and washings were combined and diluted with aqua regia (5 vol % in water), then analyzed by ICP-OES. Pt loadings are summarized in **Table A3.1**.

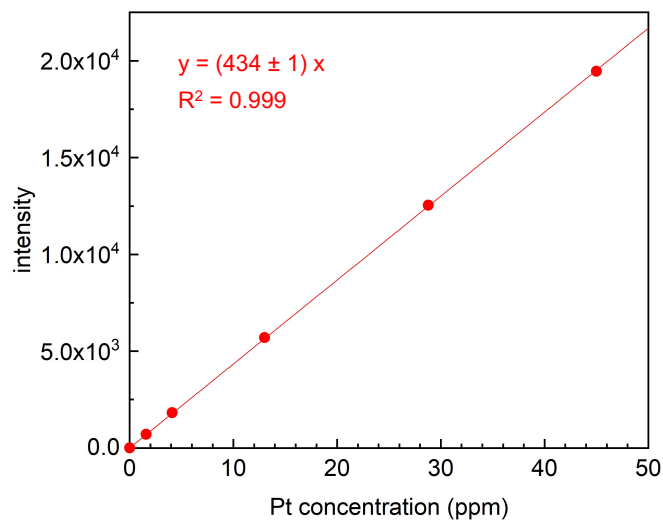


Figure A3.1. A typical calibration curve showing the ICP-OES response of Pt at 203.646 nm, using standard Pt solutions in aqua regia (5 vol% in water). The line is the least-squares fit of the equation $y = mx$ to the data.

Table A3.1. Pt loadings of various catalysts, measured by ICP-OES

Catalyst ^a	Nominal Pt Loading (wt%)	Measured Pt Loading (wt%) ^b
Pt/ZSM-5	0.99	0.96
Pt/SiO ₂ -Al ₂ O ₃	0.99	0.97
Pt/ γ -Al ₂ O ₃	0.99	1.02
Pt/ γ -Al ₂ O ₃	1.82	1.52
Pt/SiO ₂	0.99	0.97
Pt/SiO ₂ ^c	1.48	1.49
Pt/Cl-Al ₂ O ₃	1.48	1.46
Pt/F-Al ₂ O ₃	1.69	1.56
Pt/F-Al ₂ O ₃ ^d		1.54
Pt/F-Al ₂ O ₃ ^e		1.53

^a Pt was extracted in aqua regia, except where noted.

^b Average of results calculated using the Pt spectral lines at 214.423 and 203.646 nm.

^c Catalyst was digested in HF/aqua regia (v:v = 1:1).

^d Recycled once, after catalyzing the reaction of PE ($M_w = 3.5 \times 10^3$ g mol⁻¹, $D = 1.9$, 120 mg) for 8 h at 280°C.

^e Recycled twice, after catalyzing another reaction of PE ($M_w = 3.5 \times 10^3$ g mol⁻¹, $D = 1.9$, 120 mg) for 8 h at 280°C.

For some catalysts, the amount of Pt extracted by aqua regia was much lower than the nominal loading. Therefore, HF/aqua regia (v:v = 1:1) was used at 75°C for 30 min to

completely digest the SiO₂ and extract the Pt, based on previously described methods.^{7,8} The resulting solution was allowed to stand at room temperature for 12 h, then filtered through a syringe filter (pore size 0.2 mm) and washed three times with HPLC-grade H₂O (ca. 3 mL). The filtrate and washings were combined and diluted with HF/aqua regia (5% v:v in water) and analyzed by ICP-OES. A new calibration curve was constructed using standard Pt solutions, prepared from the commercial Pt standard diluted in a mixture of HF/aqua regia in HPLC-grade water (5% v:v in water).

3.8.2.2.2. Pt Dispersion

Accessible Pt surface areas in the fresh and recycled catalysts were measured by CO chemisorption, using a Micrometrics Autochem ii 2920. The catalyst (ca. 40 mg) was placed on a plug of glass wool in a U-shaped quartz reactor. A thermocouple was attached to the outside of the reactor, at the level of the middle of the bed. Complete reduction of the catalyst was ensured activated by heating in flowing H₂ (5.0 mol% in He) at a rate of 5°C min⁻¹ to 200°C, then held for 1 h before switching to He flow then cooling to room temperature. The catalyst was subjected to 30 pulses of CO (9.9 vol% in He, 124 mL each at 110°C). The amount of CO not adsorbed in each pulse was measured using a TCD detector. The Pt surface area (SA, m² g_{Pt}⁻¹), Pt dispersion (D, %), and average nanoparticle size (nm), were calculated using eqs A3.1-A3.3, assuming hemispherical Pt nanoparticles. The results are summarized in Table A3.2.

$$SA_{Pt} \text{ (m}^2 \text{ g}_{Pt}^{-1}\text{)} = (S_f N_A SA_{cross} V_{ad}) / (m W V_m) \quad (\text{A3.1})$$

$$D = (S_f M V_{ad}) / (m W V_m) \times 100\% \quad (\text{A3.2})$$

$$Pt \text{ nanoparticle size} = 6 / (d_{Pt} SA_{Pt}) \quad (\text{A3.3})$$

where the stoichiometric factor S_f (molar ratio CO/Pt_{surface}) was assumed to be unity. N_A = Avogadro's number, SA_{cross} = Pt cross-sectional area = $8.0 \times 10^{-20} \text{ m}^2$, d_{Pt} = density of Pt = $2.145 \times 10^{-20} \text{ g nm}^{-3}$, V_{ad} = volume of chemisorbed CO under STP conditions (mL), m = sample mass (g), W = weight fraction of Pt in the sample, as determined by ICP-OES ($\text{g}_{Pt}/\text{g}_{sample}$), W = Pt atomic weight = 195.1 g mol^{-1} , V_m = molar volume of CO = 22.4 L mol^{-1} at STP.

Table A3.2. Characterization of Pt nanoparticles in fresh and recycled catalysts

Catalyst	State	Loading (wt%)	Surface Area (m ² g _{Pt} ⁻¹)	Dispersion (%)	Avg NP size (nm)
Pt/HZSM-5	fresh	0.96	97	41	2.8
Pt/SiO ₂ - Al ₂ O ₃	fresh	0.97	107	43	2.6
Pt/ γ -Al ₂ O ₃	fresh	1.02	168	68	1.7
Pt/SiO ₂	fresh	0.97	108	44	2.6
Pt/SiO ₂	fresh	1.54	209	85	1.3
	recycled ^a		144	58	1.9
Pt/ γ -Al ₂ O ₃	fresh	1.52	215	87	1.3

	recycled ^a		197	80	1.4
Pt/Cl-	fresh	1.46	202	82	1.4
Al ₂ O ₃					
Pt/F-Al ₂ O ₃	fresh	1.56	172	70	1.6
Pt/F-Al ₂ O ₃	recycled ^b	1.54	145	59	1.9
Pt/F-Al ₂ O ₃	twice-recycled	1.53	141	57	2.0
	^c				

^a Recycled catalysts were removed from the reactor after converting *norm*-C₃₀H₆₂ for 12 h at 280°C. The catalysts were washed with CS₂ and isolated by filtration, evacuated overnight at 0.1 Torr, followed by calcination at 400°C in flowing O₂ and reduction in H₂ at 280°C. Pt loading was assumed to be the same as for the fresh catalyst.

^b Recycled catalyst was removed from the reactor after converting PE ($M_w = 3.5 \times 10^3$ g mol⁻¹, $\bar{D} = 1.9$) for 8 h at 280°C. The solid was washed with CH₂Cl₂ and isolated by filtration, evacuated overnight at 0.1 Torr, followed by calcination at 500°C in flowing O₂ and reduction in H₂ at 280°C.

^c Twice-recycled catalyst was removed from the reactor after converting PE ($M_w = 3.5 \times 10^3$ g mol⁻¹, $\bar{D} = 1.9$) for 8 h at 280°C. The solid was washed with CH₂Cl₂ and isolated by filtration, evacuated overnight at 0.1 Torr followed by calcination at 500°C in flowing O₂ and reduction in H₂ at 280°C.

To assess changes in the accessible Pt surface area for Pt/ γ -Al₂O₃ and Pt/SiO₂ due to their use in catalyzing reactions with *norm*-C₃₀H₆₂, CO chemisorption was performed directly on the catalysts recovered from the reactor. The Pt dispersion appeared to decrease dramatically for the recovered catalysts. However, we suspected the accuracy of the measurement was impacted by the presence of residual solvent (CS₂) used in extraction of the hydrocarbons.

Therefore, the recovered catalysts were calcined in flowing O₂ while heating to 400°C at a ramp rate of 5°C min⁻¹ and holding at 400°C for 2 h. After cooling to room temperature, the catalysts were re-reduced prior to performing CO chemisorption measurements. The Pt dispersion of Pt/ γ -Al₂O₃ decreased only slightly, from 87 to 80 %, after catalyst regeneration. In contrast, the Pt dispersion of Pt/SiO₂ decreased much more, from 85 to 58 %. Nevertheless, this change in Pt dispersion cannot account for the dramatically lower catalytic activity compared with Pt/ γ -Al₂O₃ (**Table 3.4**).

Pt/F-Al₂O₃ collected after its use in a reaction with PE was calcined in O₂ at 500°C followed by reduction in H₂ at 280°C to remove coke and unreacted PE (see **section 3.9.2.10** details on catalyst recycling). After the first recycle, the Pt dispersion of the regenerated catalyst decreased from 70 to 59 %, and the average particle size increased to 1.9 nm, consistent with the observation of larger Pt particles by TEM (**Figure A3.5**). The Pt dispersion was essentially unchanged after the second recycle, at 57 %.

3.8.2.2.3. Analysis of Pt Nanoparticle Size by Transmission Electron Microscopy

TEM images of catalysts were obtained using a ThermoFisher Talos F200X. Pt particle sizes were estimated by analysis of the high angle annular dark field (HAADF) images. Pt/Cl-Al₂O₃ (1.5 wt% Pt) and Pt/F-Al₂O₃ (1.6 wt% Pt) contain particles with average sizes of (1.0 $\pm$ 0.1) nm and (1.1 $\pm$ 0.2) nm, respectively (**Figures A3.2 and A3.3**). Both are smaller relative to the values estimated by CO chemisorption (**Table A3.2**). An overestimation of Pt particle size by CO chemisorption compared with TEM has been reported elsewhere for Pt/C in the

presence of Cl,⁹ where surface Cl preventing CO chemisorption. The average Pt particle size in Pt/F-Al₂O₃ recovered from a PE upgrading reaction at 280°C for 8 h is still (1.1 ± 0.2) nm before calcination (**Figure A3.4**). After calcination at 500°C followed by reduction in H₂ at 280°C, larger Pt particles (> 3 nm) are present but the distribution is still dominated by small particles (ca. 1 nm, **Figure A3.5a**), which is possibly due to Pt particle aggregation during the high temperature calcination. Nevertheless, the number-averaged Pt particle size increased only slightly, to (1.3 ± 0.3) nm (**Figure A3.5b**).

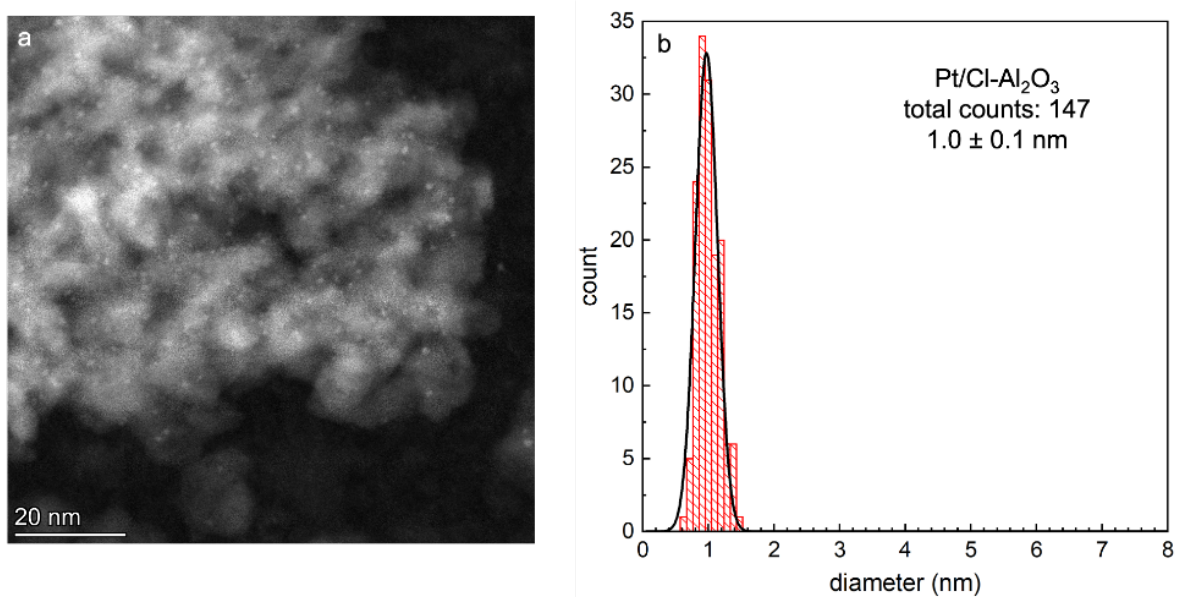


Figure A3.2. (a) HAADF-STEM image, and (b) Pt particle size histogram, for fresh, reduced Pt/Cl-Al₂O₃ (1.5 wt% Pt). The average nanoparticle size, obtained by fitting a Gaussian function to the distribution, is (1.0 ± 0.1) nm.

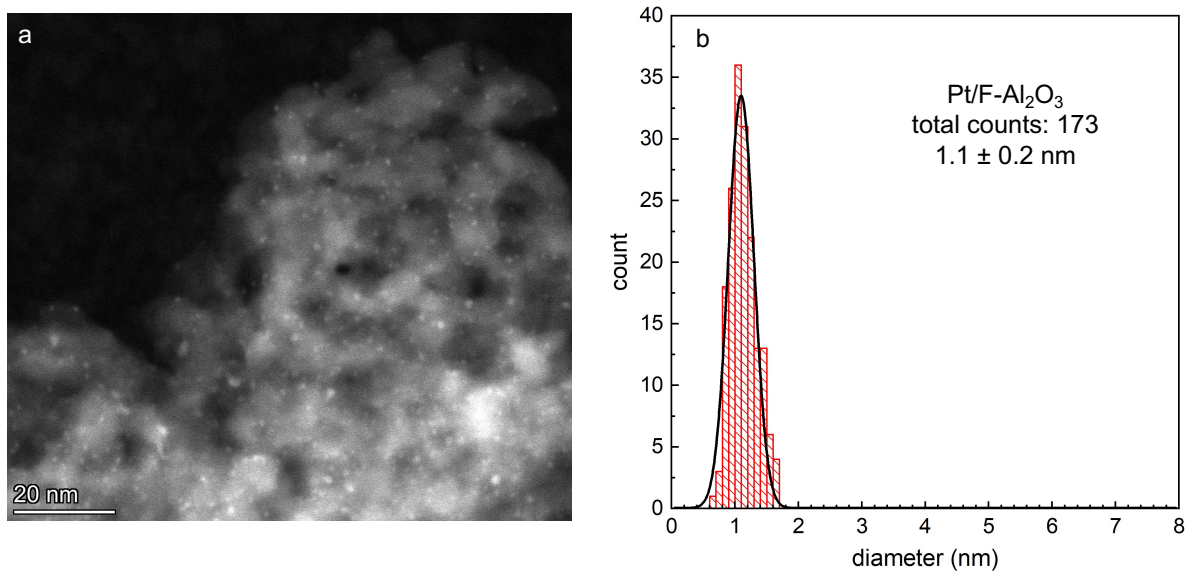


Figure A3.3. (a) HAADF-STEM image, and (b) Pt particle size histogram, for fresh, reduced Pt/F-Al₂O₃ (1.6 wt% Pt). The average nanoparticle size, obtained by fitting a Gaussian function to the distribution, is (1.1 ± 0.2) nm.

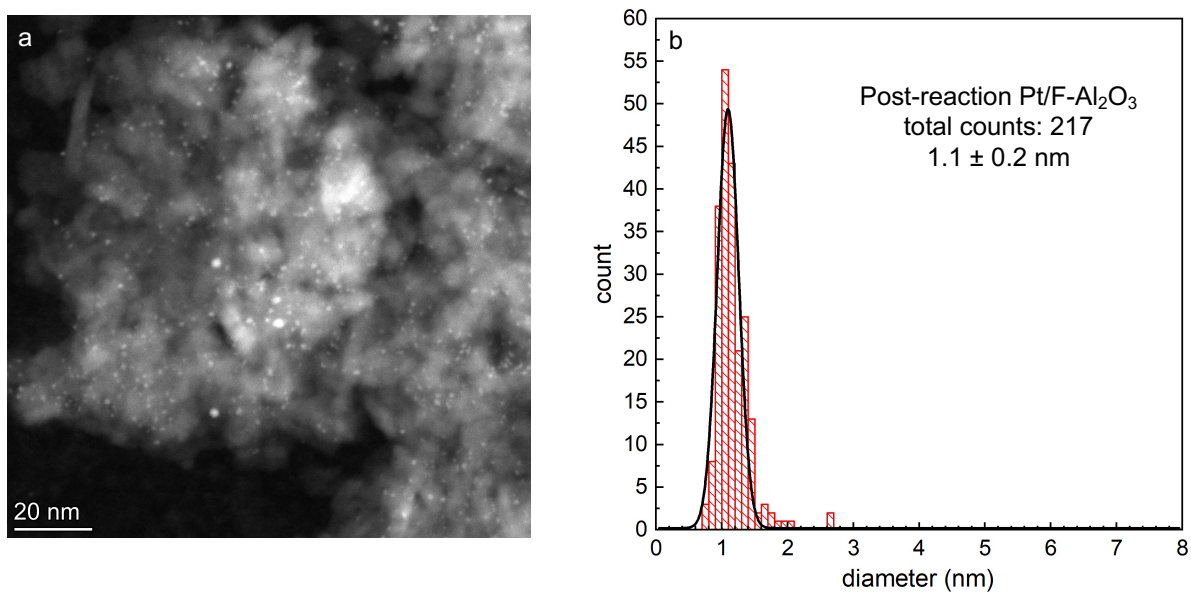


Figure A3.4. (a) HAADF-STEM image, and (b) Pt particle size histogram, for Pt/F-Al₂O₃ (1.6 wt% Pt), recovered after catalyzing the reaction of PE ($M_w = 3.5 \times 10^3$ g mol⁻¹, $D = 1.9$) at 280°C for 8 h. The average nanoparticle size, obtained by fitting a Gaussian function to the distribution, is (1.1 ± 0.2) nm.

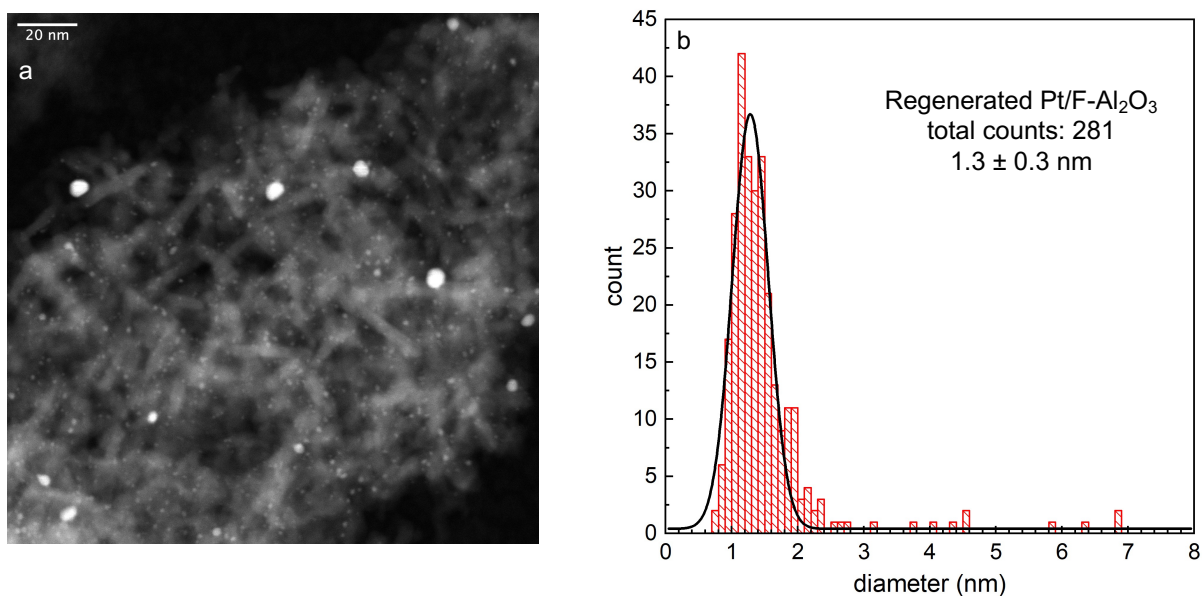


Figure A3.5. (a) HAADF-STEM image, and (b) Pt particle size histogram, for Pt/F-Al₂O₃ (1.6 wt% Pt), recovered after catalyzing the reaction of PE ($M_w = 3.5 \times 10^3$ g mol⁻¹, $D = 1.9$) at 280°C for 8 h followed by calcination in flowing O₂ at 500°C and reduction in flowing H₂ at 280°C. The average nanoparticle size, obtained by fitting a Gaussian function to the distribution, is (1.3 ± 0.3) nm.

3.8.2.3. Surface Characterization of Halogenated Aluminas and Supported Pt Catalysts

3.8.2.3.1. Physicochemical Characterization of Halogenated Aluminas

N₂ adsorption/desorption isotherms for halogenated aluminas were measured at −196°C using a Micromeritics 3Flex Porosimeter, and compared to data for unmodified γ -alumina (**Figure A3.6**). The appropriate cross-sectional area for an N₂ molecule adsorbed on a hydroxyl-terminated surface is 0.143 nm².¹⁰ All the aluminas have similar textural properties, with mesopores in the 4 nm range, mesopore volumes of ca. 0.4 cm³ g^{−1}, and negligible micropore volumes (<0.01 cm³ g^{−1}). Physicochemical properties are summarized in **Table A3.3**.

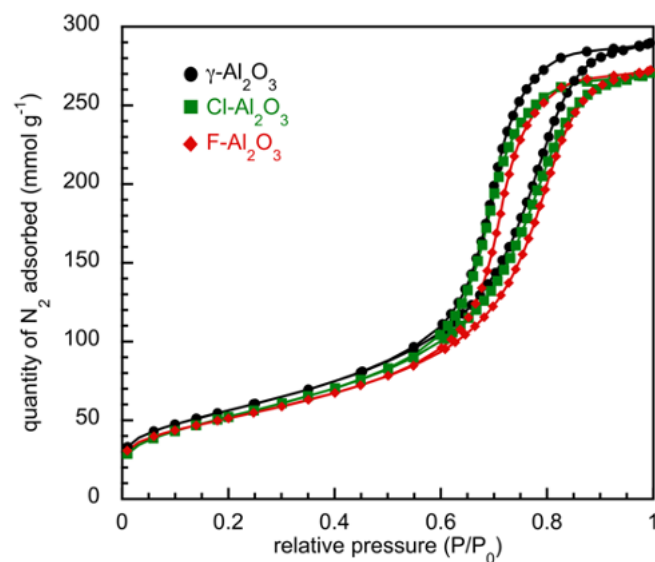


Figure A3.6. N₂ adsorption/desorption isotherms, measured at 77 K, for γ -Al₂O₃ (black circles), Cl-Al₂O₃ (1.8 wt% Cl, green squares) and F-Al₂O₃ (1.3 wt% F, red diamonds).

Table A3.3. Physicochemical properties of halogenated aluminas

Material	B.E.T. Surface	Pore Size	Pore Volume	X Density
	Area (m ² g ⁻¹)	(nm) ^a	(cm ³ g ⁻¹) ^b	(at. nm ⁻²) ^c
γ -Al ₂ O ₃	202	4.4	0.44	-
Cl-Al ₂ O ₃ (1.8 wt% Cl)	191	4.4	0.42	1.6
F-Al ₂ O ₃ (1.3 wt% F)	183	4.6	0.42	2.2

^a Calculated by the Barrett-Joyner-Halenda (B.J.H.) method, using the desorption branch of the N₂ isotherm.

^b Determined at P/P₀ = 0.99.

^c Calculated as X loading/B.E.T. surface area.

IR spectra were acquired using thin self-supporting pellets (5-mm diameter), pressed inside an Ar-filled glovebox. Spectra were recorded using a Bruker Alpha FTIR spectrometer over the range 4000–400 cm⁻¹ at a resolution of 2 cm⁻¹, accumulating 64 scans. The absorbance was normalized by the precise sample mass. Pristine γ -Al₂O₃ shows characteristic O-H stretching modes at 3790 and 3773 cm⁻¹ (**Figure A3.7**) that are associated with terminal (basic) OH groups, while bridging (acidic) OH groups appear at 3730 and 3680 cm⁻¹.¹¹ Halogenation leads to partial hydroxyl replacement by halide. The replacement of terminal OH groups is thermodynamically preferred.¹²

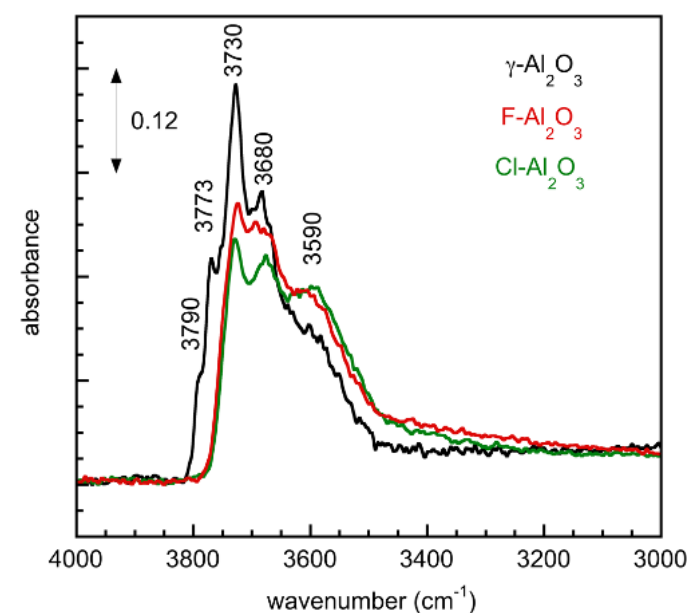


Figure A3.7. Transmission IR spectra of $\gamma\text{-Al}_2\text{O}_3$ (black), $\text{Cl-Al}_2\text{O}_3$ (1.8 wt% Cl, green), and $\text{F-Al}_2\text{O}_3$ (1.3 wt% F, red), recorded at room temperature after dehydration at ca. 10^{-2} Torr and 400°C for 8 h. All spectra are normalized by mass relative to the mass of $\gamma\text{-Al}_2\text{O}_3$ (6.0 mg).

3.8.2.3.2. IR Characterization of Catalyst Acidity

Calibration curves. Lewis and Brønsted acidity were measured by adsorption of pyridine and 2,6-dimethylpyridine (DMP), respectively. Calibration curves were constructed for each probe molecule following a literature procedure,¹³ as described below.

A precisely weighed sample of dry $\gamma\text{-Al}_2\text{O}_3$ (ca. 80 mg, of precisely weighed mass m_1) was transferred to a Schlenk tube inside a N_2 -filled glovebox. The Schlenk tube was sealed and removed from glovebox and connected to a high vacuum line. The tube was evacuated at ca. 10^{-2} Torr and 400°C for 2 h, then cooled to room temperature. A known amount of pyridine

(5.5 - 16.4 mmol, n_{py}) was introduced into the Schlenk tube. The solid was then transferred into an Ar-filled glovebox, where ca. 10 mg (of precisely weighed mass m_2) was pressed into a thin, self-supporting pellet (5 mm diameter, D). The IR spectrum was recorded and the absorbance was normalized by the precise sample mass.

When the pyridine loading is low (<250 mmol g^{-1}), the mid-IR spectrum is dominated by bands at ca. 1625, 1575, 1495 and 1455 cm^{-1} , corresponding to the ν_{8a} , ν_{8b} , ν_{19a} , and ν_{19b} modes, respectively, of pyridine interacting with Lewis acid sites (LAS). Weaker bands at ca. 1597 cm^{-1} (ν_{8a}) and 1440 cm^{-1} (ν_{19b}) are also present, corresponding to hydrogen-bonded pyridine.¹⁴ No peaks associated with pyridinium ion (pyH^+) at 1545 cm^{-1} (ν_{19b}) or 1638 cm^{-1} (ν_{8a}) were observed.

The IR region centered at ca. 1450 cm^{-1} contains three peaks at 1455, 1450, and 1443 cm^{-1} (**Figure A3.8a**). The first two peaks correspond to the ν_{19b} mode of pyridine interacting with strong and weak LAS, respectively, while the third is due to the ν_{19b} mode of H-bonded pyridine.^{14,15} The combined areas of peaks at 1455 and 1450 cm^{-1} , A_{py-LAS} , is proportional to the amount of LAS-adsorbed pyridine according to Beer's law, **eq A3.4**.

$$A_{py-LAS} = \varepsilon_{py-LAS} \cdot l \left(\frac{n_{py-LAS}}{S \cdot l} \right) = \frac{1}{S} (\varepsilon_{py-LAS} \cdot n_{py-LAS}) = \left(\frac{4}{\pi D^2} \right) (\varepsilon_{py-LAS} \cdot n_{py-LAS}) \quad (A3.4)$$

where ε_{py-LAS} is the combined apparent integrated molar extinction coefficient for the two peaks; l , S , and D are the disk thickness, its cross-sectional area, and diameter, respectively, and n_{py-LAS} is the amount of LAS-adsorbed pyridine on a disk of mass m_2 . Since the IR beam

does not sample the entire disk, the extinction coefficient is an apparent rather than a true value. However, when all experiments use the same disk size and IR beamspot size, the apparent value is proportional to the true value and can be used instead. A similar equation involving A_{py-H} and e_{py-H} can be written for the peak at 1443 cm^{-1} , **eq A3.5**, resulting in the expression for the total integrated absorbance in the region shown in **eq A3.6**:

$$A_{py-H} = \left(\frac{4}{\pi D^2} \right) (\varepsilon_{py-H} \cdot n_{py-H}) \quad (\text{A3.5})$$

$$A_{total} = A_{py-LAS} + A_{py-H} = \left(\frac{4}{\pi D^2} \right) (\varepsilon_{py-LAS} \cdot n_{py-LAS} + \varepsilon_{py-H} \cdot n_{py-H}) \quad (\text{A3.6})$$

Since e_{py-H} is unknown, we assumed $e_{py-LAS} = e_{py-H}$ to obtain **eq A3.7**:

$$A_{total} = \left(\frac{4\varepsilon_{py-LAS}}{\pi D^2} \right) (n_{py-LAS} + n_{py-H}) \quad (\text{A3.7})$$

The relationship between n_{py-LAS} and the total amount of pyridine (n_{py}) added to the original powder of mass m_1 is given in **eq A3.8**:

$$n_{py} = (m_1 / m_2) (n_{py-LAS} + n_{py-H}) \quad (\text{A3.8})$$

Measurement of A_{total} for several values of n_{py} gave the calibration curve in **Figure A3.8b**, with slope $k = 4 \text{ e m}^2 / \pi D^2 m_1$. Finally, e_{py-LAS} was calculated using **eq A3.9**:

$$e_{\text{py-LAS}} = \pi D^2 k m_1 / 4 m_2 \quad (\text{A3.9})$$

The measured value of $e_{\text{py-LAS}} = (1.31 \pm 0.06) \text{ cm mmol}^{-1}$ is consistent with previously reported values (1.11 and $1.45 \text{ cm mmol}^{-1}$).^{16,17}

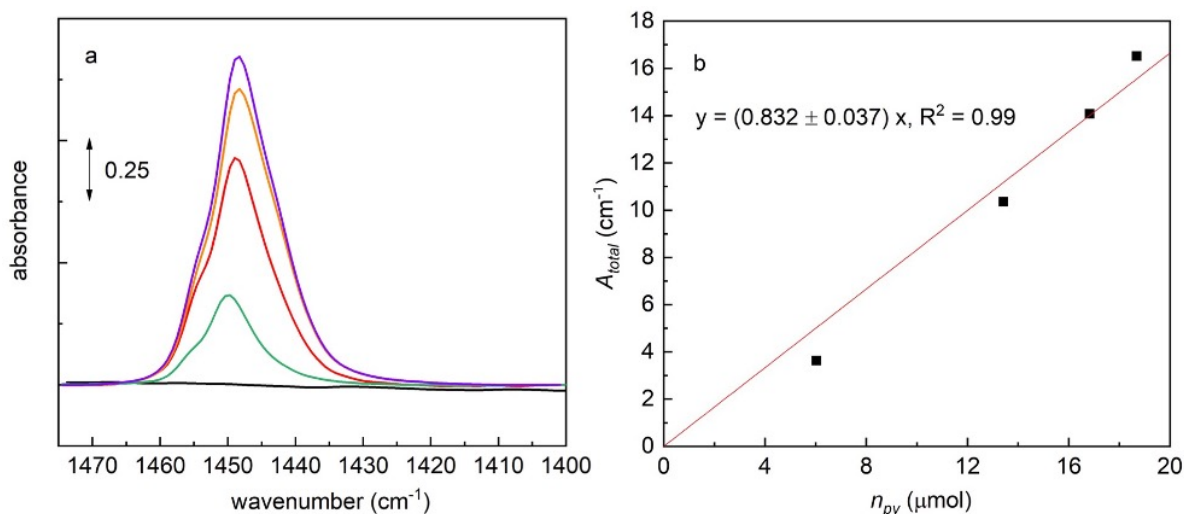


Figure A3.8. (a) Portion of the IR spectrum for pyridine (6.0 - 18.7 mmol) adsorbed on γ - Al_2O_3 (80 mg), and (b) calibration curve based on the combined peak areas at 1450 and 1455 cm^{-1} . The line is the linear least-squares fit of the equation $y = kx$ to the data.

The apparent extinction coefficient determined above for pyridine adsorbed on the LAS of γ - Al_2O_3 was used to obtain the apparent extinction coefficient for pyridine adsorbed on BAS of acidic aluminas, forming pyH^+ (1545 cm^{-1}), since the ratio of extinction coefficients $e_{\text{py-LAS}}/e_{\text{pyH}^+}$ is known (1.32),¹³ and is reported to be independent of the catalyst and acid site strength.^{13,14} The value of e_{pyH^+} is therefore $(1.01 \pm 0.05) \text{ cm mmol}^{-1}$.

Pyridine is unable to probe the Brønsted acidity of γ -Al₂O₃. The more basic 2,6-dimethylpyridine (DMP) is better suited for measuring BAS, forming DMPH⁺ on strong BAS and H-bonded DMP-H on weak BAS.¹⁸ It is also bulkier than pyridine, and therefore interacts more selectively with BAS in the presence of LAS. The procedure described above for pyridine adsorption was repeated by adsorbing precise amounts of DMP (n_{DMP}) onto dry F-Al₂O₃ (1.3 wt% F). When the DMP loading is low (<25 mmol g⁻¹), the IR spectrum in the range 1680 – 1560 cm⁻¹ shows mostly (> 87% of total peak area) bands at ca. 1650 and 1630 cm⁻¹, corresponding to the ν_{8a} and ν_{8b} modes, respectively, of DMP interacting with BAS to form DMPH⁺ (**Figure A3.9a**).^{19,20,21} Minor peaks at ca. 1617 cm⁻¹ (ν_{8a}) and 1580 cm⁻¹ (ν_{19b}) are also present, corresponding to DMP interacting with LAS.^{19,20,21}

Eq A3.10 shows the relationship between the total amount of DMP (n_{DMP}) added to the original powder of mass m_1 , the disk of mass m_2 , the amount of DMP adsorbed on BAS forming DMPH⁺ on m_2 (n_{DMPH^+}), and the amount of DMP adsorbed on LAS ($n_{\text{DMP-LAS}}$):

$$n_{\text{DMP}} = \frac{m_1}{m_2} (n_{\text{DMPH}^+} + n_{\text{DMP-LAS}}) = \frac{m_1}{m_2} \cdot n_{\text{DMPH}^+} \cdot \left(1 + \frac{n_{\text{DMP-LAS}}}{n_{\text{DMPH}^+}}\right) \quad (\text{A3.10})$$

To obtain n_{DMPH^+} , the ratio $n_{\text{DMP-LAS}}/n_{\text{DMPH}^+}$ is obtained using the reported¹⁹ ratio of extinction coefficients $\epsilon_{\text{DMPH}^+}/\epsilon_{\text{DMP-LAS}} = 1.54$, **eq A3.11**:

$$\frac{n_{\text{DMP-LAS}}}{n_{\text{DMPH}^+}} = \frac{A_{\text{DMP-LAS}} \cdot \epsilon_{\text{DMPH}^+}}{\epsilon_{\text{DMP-LAS}} \cdot A_{\text{DMPH}^+}} = 1.54 \cdot \frac{A_{\text{DMP-LAS}}}{A_{\text{DMPH}^+}} \quad (\text{A3.11})$$

Combining **eqs A3.10** and **A3.11** gives n_{DMPH^+} , according to **eq A3.12**:

$$n_{DMPH^+} = n_{DMP} \cdot \frac{m_2}{m_1} / \left(1 + \frac{n_{DMP-LAS}}{n_{DMPH^+}} \right) = \frac{m_2}{m_1} \cdot \frac{n_{DMP}}{1 + 1.54 \cdot \frac{A_{DMP-LAS}}{A_{DMPH^+}}} \quad (\text{A3.12})$$

The IR spectrum was deconvoluted into several Gaussian peaks, located at 1650, 1630, 1617, and 1580 cm^{-1} (and constrained to be these frequencies within $\pm 3 \text{ cm}^{-1}$). A_{DMPH^+} is the sum of the areas of the peaks at 1650 and 1630 cm^{-1} , while $A_{DMP-LAS}$ is the area of the peak at 1617 cm^{-1} . The dependence of A_{DMPH^+} on n_{DMPH^+} gave the calibration curve in **Figure A3.9b**, described by **eq A3.13**:

$$A_{DMPH^+} = \left(\frac{4\varepsilon_{DMPH^+}}{\pi D^2} \right) n_{DMPH^+} \quad (\text{A3.13})$$

where k is the slope of the calibration curve. Finally, ε_{DMPH^+} was calculated using **eq A3.14**:

$$\varepsilon_{DMPH^+} = \pi D^2 k / 4 \quad (\text{A3.14})$$

The measured value of $\varepsilon_{DMPH^+} = (6.9 \pm 0.3) \text{ cm mmol}^{-1}$ is consistent with a previously reported value (6.8 cm mmol^{-1}).¹⁹ The extinction coefficient for the peak at 1605 cm^{-1} , representing DMP adsorption on weak BAS to give hydrogen-bonded DMP (DMP-H), was

obtained using the reported ratio of extinction coefficients for DMPH^+ and DMP-H (3.6).¹⁹

The value for DMP-H is therefore $(1.93 \pm 0.07) \text{ cm mmol}^{-1}$.

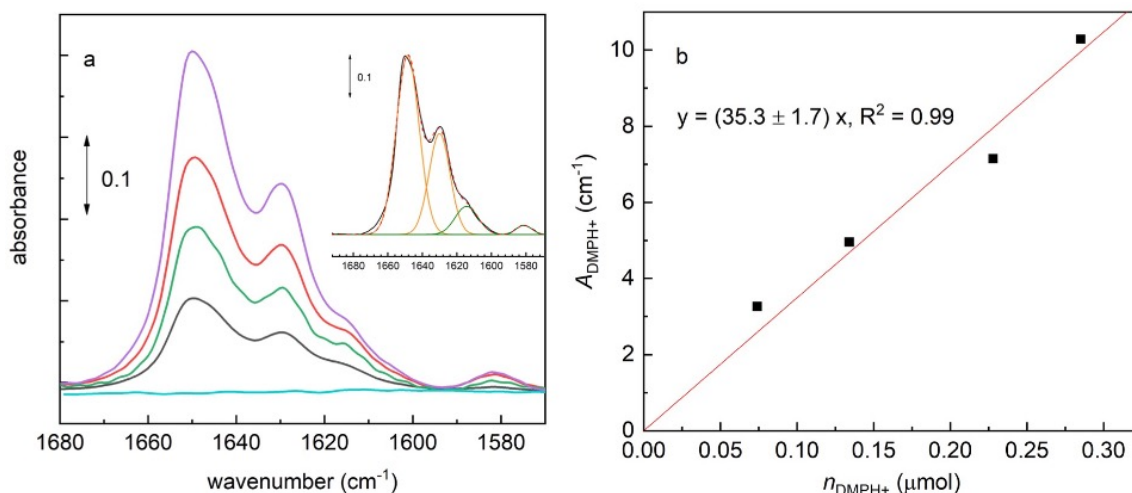


Figure A3.9. (a) Portion of the IR spectrum showing various amounts (0.08 – 0.29 mmol) DMP adsorbed on the BAS (DMPH^+) and LAS (DMP-LAS) of $\text{F-Al}_2\text{O}_3$ (10 mg, 1.3 wt% F), and (b) calibration curve based on the integrated IR absorbance of the peaks at 1650 (ν_{8a} of DMPH^+) and 1630 cm^{-1} (ν_{8b} of DMPH^+). The line is a linear least-squares fit of the equation $y = kx$ to the data. The insert in (a) shows the peak deconvolution, performed using four Gaussian peaks, at 1650 (orange), 1630 (orange), 1617 (green), and 1580 (green) cm^{-1} , and their sum (red dashed line).

Quantification of LAS. To distinguish between strong and weak LAS, adsorption of pyridine was followed by desorption at either 150 or 350°C. Each catalyst (ca. 80 mg) was dried by evacuation at ca. 10^{-2} Torr and 400°C for 2 h, then cooled to room temperature. Excess pyridine vapor was introduced at room temperature and allowed to equilibrate for 15

min. The mixture was then evacuated at ca. 10^{-2} Torr for 30 min while heating to remove physisorbed pyridine (150°C) or physisorbed and weakly chemisorbed pyridine (350°C). Pyridine still adsorbed after heating at 350°C was used to obtain the number of strong LAS, while the difference between the amounts of pyridine remaining adsorbed after heating at 150 or 350°C represents the number of weak LAS (**Figures A3.10-A3.11, A3.14**).¹⁵ The results are shown in **Tables 3.2-3.3**.

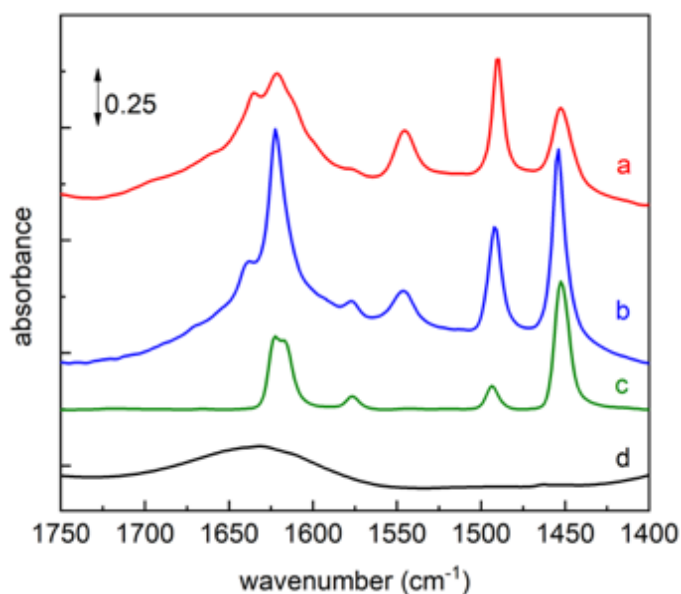


Figure A3.10. IR spectra of (a) Pt/HZSM-5 (1.0 wt% Pt, red), (b) Pt/SiO₂-Al₂O₃ (1.0 wt% Pt, blue), (c) Pt/ γ -Al₂O₃ (1.0 wt% Pt, green), and (d) Pt/SiO₂ (1.0 wt% Pt, black), each recorded after adsorption of excess pyridine at room temperature, followed by desorption at 150°C and ca. 10^{-2} Torr for 30 min. All spectra are normalized by mass relative to Pt/ γ -Al₂O₃ (10.0 mg), and are offset vertically for clarity. The broad band at 1630 cm⁻¹ in the spectra of the silica-containing materials (a, b, d) corresponds to a silica lattice overtone.²²

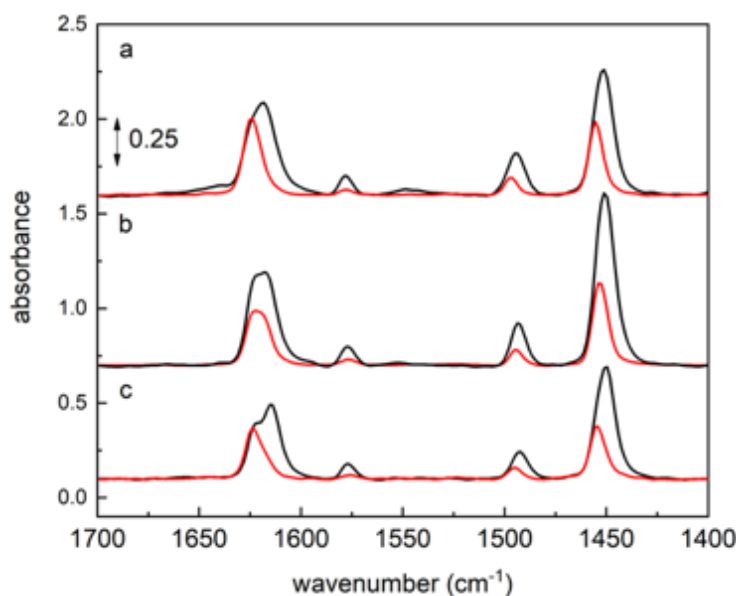


Figure A3.11. IR spectra of (a) F-Al₂O₃, (b) Cl-Al₂O₃, and (c) γ-Al₂O₃, recorded after pyridine adsorption at room temperature, followed by desorption at either 150°C (black) or 350°C (red) at ca. 10⁻² Torr for 30 min. All spectra are normalized by mass relative to γ-Al₂O₃ (10.0 mg), and are offset vertically for clarity.

Quantification of BAS. To distinguish between weak and strong BAS, adsorption of DMP was followed by desorption at 150°C. Each catalyst (ca. 80 mg) was evacuated at ca. 10⁻² Torr and 400°C for 2 h, then cooled to room temperature. Excess DMP vapor was introduced at room temperature and allowed to equilibrate for 15 min. The mixture was then evacuated at ca. 10⁻² Torr for 30 min while heating at 150°C to remove physisorbed DMP. The amount of DMP still adsorbed after heating at 150°C as DMPH⁺ and as H-bonded DMP-H represents

the number of strong and weak BAS, respectively. The results are shown in **Figures A3.12-A3.14** and **Table A3.4**.

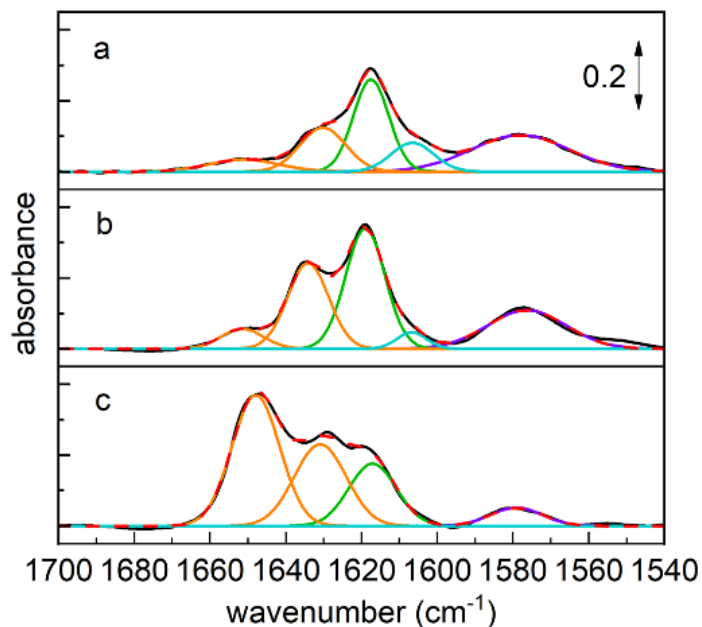


Figure A3.12. IR spectra (black) of (a) γ - Al_2O_3 , (b) $\text{Cl-Al}_2\text{O}_3$ (1.8 wt% Cl), and (c) $\text{F-Al}_2\text{O}_3$ (1.3 wt% F), each recorded after adsorption of excess DMP at room temperature, followed by desorption at 150°C and ca. 10^{-2} Torr for 30 min. Spectra are normalized by mass relative to γ - Al_2O_3 (10.0 mg). The deconvolution shows peaks at 1650 (orange), 1630 (orange), 1617 (green), 1605 (light blue), and 1580 (purple) cm^{-1} , as well as their sum (red dashed line).

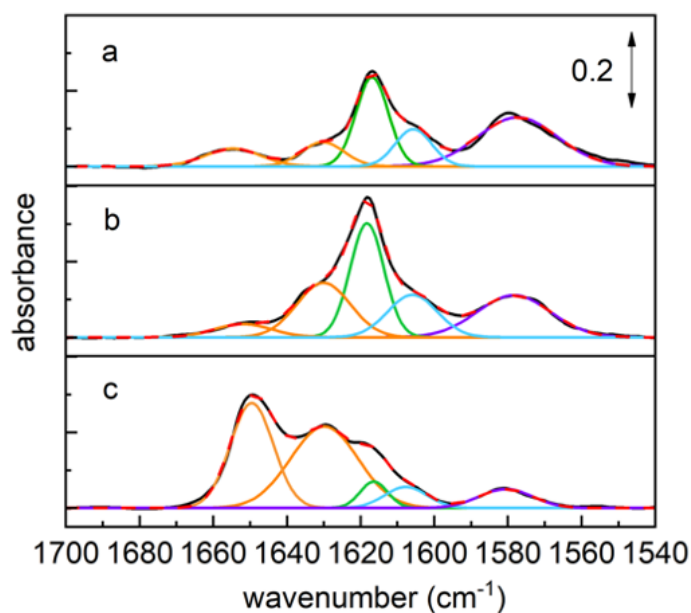


Figure A3.13. IR spectra (black) of (a) Pt/ γ -Al₂O₃ (1.5 wt%), (b) Pt/Cl-Al₂O₃ (1.5 wt% Pt, 1.4 wt% Cl), and (c) Pt/F-Al₂O₃ (1.6 wt% Pt, 0.8 wt% F), each recorded after adsorption of excess DMP at room temperature, followed by desorption at 150°C and ca. 10^{-2} Torr for 30 min. Spectra are normalized by mass relative to γ -Al₂O₃ (10.0 mg). The deconvolution shows peaks at 1650 (orange), 1630 (orange), 1617 (green), 1605 (light blue), 1580 cm⁻¹ (purple), as well as their sum (red dashed line).

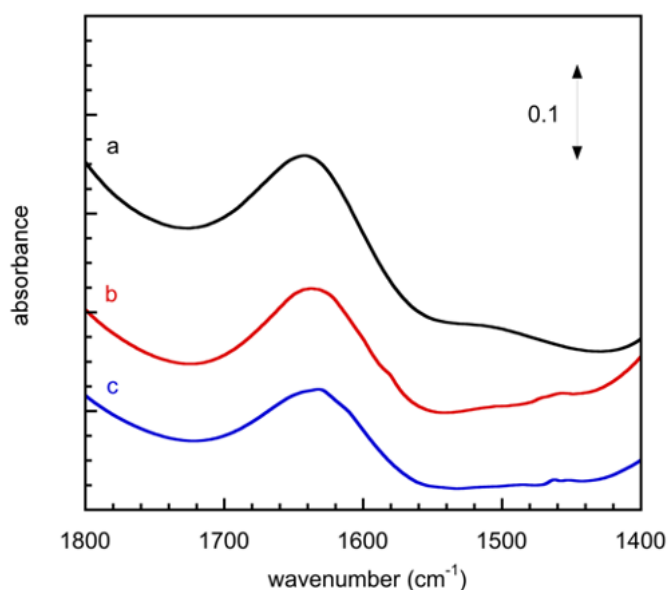


Figure A3.14. IR spectra of (a) Pt/SiO₂ (1.5 wt% Pt), (b) with adsorbed DMP, and (c) with adsorbed pyridine. Spectra were recorded at room temperature, after desorption of weakly adsorbed molecules (where applicable) at 150°C and ca. 10⁻² Torr for 30 min. Spectra are normalized by mass relative to Pt/SiO₂ (10.0 mg) and offset vertically for clarity.

Table A3.4. Quantitative assessment of Brønsted acid sites (BAS) for various catalysts

Catalyst	Pt Loading (wt%)	X Loading (X = Cl, F) (wt%) ^a	BAS (μmol g ⁻¹)	
			DMP ^b	Py ^c
Pt/SiO ₂	1.5	-	0	-
Pt/γ-Al ₂ O ₃	1.5	-	6(1)	-
Pt/Cl-Al ₂ O ₃	1.5	1.45(4)	12(1)	-
Pt/F-Al ₂ O ₃	1.6	0.76(8)	28(2)	-

Pt/F-Al ₂ O ₃ ^d	1.5	0.74	27(2)	-
Pt/F-Al ₂ O ₃ ^e	1.5	0.73	27(2)	-
γ-Al ₂ O ₃	-	-	9(1)	0
Cl-Al ₂ O ₃	-	1.77(6)	14(1)	0
F-Al ₂ O ₃	-	0.74(7)	28(2)	-
F-Al ₂ O ₃	-	1.33(6)	34(2)	6(1)
Pt/SiO ₂	1.0	-	-	0
Pt/γ-Al ₂ O ₃	1.0	-	-	0
Pt/SiO ₂ -Al ₂ O ₃	1.0	-	-	41(2)
Pt/HZSM-5	1.0	-	-	63(3)

^a Determined by flask combustion/ion chromatography. Values are the average from duplicate experiments, with standard deviations from duplicate experiments in parentheses.

^b Obtained from the IR spectrum of adsorbed 2,6-dimethylpyridine (DMP), after desorption at 150°C under vacuum (10⁻² Torr), via integration of the peaks at 1650 and 1630 cm⁻¹ (DMPH⁺, strong BAS). Values in parentheses represent uncertainties propagated from the IR calibration (**Figure A3.9b**).

^c Obtained from the IR spectrum of adsorbed pyridine (Py), after desorption at 150°C and 10⁻² Torr, via the peak area at 1545 cm⁻¹ (BAS). Uncertainties (in parentheses) are propagated from uncertainties in the extinction coefficients (**Figure A3.8b**).

^d Once-recycled catalyst, recovered from a reaction with PE ($M_w = 3.5 \times 10^3$ g mol⁻¹, $D = 1.9$) at 280°C for 8 h, followed by calcination in flowing O₂ at 500°C and reduction in flowing H₂ (5.0 vol% in Ar) at 280°C.

^e Twice-recycled catalyst.

3.8.2.4. Catalytic Conversion of Polyethylene and Model Compounds

3.8.2.4.1. Catalytic Conversion of Polyethylene

A stainless steel autoclave (90 mL, Parr Series 5000 Multiple Reactor System) equipped with an addition port on the lid was loaded with PE ($M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) and a freshly-reduced Pt catalyst (0.200 g, Pt/ γ -Al₂O₃, Pt/Cl-Al₂O₃, or Pt/F-Al₂O₃), or where specified, a physical mixture of Pt/ γ -Al₂O₃ (0.200 g) and F-Al₂O₃ (0.100 g) inside an Ar-filled glove-box. The contents were stirred magnetically at ca. 675 rpm, using a Pyrex-encapsulated stir bar. Timing of the reaction began when the internal temperature reached the set temperature, 250°C, after ca. 30 min. Since the internal thermocouple is located above the solids in the reactor, it reflects the temperature of the gas phase rather than the solid/liquid phase. The external temperature of the autoclave was measured to be $(280 \pm 5)^\circ\text{C}$. Prior to opening the autoclave, it was cooled to room temperature by immersing the bottom of the vessel in a room temperature water bath for 30 min.

Overall product yields. To characterize volatile reaction products, the autoclave and a Schlenk flask capped with a white rubber septum were connected via Tygon tubing to a glass vacuum line equipped with a pressure gauge and a gas sampling port. The Schlenk flask and lines were evacuated (10^{-2} Torr), then isolated from the pumping system. The gases in the autoclave were expanded into the line and Schlenk flask. H₂ analysis by GC-TCD was achieved by removing an aliquot of gas (400 μL) via the gas sampling port using a gas-tight syringe. The Ar (1 atm) present in the autoclave at the start of the reaction was used as the internal standard for quantification of H₂ remaining in the reactor after reaction. Propene (400

mL, 200-400 mbar) was injected into the Schlenk tube for use as an internal standard prior to removing a gas aliquot (200 mL) for light hydrocarbon analysis (C_{1-8}) by GC-FID.

To collect the liquid products, methylene chloride (DCM, 5 mL) was added to the reactor at room temperature through the addition port, dissolving hydrocarbons condensed on the inner reactor lid. The solution mixture was transferred by pipette onto a fine glass frit (4.0-5.5 mm) and filtered. The solid remaining on the frit was washed with hot DCM (5 mL) to dissolve hydrocarbons present in the solid residue. The filtrate was analyzed by GC-FID before removing the solvent, to ensure detection of light hydrocarbons (C_{7-11}). After evaporating the solvent under reduced pressure (0.1 Torr, 1 h), the liquid was redissolved in DCM and analyzed again by GC-FID to identify by difference the amount of liquid hydrocarbons lost during the solvent evaporation. Hydrocarbon products were recovered by evaporating the solvent again under reduced pressure (0.1 Torr, 1 h). The total liquid yield is the sum of liquid products detected before and after solvent removal. An aliquot of the liquid remaining after solvent removal (~2 mg) was dissolved in 1,1,2,2-tetrachloroethane- d_2 (TCE- d_2) for analysis by 1H NMR. A second aliquot (~6 mg) was dissolved in $CHCl_3$ containing 0.25 vol% triethylamine (1.5 mL) for analysis by GPC. A third aliquot (~5 mg) was dissolved in 0.2 mL DCM for analysis by GC-MS.

The insoluble material remaining on the frit, including the catalyst and insoluble hydrocarbons, was recovered and weighed. The mass of insoluble hydrocarbons was calculated by subtracting the initial mass of the catalyst. Gas, liquid and solid residue yields are shown in **Table A3.5**.

Table A3.5. Hydrocarbons recovered after catalytic conversion of PE ^a

Catalyst ^b	Gas (wt%)	Liquid (wt%)	Solid (wt%)
Pt/ γ -Al ₂ O ₃	2.4 (0.2)	44.5 (0.5)	46.5 (1.2)
Pt/Cl-Al ₂ O ₃	4.4 (0.2)	71.5 (0.2)	16.4 (0.9)
Pt/F-Al ₂ O ₃	7.1 (0.6)	70.8 (0.8)	11.5 (1.4)
Pt/ γ -Al ₂ O ₃ + F-Al ₂ O ₃	9.2 (0.9)	69.7 (1.0)	9.5 (0.5)
Pt/F-Al ₂ O ₃ ^c	12.8 (0.4)	66.0 (0.8)	13.3 (1.2)

^a Reaction conditions: PE (0.120 g, $M_w = 3.5 \times 10^3$ g mol⁻¹, $D = 1.9$), catalyst (0.200 g), except where noted, after 8 h at 280°C, Ar. Uncertainties shown in parentheses represent the standard deviation of duplicate experiments.

^b 0.200 g Pt/ γ -Al₂O₃ (1.5 wt% Pt), Pt/Cl-Al₂O₃ (1.5 wt% Pt, 1.4 wt% Cl), or Pt/F-Al₂O₃ (1.6 wt% Pt, 0.8 wt% F), or a physical mixture of 0.200 g Pt/ γ -Al₂O₃ (1.5 wt% Pt) and 0.100 g F-Al₂O₃ (1.3 wt% F).

^c Reaction with PE ($M_w = 2.6 \times 10^4$ g mol⁻¹, $D = 3.9$).

3.8.2.4.2. Catalytic Conversion of Triacontane and 1-Octadecene

Bifunctional catalytic conversion of triacontane. In a typical experiment, a stainless steel mini-autoclave (10 mL) equipped with a gas sampling port (resulting in 13 mL total volume) was loaded with *norm*-C₃₀H₆₂ (0.120 g), a freshly-reduced Pt catalyst (0.100 or 0.200 g), and the desired amount of modified alumina (Cl-Al₂O₃ or F-Al₂O₃, various amounts up to 0.100 g) inside an Ar-filled glovebox. The reactor was sealed, removed from the glovebox, and placed in a pre-heated muffle furnace (Thermo Scientific Lindberg/Blue M BF51848C) at

280°C. After heating for the designated time, the reactor was removed and rapidly cooled to room temperature (within 10 min) using a jet of compressed air.

Volatiles (C₁₋₈) were collected and quantified using the procedure described in the previous section. Solids were collected on a spatula and transferred onto a fine frit, washed with CS₂ (ca. 20 mL), and filtered. The filtrate was diluted with CS₂ in a volumetric flask. An aliquot (1 mL) was filtered through a 0.2 mm filter for GC-FID analysis of liquid hydrocarbons (C₆₋₃₀). A second aliquot (2 mL) was transferred to a vial for solvent removal in a rotary evaporator (30°C, 350 Torr), then dissolved in TCE-*d*₂ for analysis by ¹H NMR. A third aliquot (2 mL) was transferred to a vial for solvent removal in a rotary evaporator (30°C, 350 Torr), followed by analysis by GC-MS. A fourth aliquot (ca. 15 mL) was transferred to a vial for solvent removal in a rotary evaporator (30°C, 350 Torr), then dissolved in CDCl₃ with the addition of Cr(acac)₃ (80 mM) for quantitative analysis by ¹³C NMR. Insoluble material recovered from the frit was dried by evacuation overnight at 0.1 Torr. The mass of the solid phase corresponded to the catalyst mass, therefore the reaction generates a negligible amount of CS₂-insoluble hydrocarbons (< 1 wt%); the hydrocarbon product distribution consists only of hydrocarbons detected in the gas and liquid phases (**Table A3.8**).

Catalytic conversion of 1-octadecene. A stainless steel mini-autoclave (10 mL) was loaded with 1-octadecene (0.120 g) and Pt/SiO₂ (0.200 g, 1.5 wt% Pt) or an alumina (γ-Al₂O₃, 1.8 wt% Cl-Al₂O₃, or 1.3 wt% F-Al₂O₃, 0.200 g) inside an Ar-filled glovebox. The reactor was sealed, removed from the glovebox, and placed into a pre-heated muffle furnace (Thermo Scientific Lindberg/Blue M BF51848C) at 280°C. After 4 or 12 h, the reactor was actively cooled by a jet of room temperature air. Hydrocarbons were dissolved in CS₂ (ca. 5 mL), and

the solution was passed through a 0.2 mm filter to remove traces of catalyst. The solvent was removed using a rotary evaporator (30°C, 350 Torr). Hydrocarbons were redissolved in CDCl₃ for characterization by ¹H NMR (Figure A3.15).

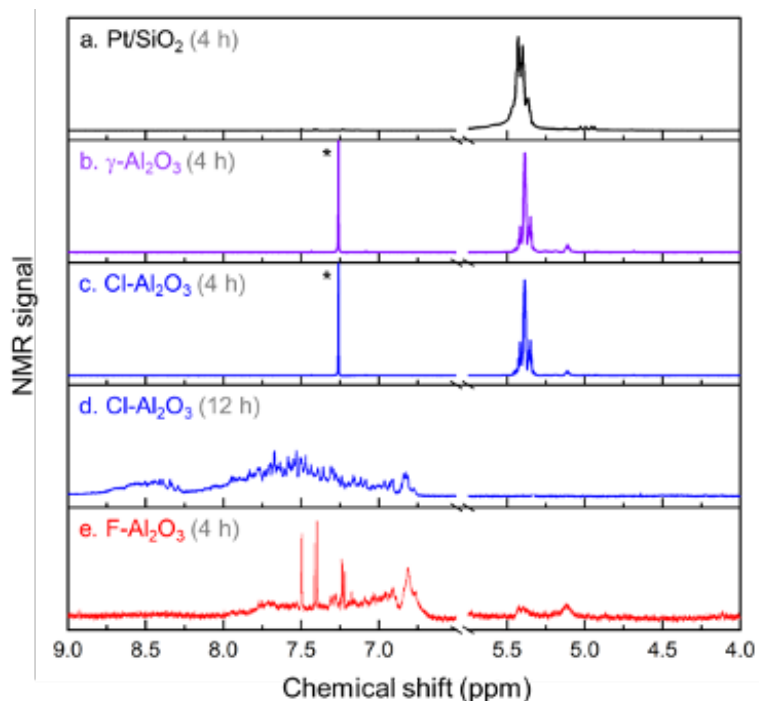


Figure A3.15. ¹H NMR spectra of 1-octadecene (0.120 g), after heating at 280°C in the presence of (a) Pt/SiO₂ (0.200 g, 1.5 wt% Pt, black) for 4 h, or an alumina (0.200 g, no Pt): (b) γ-Al₂O₃ (purple) for 4 h, (c) Cl-Al₂O₃ (1.8 wt%, blue) for 4 h, or (d) for 12 h, or (e) F-Al₂O₃ (1.3 wt%) for 4 h. * indicates the CDCl₃ solvent. Spectrum (c) and (d) was recorded in 1,1,2,2-tetrachloroethane-d₂ to avoid overlap of CHCl₃ signals with the aromatic signals. Aromatics are barely detectable in the first three spectra.

3.8.2.5. Analysis of H₂ and Gaseous Hydrocarbons by Gas Chromatography

H₂ was quantified on a Shimadzu GC-8AIT gas chromatograph equipped with a packed column (ShinCarbon ST 80/100, 2 m x 2 mm) and a thermal conductivity detector (TCD). The column, injector and detector temperatures were all 130°C. The TCD current was 70 mA and the head pressure was 300 kPa (N₂). Ar present in the reactor was used as the internal standard. The linear responses of the TCD signal to the injected volumes of H₂ and Ar were confirmed using standard H₂/Ar gas mixtures. The response factors were obtained as described previously.³ A representative chromatogram is shown in **Figure A3.16**.

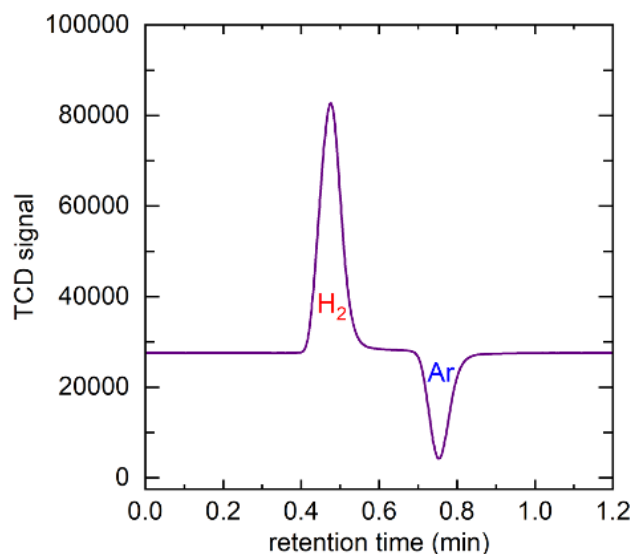


Figure A3.16. GC-TCD chromatogram of gas recovered from catalytic conversion of PE ($M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) using Pt/Cl-Al₂O₃ (1.5 wt% Pt, 1.4 wt% Cl) after 8 h at 280°C under Ar (3.8 mmol).

Hydrocarbons in the gas fraction (C₁₋₈) were analyzed qualitatively and quantitatively on a Shimadzu GC-2010 gas chromatograph equipped with a capillary column (Supelco Alumina Sulfate plot, 30 m x 0.32 mm) and a flame ionization detector (FID). The injector and detector temperatures were both 200°C. The temperature program was: 90°C (hold 3 min), ramp 20°C/min to 180°C (hold 20 min). The yields of each hydrocarbon were calculated assuming all have the same relative carbon response factor.²³

When propene was not a reaction product (i.e., with the bifunctional catalysts, **Figures A3.17-A3.18**), it was used as an internal standard. In experiments with acid catalysts, where propene and other gaseous alkenes are formed (**Figures A3.18-A3.19**), a known amount of propene was also added as an internal standard. The peak area (A) was measured relative to the area for butanes (*norm*-butane and *iso*-butane) before and after standard addition (**eqs A3.15-A3.17**). The yields of gaseous hydrocarbons are summarized in **Table A3.8**.

$$\text{without added propene: } A_{\text{propene}}/A_{\text{butanes}} = 3n_{\text{propene}}/(4n_{\text{butanes}}) = x \quad (\text{A3.15})$$

$$\text{with added propene: } A'_{\text{propene}}/A'_{\text{butanes}} = 3(n_{\text{propene}} + n_{\text{added propene}})/(4n_{\text{butanes}}) = y \quad (\text{A3.16})$$

$$n_{\text{propene}} = n_{\text{added propene}}x/(y-x) \quad (\text{A3.17})$$

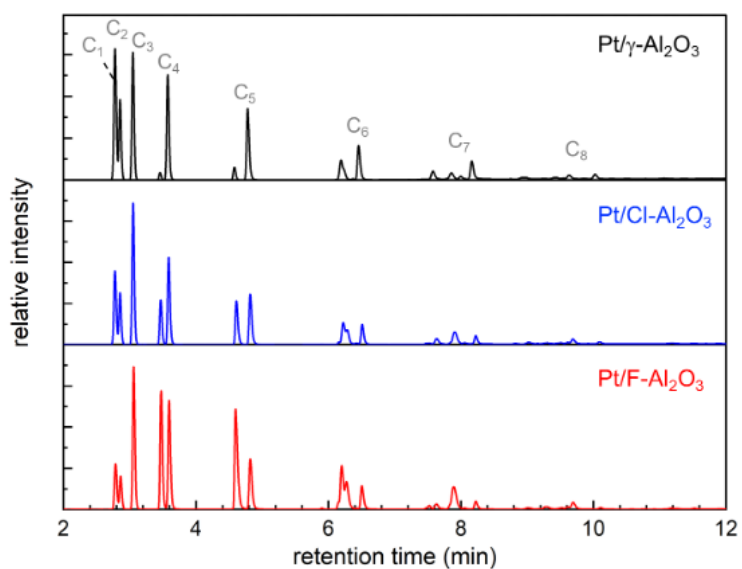


Figure A3.17. GC-FID of gas products recovered from catalytic conversion of PE (0.120 g, $M_w = 3.5 \times 10^3$ g mol⁻¹, $D = 1.9$) using Pt/γ-Al₂O₃ (0.200 g, 1.5 wt% Pt, black), Pt/Cl-Al₂O₃ (0.200 g, 1.5 wt% Pt, 1.4 wt% Cl, blue), or Pt/F-Al₂O₃ (0.200 g, 1.6 wt% Pt, 0.8 wt% F, red) for 8 h at 280°C under Ar.

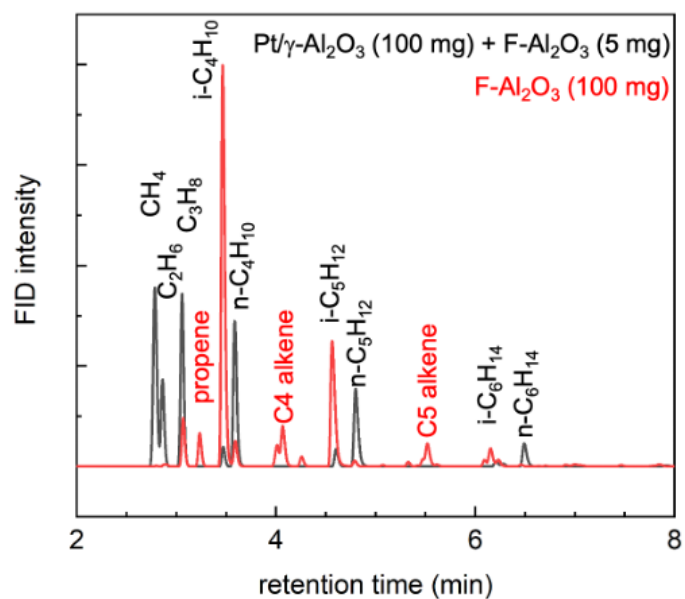


Figure A3.18. GC-FID of gas products recovered from catalytic conversion of *norm*-C₃₀H₆₂ (0.120 g) after 12 h at 280°C under Ar, using a physical mixture of Pt/ γ -Al₂O₃ (0.100 g, 1.5 wt% Pt) and F-Al₂O₃ (0.005 g, 1.3 wt% F) (black), or F-Al₂O₃ alone (0.100 g, 1.3 wt% F, red).

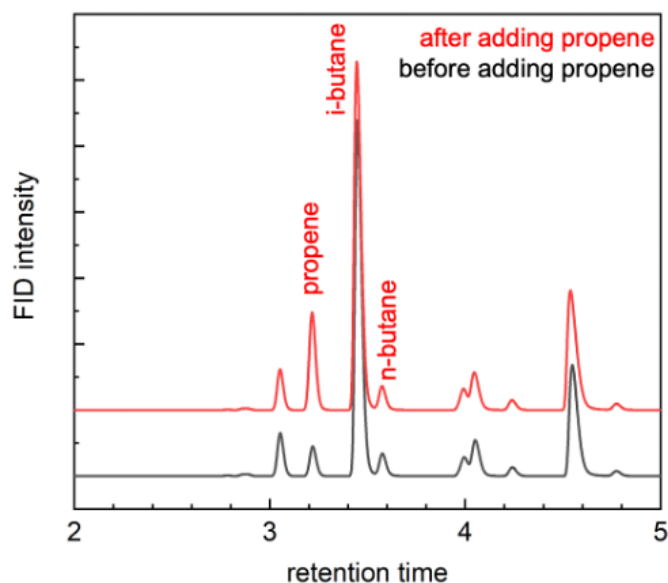


Figure A3.19. GC-FID of gas products recovered after catalytic conversion of *norm*-C₃₀H₆₂ (0.120 g) after 12 h at 280°C under Ar, catalyzed by F-Al₂O₃ (0.100 g, 1.3 wt% F), without (black) or with (red) the addition of propene (3.2 mmol) as an internal standard at the end of the reaction.

3.8.2.6. Liquid Hydrocarbons Analysis

3.8.2.6.1. Liquid Products from Catalytic Conversion of Polyethylene

Analysis by GC-FID. Extracted hydrocarbons that are present only prior to solvent evaporation (C₇₋₁₁) were quantified on an Agilent 6890N Network gas chromatograph

equipped with an Agilent DB-5 capillary column (fused silica, 30 m x 0.25 mm x 0.25 mm) and an FID detector. The inlet and detector temperatures were 300 and 280°C, respectively. The temperature ramp program was: 40°C (hold 3 min), ramp 25°C /min to 320°C (hold 10 min). The flow rate was 1.0 mL/min (He) with a 5:1 split ratio. The total peak areas corresponding to C₇₋₁₁ before and after solvent evaporation (**Figure A3.20**) were measured using an external standard (*norm*-octane in DCM, see the calibration curve in **Figure A3.21**). The difference corresponds to hydrocarbons lost during solvent removal. Their mass was calculated assuming the same relative carbon response factor (*f*) for all hydrocarbons.²³

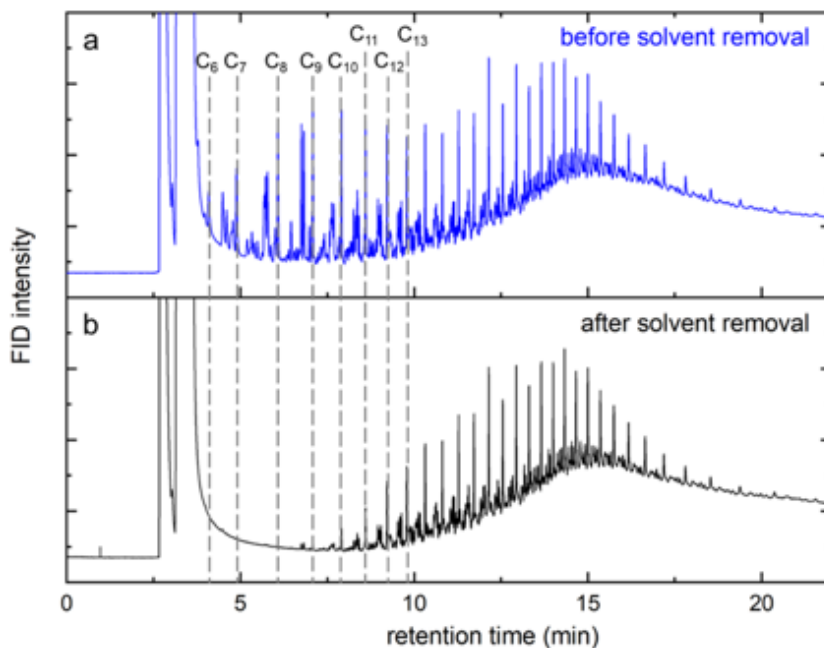


Figure A3.20. GC-FID of liquid products recovered from PE conversion catalyzed by Pt/Cl-Al₂O₃ (0.200 g, 1.5 wt% Pt, 1.4 wt% Cl) for 8 h at 280°C under Ar, (a) before, and (b) after solvent removal.

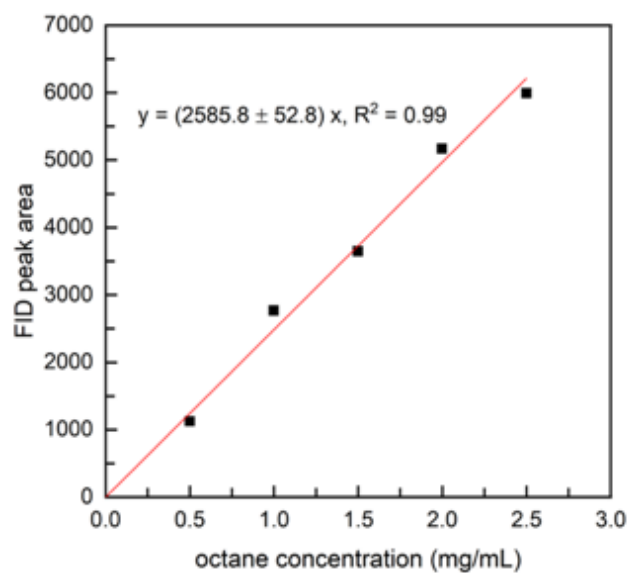


Figure A3.21. Calibration curve for the octane response of the flame ionization detector. The line is a least-squares fit of the equation $y = mx$ to the data.

The average carbon number in the liquid hydrocarbons remaining after solvent removal was calculated for comparison with the value obtained by GPC (see next section). An example is shown in **Figure A3.22** and **Table A3.6**.

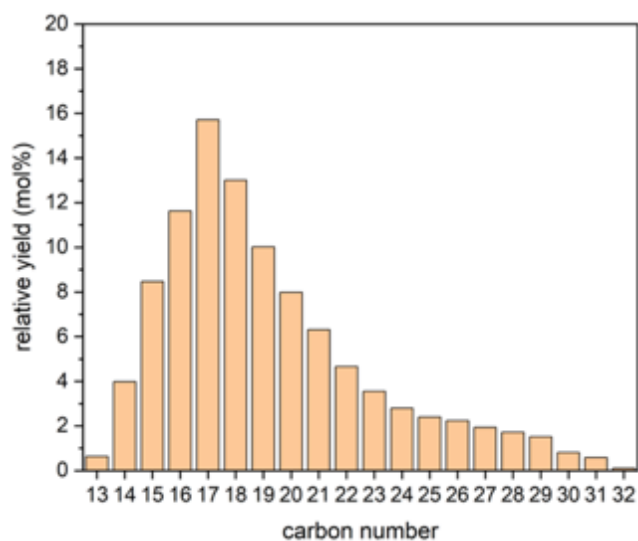


Figure A3.22. Distribution of liquid hydrocarbon products by carbon number, from conversion of PE (0.120 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) catalyzed by a physical mixture of Pt/ γ -Al₂O₃ (0.200 g) and F-Al₂O₃ (0.100 g, 1.3 wt%) for 8 h at 280°C under Ar, after extraction and solvent removal.

Analysis by gel permeation chromatography. The molecular weight distribution of unreacted PE and the liquid hydrocarbon products were analyzed on an Agilent PL-GPC 220 gel permeation chromatograph, equipped with a PL-Gel Mixed B guard column, three PL-Gel Mixed B columns, and a refractive index (RI) detector. Samples were dissolved in 1,2,4-trichlorobenzene (TCB) containing di(*tert*-butyl)hydroxytoluene (BHT, 0.01 wt%), by heating at 150°C for at least 1 h. Elution was achieved using TCB (with BHT) at 150°C and 1.0 mL min⁻¹. The molecular weight response was calibrated with monomodal, linear polyethylene standards (Varian).

Molecular weight distributions of aromatic chromophores were analyzed by GPC with UV detection. Analyses were conducted on a Waters 2690 HPLC equipped with two Agilent Columns (PLgel, 5 mm MiniMIX-D, 250×4.6 mm) and a guard column (MW linear range 200 - 400,000 g mol⁻¹), a Waters 2410 refractive index (RI) detector and a Waters 2998 photodiode array detector (PDA). Chloroform containing 0.25 vol% triethylamine was used as the mobile phase at room temperature and 0.35 mL min⁻¹. Calibration was achieved using polystyrene standards (Agilent EasiVial kit, linear response for molecular weights in the range 200 - 400,000 g mol⁻¹).

GPC results for liquid products after solvent removal were analyzed using PE calibration standards (except where noted). The results are summarized in **Table A3.6**. Product distributions were monomodal, with the exception of one sample made using Pt/Cl-Al₂O₃, which showed a bimodal distribution. In the latter case, it appears that a portion of the (largely) intact polymer became solubilized due to extensive, acid-catalyzed skeletal isomerization, and was then carried along into the GPC analysis of the liquid products. A typical monomodal distribution as well as the sole bimodal distribution are shown in **Figure A3.23**.

Table A3.6. GPC analyses ^a of liquid hydrocarbons recovered from catalytic conversion of PE ^b

Catalyst	Liq. Yield (wt%)	Low molecular weight fraction			High molecular weight fraction		
		M_n	M_w	$\bar{D}$	M_n	M_w	$\bar{D}$
Pt/ γ -Al ₂ O ₃	44	725	1562	2.2			
Pt/Cl-Al ₂ O ₃	70	350	418	1.2	932	2426	2.6
		400 ^c	1572 ^c	3.9 ^c			
		332 ^d	1450 ^d	4.4 ^d			
Pt/F-Al ₂ O ₃	64	330	353	1.1			
Pt/F-Al ₂ O ₃ ^e	59	319	354	1.1			
Pt/ γ -Al ₂ O ₃ + F-Al ₂ O ₃	61	241	254	1.1			

^a Analyzed using PE calibration standards with RI detector (except where noted). M_n , M_w values in g mol⁻¹. $\bar{D} = M_w / M_n$.

^b Reaction conditions: PE (0.120 g, $M_w = 3.5 \times 10^3$ g mol⁻¹, $\bar{D} = 1.9$), Pt catalyst (0.200 g, Pt/ γ -Al₂O₃, Pt/Cl-Al₂O₃, Pt/F-Al₂O₃) or a physical mixture of Pt/ γ -Al₂O₃ (0.200 g, 1.5 wt% Pt) and F-Al₂O₃ (0.100 g, 1.3 wt% F), 8 h at 280 °C.

^c Also analyzed using polystyrene calibration standards, with RI detector.

^d Also analyzed using polystyrene calibration standards, with UV detector.

^e Reaction with higher molecular weight PE (0.120 g, $M_w = 2.6 \times 10^4$ g mol⁻¹, $\bar{D} = 3.9$).

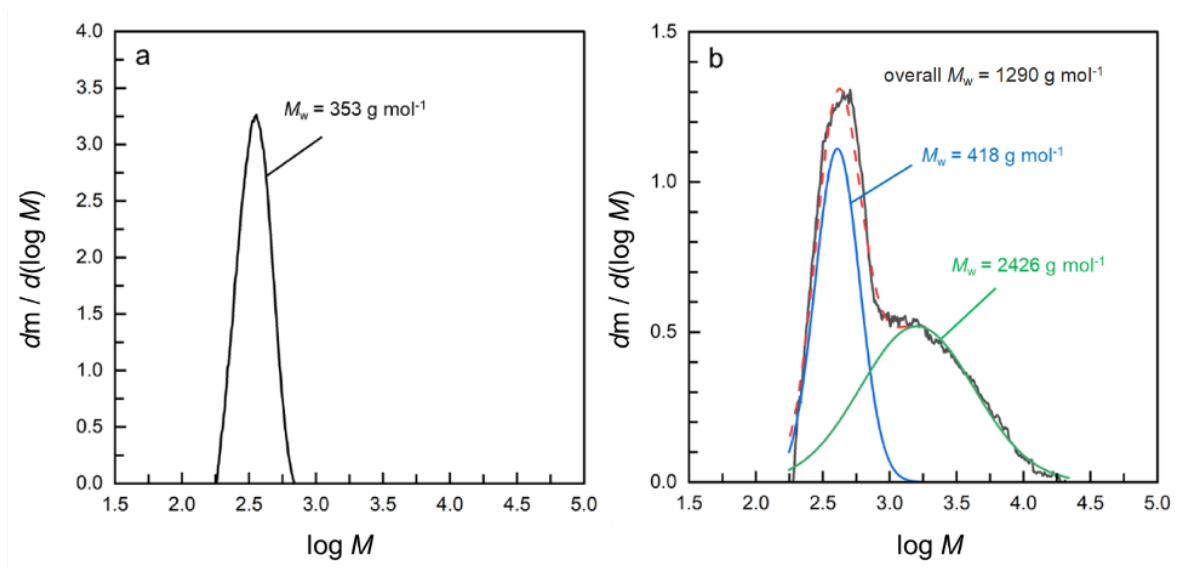


Figure A3.23. GPC chromatograms (obtained using PE calibration standards with RI detection) for liquid hydrocarbons recovered from the catalytic conversion of PE (0.120 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $\bar{D} = 1.9$), using (a) Pt/F-Al₂O₃, and (b) Pt/Cl-Al₂O₃, after 8 h at 280°C under Ar. The chromatogram in (b) was deconvoluted into two Gaussian peaks (green and blue). Their sum is shown as the red dashed line.

3.8.2.6.2. Analysis of Halogen Content in Liquid Hydrocarbons

To assess the leaching of halogen from catalyst into liquid hydrocarbon products during the PE reactions, the Cl and F contents in the liquid were determined by flask combustion/ion chromatography (Atlantic Microlab, Inc., Norcross, GA). Negligible Cl or F was detected in the liquid hydrocarbons (**Table A3.7**).

Table A3.7. Quantitative analysis of halogen content in liquid hydrocarbon products ^a
Pt catalyst **Halogen content (Cl or F, wt%) ^b**

Pt/Cl-Al ₂ O ₃	<0.25
Pt/F-Al ₂ O ₃	0.0
Once-recycled Pt/F-Al ₂ O ₃ ^c	0.0
Pt/ γ -Al ₂ O ₃ + F-Al ₂ O ₃ ^d	0.0

^a Liquids were recovered after reaction of PE (0.120 g, $M_w = 3.5 \times 10^3$ g mol⁻¹, $\bar{D} = 1.9$) catalyzed by Pt catalyst (0.200 g, 1.5 wt% Pt) at 280°C for 8 h.

^b Determined by flask combustion/ion chromatography.

^c Pt/F-Al₂O₃ recycled after a PE upgrading reaction at 280°C for 8 h, followed by further calcination in flowing O₂ at 500°C and reduction in flowing 5.0 vol% H₂/Ar at 280°C.

^d Physical mixture of the two catalysts: Pt/ γ -Al₂O₃ (0.200 g, 1.5 wt% Pt) and F-Al₂O₃ (0.100 g, 1.3 wt% F).

3.8.2.6.3. Analysis of Liquid Products from Catalytic Conversion of Triacontane

Analysis by GC-MS. An aliquot of the liquid products dissolved in CS₂ (2 mL) was transferred to a vial for solvent removal in a rotary evaporator (30°C, 350 Torr), then analyzed on a Shimadzu GC-2010 gas chromatograph equipped with an Agilent DB-5 MS capillary column ((5%-phenyl)-methylpolysiloxane, 30 m x 0.25 mm x 0.25 μ m) coupled to a QP2010 Mass Spectrometer. The injector and detector temperatures were 250°C. The temperature ramp program was: 60°C (hold 2 min), ramp 15°C per min to 270°C, hold 50 min. Examples of GC-MS analysis are shown in **Figures A3.28-A3.29** and **A3.35**.

The majority of liquid products obtained from reactions of *norm*-C₃₀H₆₂ are isomers of linear C₃₀, and normal and branched alkanes in the range C₆₋₂₉. They were identified by GC-MS with the aid of a mass spectral library (NIST 107), and by matching retention times with *norm*-hexane and a *norm*-alkane standard mixture (C₇-C₄₀). Alkylaromatics are minor products, as evidenced by the lack of signals in the 6.5-9 ppm region of the ¹H NMR spectrum.

Analysis by GC-FID. The hydrocarbons were quantified on an Agilent 6890N Network gas chromatograph equipped with an Agilent DB-5 capillary column (fused silica, 30 m x 0.25 mm x 0.25 mm) and an FID detector. The inlet and detector temperatures were 300 and 280°C, respectively. The temperature ramp program was: 40°C (hold 3 min), ramp 25°C /min to 320°C (hold 10 min). The flow rate was 1.0 mL/min (He) with a 5:1 split ratio. The same relative carbon response factor (*f*) was assumed for all hydrocarbons.²³ *norm*-Octadecane in CS₂ was used as an external standard. Peak areas were measured by injection of several *n*-octadecane solutions of different concentrations, giving the calibration curve in **Figure A3.24**.

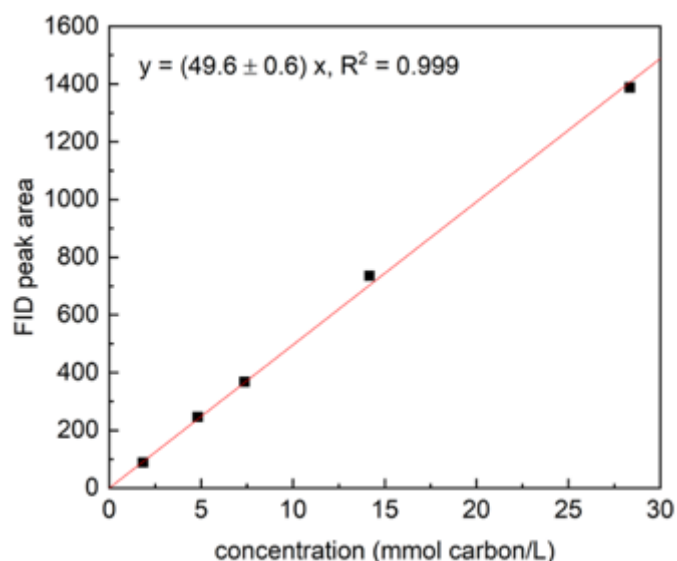


Figure A3.24. Calibration curve for *norm*-octadecane response of the flame ionization detector. The line is a least-squares fit of the equation $y = mx$.

Since a large number of hydrocarbon isomers have similar retention times (**Figure A3.25**), and because the *norm*-alkane has the highest boiling point of all C_i isomers, all peaks between *norm*- $C_{i-1}H_{2i-2}$ and *norm*- C_iH_{2i+2} were assumed to have carbon number i . Where individual peaks are resolved, the number of moles of each hydrocarbon (n_i) was calculated from its peak area (A_i) and volume of the solution (V_0), **eq A3.18**. The liquid phase analysis is combined with the gas phase analysis in **Table A3.8**. The mass of each type of hydrocarbon (m_i) was calculated assuming the molecular weight to be that of the alkane ($14i + 2$), **eq A3.19**. The total recovered mass of hydrocarbons, $m(total)$ %, including both gas and liquid fractions, was calculated using **eq A3.20**. The number-averaged carbon number for the liquid fraction, $\bar{i}$, was calculated using **eq A3.21**. The results are summarized in **Tables A3.10** and **A3.11**.

$$n_i = A_i V_0 / (f i) \quad (A3.18)$$

$$m_i = n_i (14i + 2) \quad (A3.19)$$

$$m(total)\% = \frac{\sum_1^8 m_i(gas) + \sum_6^{30} m_i(liquid)}{m_{C_{30}H_{62}}} \quad (A3.20)$$

$$\bar{i} = \frac{\sum_6^{30} n_i \cdot i}{\sum_6^{30} n_i} \quad (A3.21)$$

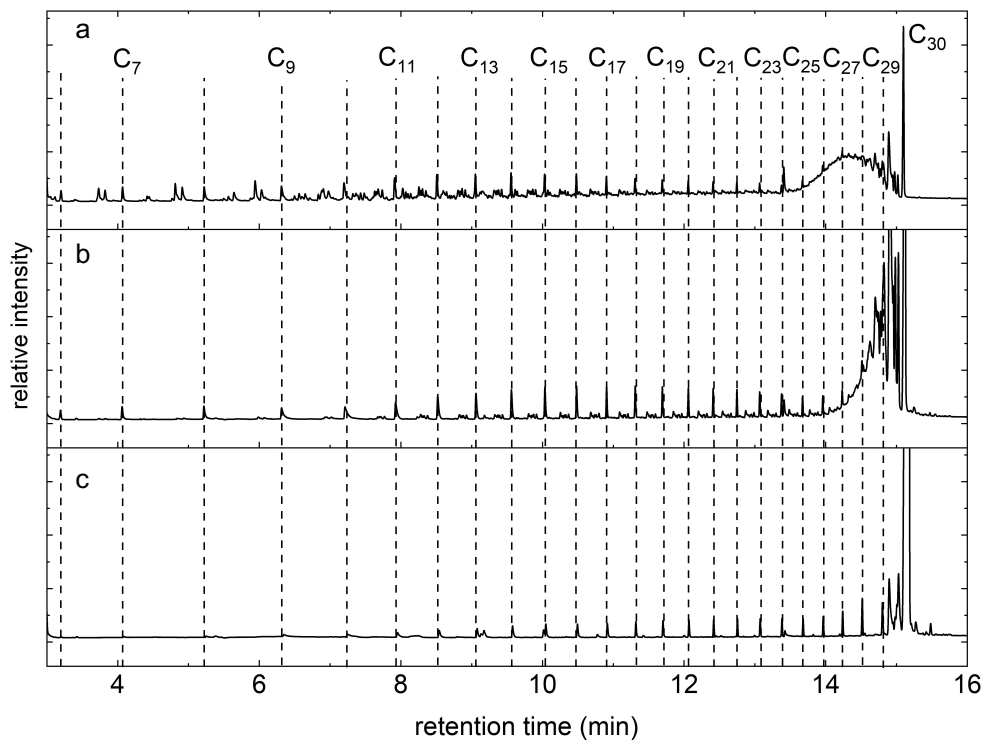


Figure A3.25. GC-FID of liquid products obtained from the reaction of *norm*-C₃₀H₆₂ catalyzed by (a) a physical mixture of Pt/ γ -Al₂O₃ (0.100 g, 1.5 wt%) and F-Al₂O₃ (0.100 g, 1.3 wt%), (b) a physical mixture of Pt/ γ -Al₂O₃ (0.100 g, 1.5 wt%) and Cl-Al₂O₃ (0.100 g, 1.8 wt%), (c) Pt/ γ -Al₂O₃ (0.100 g, 1.5 wt%). All reactions were conducted for 12 h at 280°C under Ar. The retention times of the *norm*-alkanes are indicated by dotted lines; odd carbon numbers are labeled.

Table A3.8. Overall molar hydrocarbon distributions^a recovered from conversion of *norm*-C₃₀H₆₂ by various catalyst combinations^b

Pt catalyst												
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Pt catalyst ^e												
Pt catalyst ^e												
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	0.2(1)	1.1	1.9(6)	5.5(7)	7.9(2.4)	1.1(8)	1.3(6)	3.4(1.3)	0.7	11.1	2.6(3.4)	1.3(2)
9	0.4(1)	2.1	2.4(1.1)	6.8(5)	9.2(3.0)	1.6(1.1)	1.7(5)	3.8(6)	0.6	11.4	1.6(9)	0.6(7)
10	0.4(1)	2.3	3.0(3)	7.2(2)	10.0(3.1)	1.8(8)	1.9(4)	4.4(1.1)	1.0	14.8	0.9(1.1)	0.7(1)
11	0.4(1)	1.7	3.2(1)	6.8(1.0)	9.9(3.5)	1.9(7)	1.9(4)	4.6(1.2)	0.1	9.8	1.1(1.2)	0.6(5)
12	0.5(1)	2.7	3.1(1)	6.7(1.2)	9.6(3.6)	2.5(5)	2.2(3)	5.0(1.3)	0.7	9.7	0.8(1.0)	1.2(1)
13	0.5(1)	2.0	2.9(1)	6.0(1.4)	8.0(2.5)	2.1(3)	1.9(3)	4.5(1.3)	0.1	5.7	0.6(4)	0.2(2)
14	0.9(5)	2.9	2.7(1)	5.8(1.3)	8.7(4.0)	2.2(3)	2.2(2)	4.5(1.2)	0.5	6.2	1.0(7)	1.0(3)
15	1.1(3)	2.2	2.2(3)	5.2(1.3)	7.2(3.0)	2.0(2)	2.0(3)	4.2(1.1)	0.1	4.5	0.8(8)	0.6(1)
16	0.5(1)	1.6	2.2(2)	4.6(1.2)	5.8(1.8)	1.8(3)	1.8(2)	3.8(1.0)	0.1	2.1	0.1(1)	0.1(1)
17	0.6(1)	1.6	1.9(5)	4.2(1.1)	5.3(1.6)	1.6(3)	1.7(1)	2.8(3)	0.0	2.1	0.2(2)	0.2(2)
18	0.5(1)	1.3	1.8(8)	4.0(1.2)	5.1(1.2)	1.5(2)	1.5(1)	3.6(6)	0.1	1.5	0.1(1)	0.1(1)
19	0.5(1)	1.3	1.5(7)	3.5(5)	3.8(1.1)	1.4(3)	1.4(1)	2.9(7)	0.1	0.8	0.2(2)	0.1(1)
20	0.5(1)	1.3	1.5(8)	3.0(1.0)	3.6(9)	1.4(3)	1.4(1)	2.9(4)	0.1	0.3	0.1(1)	0.1(1)
21	0.4(1)	1.1	1.5(6)	3.3(8)	3.7(8)	1.3(3)	1.3(1)	3.1(4)	0.0	0.4	0.1(1)	0.2(1)
22	0.5(1)	1.2	1.6(6)	2.8(6)	2.8(1)	1.3(3)	1.3(1)	2.2(2)	0.1	0.7	0.1(1)	0.1(1)
23	0.4(1)	1.0	1.6(5)	2.3(8)	2.7(9)	1.1(2)	1.2(1)	2.4(1)	0.1	0.8	0.1(1)	0.2(1)

24	0.3(1)	0.8	2.1(6)	2.9(1)	3.0(4)	1.3(1)	1.0(1)	2.1(1)	0.3	1.2	0.1(1)	0.1(1)
25	0.6(3)	1.0	2.5(1.4)	2.1(2)	2.9(1.1)	1.2(8)	1.5(1)	2.9(5)	0.1	1.1	0.4(2)	0.8(3)
26	0.4(1)	1.2	8.7(5.9)	5.8(2)	5.9(1)	1.1(2)	1.3(1)	3.8(2.3)	0.2	13.4	0.1(1)	0.1(1)
27	0.4(1)	2.6	7.1(4.1)	11.1(1.1)	9.2(1.5)	1.4(2)	2.1(2)	7.3(4.7)	0.2	2.0	0.2(1)	0.2(1)
28	0.6(1)	5.2	14.8(2.9)	10.5(1.8)	11.2(5.8)	3.6(4)	7.7(6)	15.0(6.4)	0.6	13.7	0.3(1)	0.4(1)
29	2.8(2)	23.7	24.3(6)	11.0(3.9)	7.5(6.2)	34.4(10.8)	40.9(1.2)	24.6(1.6)	0.2	11.7	0.3(1)	0.4(1)
30	81.2(4.4)	34.4	14.0(1.0)	4.0(2.6)	2.9(1.8)	39.5(7)	24.1(1)	11.5(3.7)	94.9	6.7	79.0(3.5)	94.3(1.2)

^a Reported as $100n_i/n_{C30}$ (%), where n_{C30} is the initial moles of *norm*-C₃₀H₆₂.

^b Reactions were catalyzed by ^c Pt/ γ -Al₂O₃ (0.100 g, 1.5 wt% Pt), or ^d Pt/SiO₂ (0.100 g, 1.5 wt% Pt), or with ^e no Pt catalyst, mixed with various amounts (0-100 mg) of acid catalyst after 12 h at 280°C under Ar. Each number followed by a value in parentheses is the average of duplicate experiments, where the value in parentheses represents the standard deviation. Products with carbon numbers 1-5 were obtained by gas phase analysis; 6-8 by combining both gas and liquid phase, and from 9-30 by liquid phase analysis.

^f F-Al₂O₃ (1.3 wt% F).

^g Cl-Al₂O₃ (1.8 wt% Cl).

When an acid catalyst is present in addition to Pt/ γ -Al₂O₃, the GC-FID of the liquid hydrocarbon products recovered from the reaction of *norm*-C₃₀H₆₂ also shows a broad peak between 13.6 and 15.1 min (**Figure A3.25a,b**). These retention times should correspond to alkane isomers with *i* (carbon number) values from C₂₅ to C₃₀. Their analysis was performed by integrating the areas demarcated by the sharp *norm*-alkane peaks (Method 1). Alternatively, assuming that the broad peak corresponds exclusively to different C₃₀ isomers, the deconvolution shown in **Figure A3.26** was used to estimate the total C₃₀ remaining after reaction (Method 2). Product distributions obtained using each method are shown in **Table A3.9**. The total number of C-C bond scissions (see **section 3.8.2.11** Rate of C-C bond scission) calculated using the first method, 335 mmol, is slightly (4 %) lower than the second method (348 mmol).

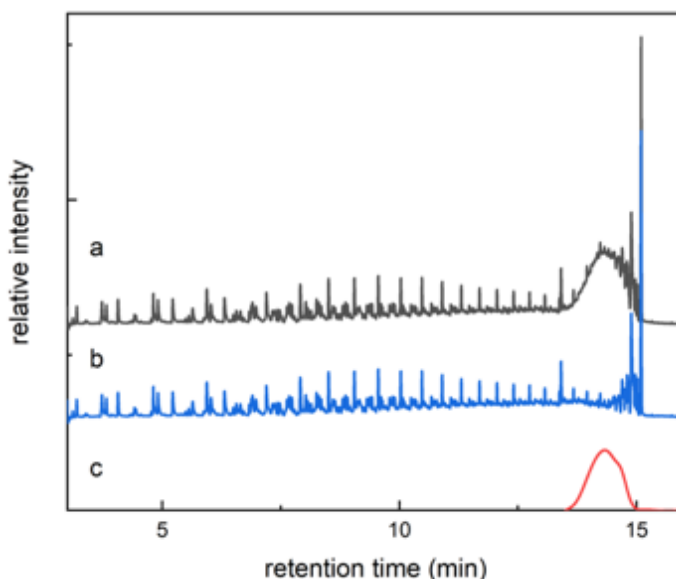


Figure A3.26. Deconvolution of GC-FID for liquid products obtained after 12 h at 280°C under Ar, in the reaction of *norm*-C₃₀H₆₂ catalyzed by a physical mixture of Pt/ γ -Al₂O₃ (0.100

g, 1.5 wt% Pt) and F-Al₂O₃ (0.100 g, 1.3 wt% F): (a) the original chromatogram, (b) contribution of narrow signals to the chromatogram, (c) contribution of the broad peak to the chromatogram.

Table A3.9. Estimated molar fractions of C₂₅₋₃₀ hydrocarbons recovered from the reaction of *norm*-C₃₀H₆₂ (0.120 g) catalyzed by a physical mixture of Pt/ γ -Al₂O₃ (0.100 g, 1.5 wt% Pt) and F-Al₂O₃ (0.100 g, 1.3 wt% F) after 12 h at 280°C under Ar

<i>i</i>	100 n _i /n ₀ (%)	
	Method	Method
	1	2
25	2.5	2.3
26	6.2	3.0
27	10.5	2.5
28	13.5	2.6
29	9.2	3.6
30	4.0	31.7
25-30	45.9	45.7

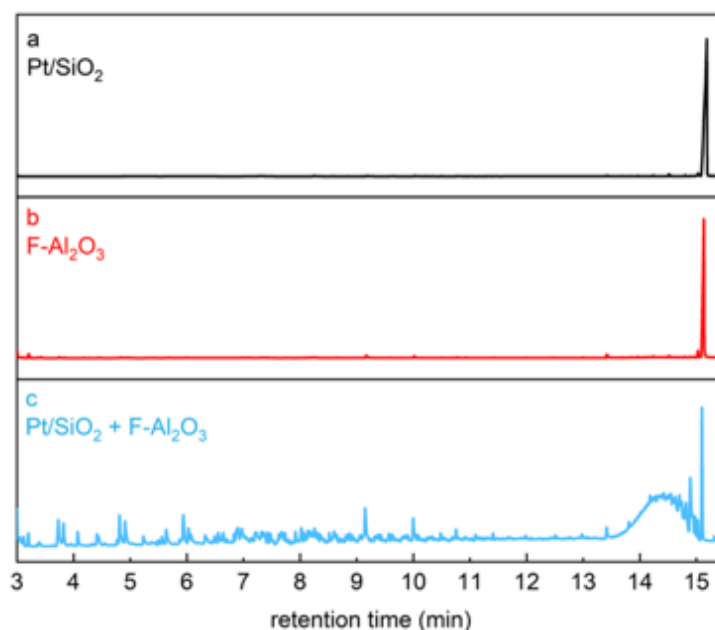


Figure A3.27. GC-FID of liquid products recovered from the reaction of *norm*-C₃₀H₆₂ (0.120 g) catalyzed by (a) Pt/SiO₂ (0.100 g, 1.5 wt%), (b) F-Al₂O₃ (0.100 g, 1.3 wt%), or (c) a physical mixture of Pt/SiO₂ (0.100 g, 1.5 wt% Pt) and F-Al₂O₃ (0.100 g, 1.3 wt% F), after 12 h at 280°C under Ar.

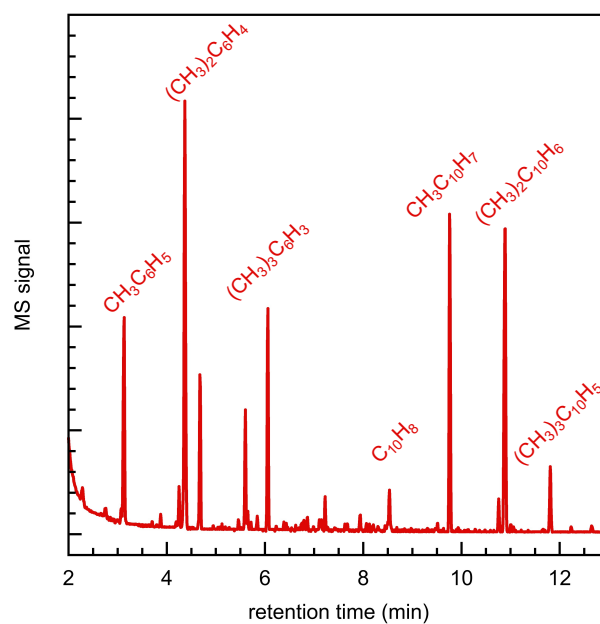


Figure A3.28. GC-MS of liquid products obtained from the reaction of *norm*- $C_{30}H_{62}$ (0.120 g) catalyzed by Pt/HZSM-5 (0.200 g, 1.0 wt% Pt) after 24 h at 280°C under Ar. The major peaks are methyl-substituted benzenes or naphthalenes, as indicated. They were assigned using the NIST MS library. The most probable chemical structures are indicated in **Figure A3.29**.

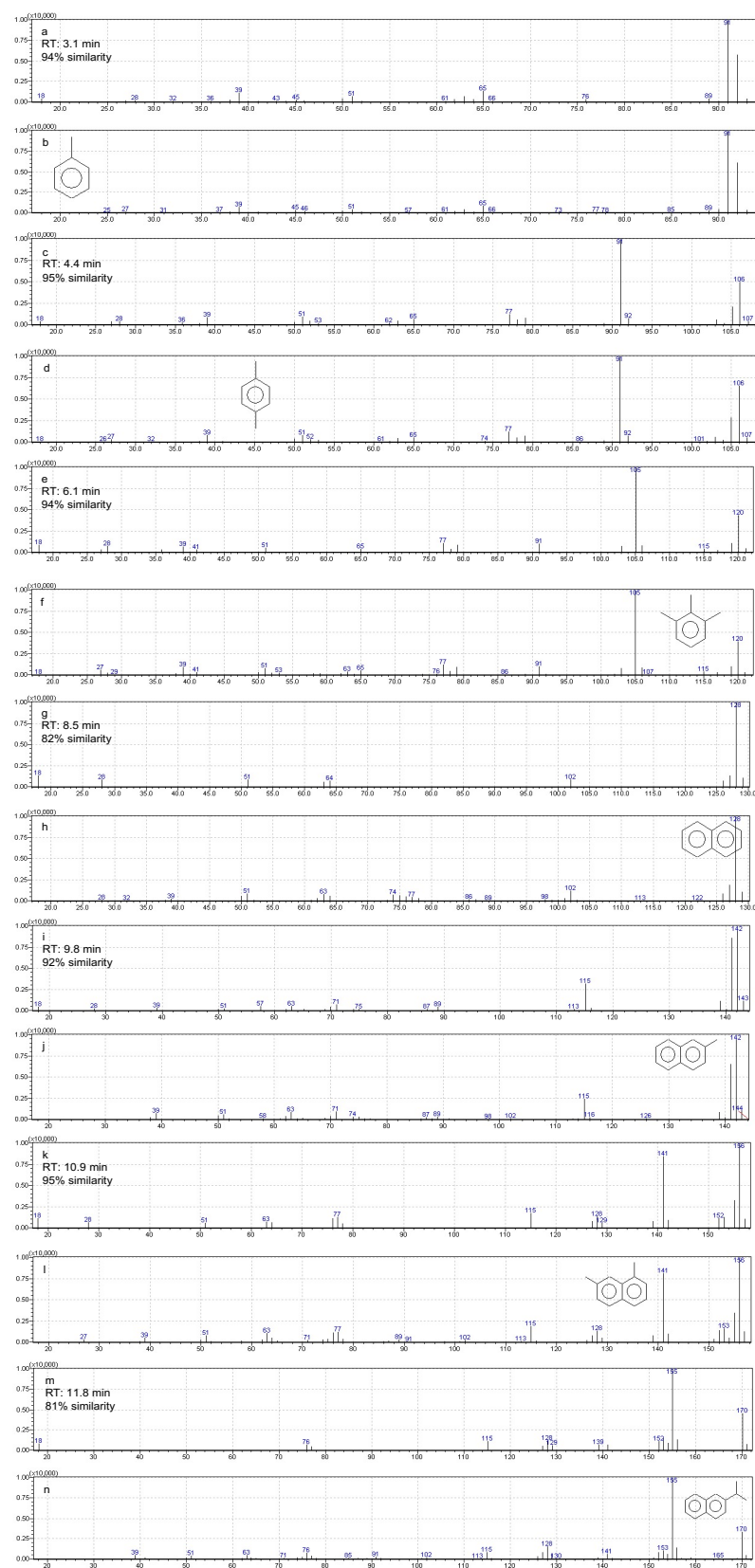


Figure A3.29. Comparison of mass spectra for products (a, c, e, g, i, k, m) with those from the NIST MS library (b, d, f, h, j, l, n). The reaction of *norm*-C₃₀H₆₂ (0.120 g) catalyzed by Pt/HZSM-5 (0.200 g, 1.0 wt% Pt) was conducted at 280°C for 24 h under Ar.

3.8.2.7. Analysis of Aromatic Yields and Substitution Patterns

NMR spectroscopic analysis. ¹H NMR spectra of liquid products recovered from the reactions of *norm*-C₃₀H₆₂ and PE were recorded on a Varian Unity Inova AS600 spectrometer, and analyzed by MestReNova (v11.0.1, Mestrelab Research S. L.). Representative spectra are shown in **Figures A3.30-A3.31** and **A3.37**. Quantitative ¹³C NMR spectra of liquid products from the catalytic reaction of *norm*-C₃₀H₆₂ were recorded on a Bruker Avance NEO 500MHz spectrometer, then analyzed using the software MestReNova. A representative example is shown in **Figure A3.38**.

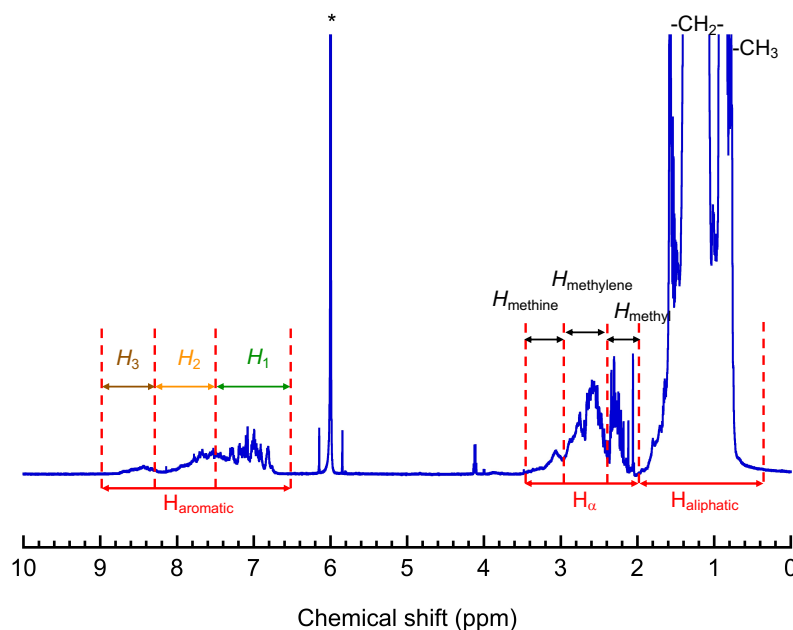


Figure A3.30. ^1H NMR spectrum of liquid hydrocarbons formed during the conversion of *norm*- $\text{C}_{30}\text{H}_{62}$ catalyzed by a physical mixture of $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ (0.100 g, 1.5 wt% Pt) and $\text{F-Al}_2\text{O}_3$ (0.100 g, 1.3 wt% F), after 12 h at 280°C . * indicates the solvent peak (residual protons in $\text{TCE-}d_2$).

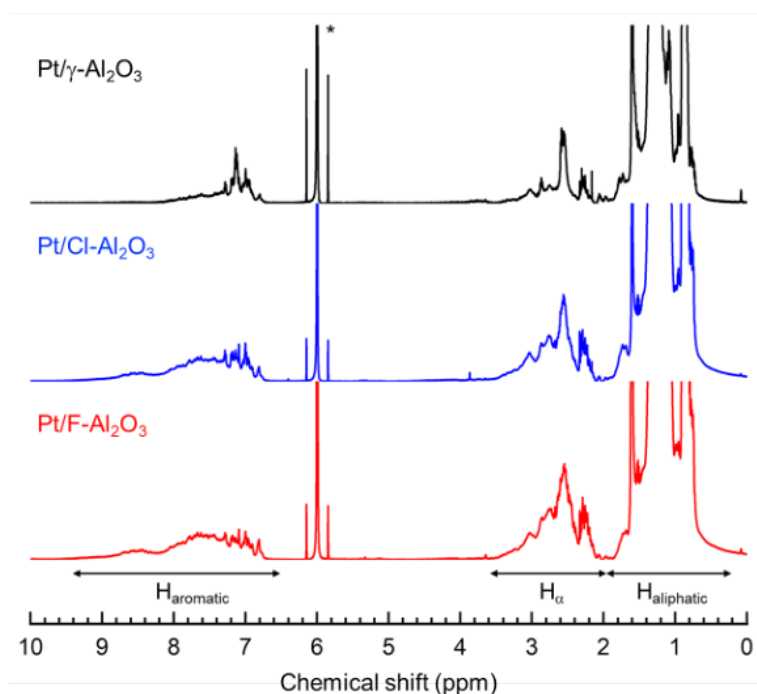


Figure A3.31. ^1H NMR spectrum of liquid hydrocarbons formed during the conversion of PE (0.120 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) catalyzed by $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ (0.200 g, 1.5 wt% Pt, black), $\text{Pt}/\text{Cl-Al}_2\text{O}_3$ (0.200 g, 1.5 wt% Pt, 1.4 wt% Cl, blue) and $\text{Pt}/\text{F-Al}_2\text{O}_3$ (0.200 g, 1.6 wt% Pt, 0.8 wt% F, red) after 8 h at 280°C . * indicates the solvent peak (residual protons in $\text{TCE-}d_2$). For assignments and integration regions, see **Figure A3.30**.

In the aromatic region, three types of aromatic ^1H signals are present: 6.5-7.5 ppm (H_1 , alkylbenzenes, -naphthalenes, -phenanthrenes), 7.5-8.3 ppm (H_2 , alkylnaphthalenes, -phenanthrenes), and 8.3-9.0 ppm (H_3 , alkylphenanthrenes).^{24,25} The presence of a significant amount of anthracenes or larger fused aromatics (e.g., chrysenes) was ruled out by UV-vis (**Figure A3.39**). Nevertheless, the large number of possible contributing structures makes it challenging to deduce the yield and selectivity for each type of aromatic from the ^1H NMR spectrum alone.

To evaluate the average number of alkyl substituents on the aromatic rings, the ratio of H_a signals (2.0-3.5 ppm) to aromatic signals (H_{arom} , 6.5-9.0 ppm), H_a/H_{arom} , was assessed by ^1H NMR. The ratio is ca. 1.5 (**Tables A3.11** and **A3.12**). Dialkylsubstituted aromatics should have a ratio between 0.5 and 1.0 (**Figure A3.32a**). To explain the higher ratio observed experimentally, we observe that bifunctional catalysts promote the skeletal isomerization of hydrocarbon chains, creating methyl branches.²⁶ Dehydrogenation is most favorable at the site of the methyl branch, creating a more substituted alkene. Aromatization of methyl-branched alkenes generates methyldialkylbenzenes and methyldialkylnaphthalenes with H_a/H_{aro} ratios of 2.3 and 1.4, respectively (**Figure A3.32b**). Evidence for methyl substituents is seen in the intense ^1H NMR signals at 2.0-2.5 ppm (**Figures A3.30-A3.31**).

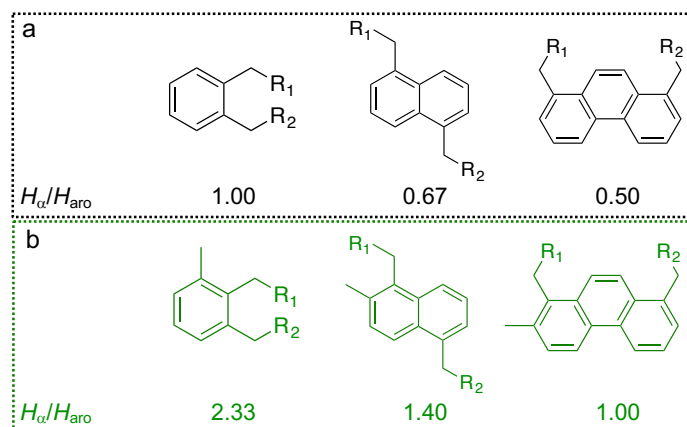
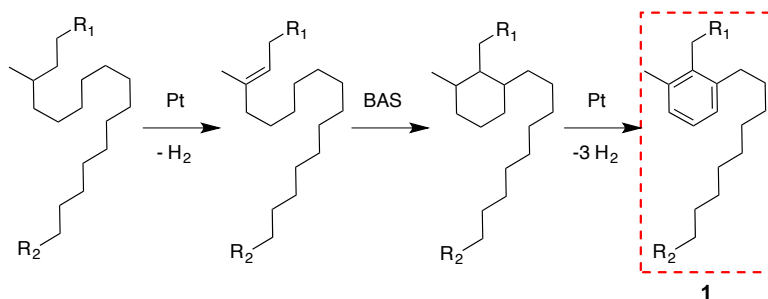


Figure A3.32. Plausible substitution patterns and their corresponding H_a/H_{arom} ratios for (a) dialkylbenzenes, -naphthalenes, and -phenanthrenes, and (b) methyldialkylbenzenes, -naphthalenes, and -phenanthrenes.

The expected mechanism for aromatic ring formation can provide some guidance in terms of expected substitution patterns. **Figure A3.33** shows how the first aromatic ring is assumed to form by ring closure at a branch point along the alkane chain, followed by dehydrogenation to give a 1,2-dialkyl-3-methylbenzene (**1**). Dehydrogenation, Friedel-Crafts alkylation, and further dehydrogenation converts **1** to a 1,5-dialkyl-2-methylnaphthalene (**2**). Repeating this process yields a 1,8-dialkyl-2-methylphenanthrene (**3**).



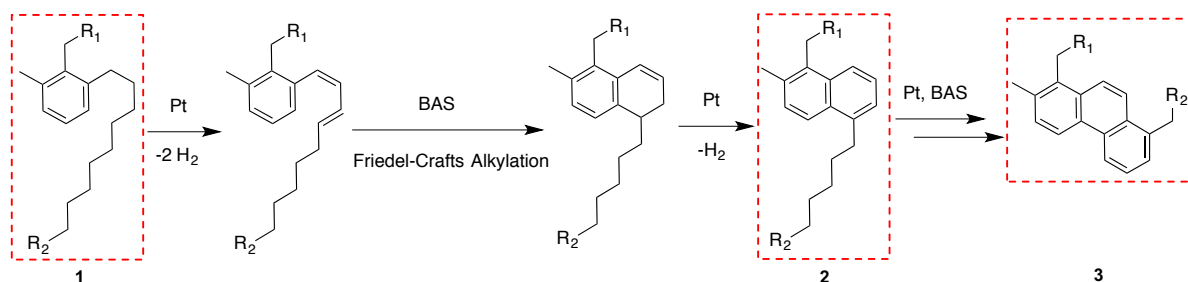


Figure A3.33. Proposed mechanism for conversion of long-chain methyl-branched alkanes to methyldialkylaromatics (boxed in red).

The potential contributions of methyldialkyl-substituted aromatics to the ^1H NMR signals in the aromatic region are summarized in **Figure A3.34**.

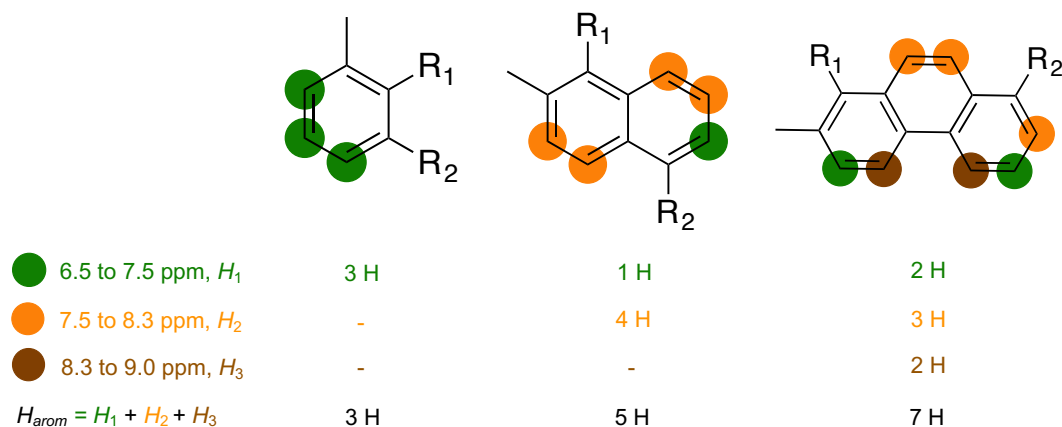


Figure A3.34. Predicted chemical shifts for aromatic protons in methyldialkyl-substituted benzenes, -naphthalenes, and -phenanthrenes, showing the assignments of the expected ^1H signals for each structure type to one of the three aromatic regions (H_1 , green; H_2 , orange; H_3 , brown), and the relative contributions of each type of aromatic proton to each structure type.

The experimental ratios $H_1 : H_2 : H_3$ were obtained by integrating the relevant aromatic regions in the ^1H NMR spectrum. These values were related to the molar amounts (n_j) for each aromatic structure type to estimate the relative molar selectivities (where $S_j = n_j/n_{\text{total}}$), **eqs A3.22-A3.25**.

$$H_1 = 3 n_{\text{ben}} + 1 n_{\text{nap}} + 2 n_{\text{phe}} \quad (\text{A3.22})$$

$$H_2 = 4 n_{\text{nap}} + 3 n_{\text{phe}} \quad (\text{A3.23})$$

$$H_3 = 2 n_{\text{phe}} \quad (\text{A3.24})$$

$$S_{\text{phe}} : S_{\text{nap}} : S_{\text{ben}} = n_{\text{phe}} : n_{\text{nap}} : n_{\text{ben}} = 1/2 H_3 : 1/4 (H_2 - 3/2 H_3) : 1/3 H_1 - 1/12 H_2 - 5/24 H_3 \quad (\text{A3.25})$$

The fractional selectivities (S_j) for all hydrocarbon products must sum to 1 (**eq A3.26**). To estimate S_{alk} , we use the fraction of aromatic protons, $H_{\text{arom}}/H_{\text{total}}$, calculated from the empirical formulas and selectivities for each aromatic structure type (**eq A3.27**), where the value of $H_{\text{arom}}/H_{\text{total}}$ is obtained by integrating the relevant regions of the ^1H NMR spectrum.

$$S_{\text{phe}} + S_{\text{nap}} + S_{\text{ben}} + S_{\text{alk}} = 1 \quad (\text{A3.26})$$

$$\frac{H_{\text{arom}}}{H_{\text{total}}} = (3S_{\text{ben}} + 5S_{\text{nap}} + 7S_{\text{phe}}) / [(2\bar{i} - 6)S_{\text{ben}} + (2\bar{i} - 12)S_{\text{nap}} + (2\bar{i} - 18)S_{\text{phe}} + (2\bar{i} + 2)S_{\text{alk}}] \quad (\text{A3.27})$$

Here, the individual number-averaged carbon numbers for each type of hydrocarbon product are assumed to be the same as the average carbon number $\bar{i}$ for the entire distribution. This assumption was justified by examination of the characteristic ion chromatograms in the GC-MS. All show distributions similar to that of the total ion chromatogram (one example is shown in **Figure A3.35**). The values of S_{ben} , S_{nap} , S_{phe} , and S_{alk} were therefore obtained by solving eqs A3.26 and A3.27 simultaneously.

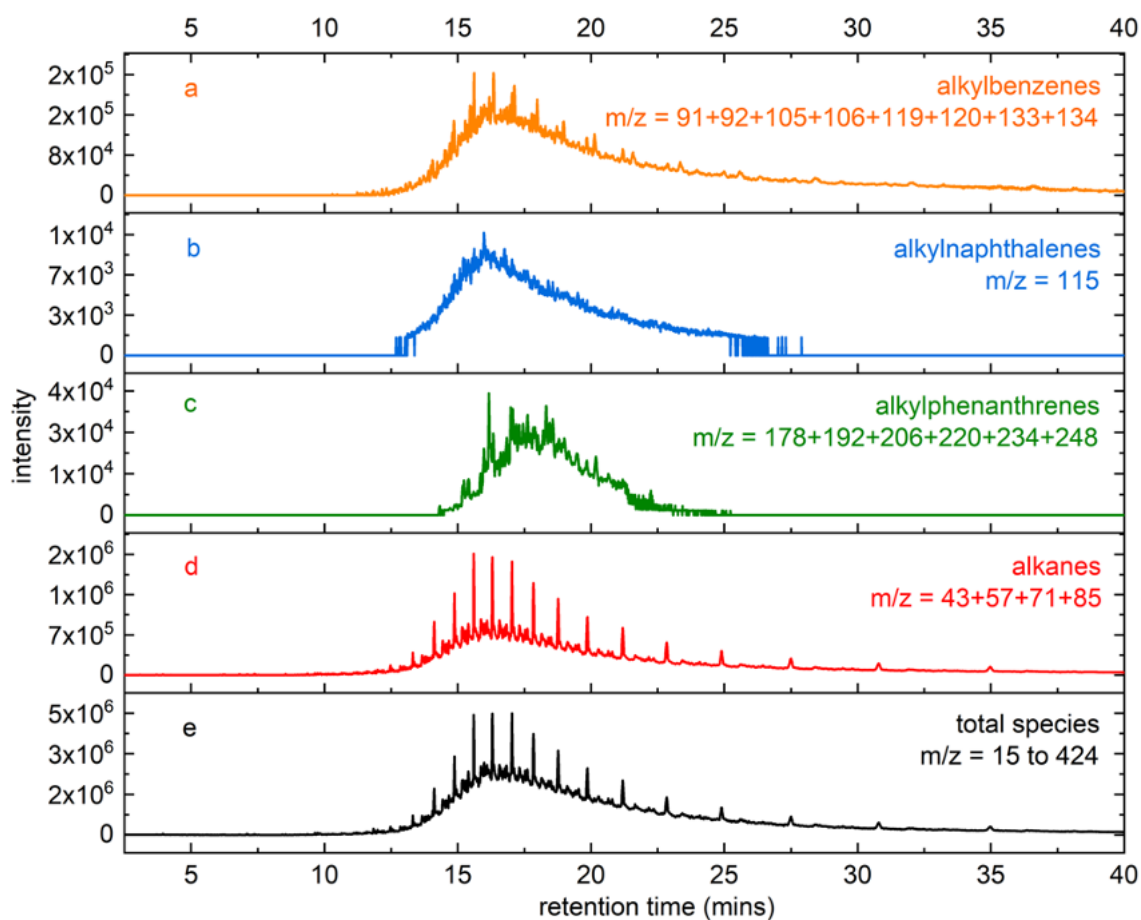


Figure A3.35. Ion chromatograms isolated from the GC-MS of liquid products obtained from the reaction of PE (0.120 g, $M_w = 3.5 \times 10^3$ g mol⁻¹, $D = 1.9$) catalyzed by Pt/F-Al₂O₃ (0.200

g, 1.6 wt% Pt, 0.8 wt% F) after 8 h at 280°C under Ar. The characteristic ion intensities are summed for (a) alkylbenzenes,²⁷ (b) alkylnaphthalenes,²⁸ (c) alkylphenanthrenes,²⁹ and (d) alkanes,³⁰ as well as for (e) the total ion chromatogram.

Our assumption that the average carbon number is similar for alkanes, alkylbenzenes, alkylnaphthalenes and alkylphenanthrenes was tested more quantitatively by analyzing the ion chromatograms in **Figure A3.35**. The carbon number of each type of hydrocarbon product was estimated using the method described in **section 3.8.2.6.3**. First, we assumed that the MS response factor depends only on the type of hydrocarbon (e.g., alkane, alkylbenzene), and not on the molecular weight. The resulting values calculated for $\overline{i_{ben}}$, $\overline{i_{nap}}$, $\overline{i_{phe}}$, $\overline{i_{alk}}$, and $\bar{i}$ (number-averaged carbon number for overall hydrocarbons) are 25.2, 23.4, 23.8, 24.8, and 24.9, respectively. Alternatively, if we assume that the MS response factor for each type of hydrocarbon (e.g., alkane, alkylbenzene) also depends on molecular weight, the calculated values for $\overline{i_{ben}}$, $\overline{i_{nap}}$, $\overline{i_{phe}}$, $\overline{i_{alk}}$, and $\bar{i}$ are 24.6, 23.0, 23.7, 24.0, and 24.2, respectively. Both results suggest that $\overline{i_{ben}} \approx \overline{i_{nap}} \approx \overline{i_{phe}} \approx \overline{i_{alk}} \approx \bar{i}$.

In addition, GPC analysis using both RI and UV detectors showed similar distributions (one example is presented in **Figure A3.36**), showing that the carbon number distribution for the UV-active products is similar to that for the non-UV-active products. This result further supports the assumption that $\overline{i_{ben}} \approx \overline{i_{nap}} \approx \overline{i_{phe}} \approx \overline{i_{alk}} \approx \bar{i}$. Furthermore, since the molar extinction coefficients at 269 nm for phenanthrene ($1.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and naphthalene ($5 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) are much larger than that of benzene ($<100 \text{ M}^{-1} \text{ cm}^{-1}$),³¹ this analysis shows that $\bar{i} \approx 1/2(\overline{i_{nap}} + \overline{i_{phe}})$ in the liquid products.

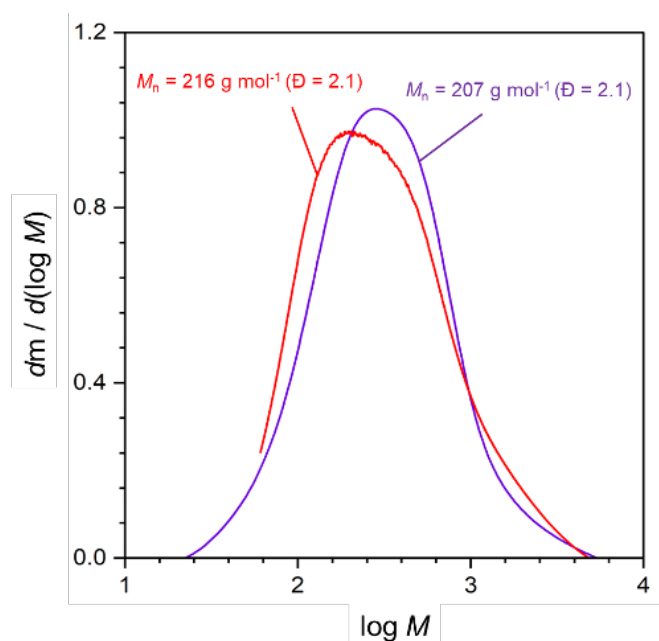


Figure A3.36 GPC chromatogram of liquid hydrocarbons recovered from catalytic conversion of PE (0.120 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $\bar{D} = 1.9$) using Pt/F- Al_2O_3 (0.200 g, 1.6 wt% Pt, 0.8 wt% F) for 8 h at 280°C. The analyses were conducted using RI (purple) and UV (red) detectors at 269.1 nm.

Molar yields of individual aromatic products and total aromatics were calculated using eqs A3.28-A3.29, respectively where $\sum_6^{30} n_i$ represents the moles of total hydrocarbons present in the liquid after reaction, and n_{C30} represents the initial moles of *norm*- $\text{C}_{30}\text{H}_{62}$. (To minimize errors caused by incomplete product recovery, the unrecovered mass in each experiment was assumed to have the same compositional distribution as the detected products and the selectivities were renormalized using the term $1/m\%$ in eq A3.28.) The results are summarized in **Tables A3.10** and **A3.11**.

$$\frac{n_j}{n_{C30}} (mol\%) = \frac{1}{m\%} \cdot \frac{S_j \sum_6^{30} n_i}{n_{C30}} \times 100\% \quad (A3.28)$$

$$n_{arom} / n_{C30} (\%) = n_{ben} / n_{C30} (\%) + n_{nap} / n_{C30} (\%) + n_{phe} / n_{C30} (\%) \quad (A3.29)$$

Table A3.10. Selectivity for various types of hydrocarbons in the catalytic conversion of *norm*-C₃₀H₆₂ by various Pt catalysts ^a

Catalyst	Gases (wt%) ^b	Liquids (wt%) ^b	Insoluble hydrocarbons (wt%) ^c	H _{arom} /H _{total} (%) ^d	$\bar{i}$ ^e	S _{arom} (mol%) ^f
Pt/ZSM-5	73.9	7.8	8	7.2	11.9	90 ^g
Pt/SiO ₂ - Al ₂ O ₃	18.0	56.0	22	5.2	12.1	25
Pt/ γ -Al ₂ O ₃	4.0	81.2	n.d.	1.8	18.8	20
Pt/SiO ₂	0.1	87.2	n.d.	0.1	29.8	2

^a Reaction conditions: *norm*-C₃₀H₆₂ (0.120 g), Pt catalyst (0.200 g, 1.0 wt% Pt) at 280°C after 24 h under Ar.

^b Measured by GC-FID analysis of the headspace (gas yield) and CS₂-soluble products (liquid yield). Yields were calculated using $m(gas)\% = \frac{\sum_1^8 m_i(gas)}{m_{C30H62}}$ and $m(liquid)\% = \frac{\sum_6^{30} m_i(liquid)}{m_{C30H62}}$.

^c Measured by weighing the CS₂-insoluble residue and subtracting the known mass of catalyst.

^d Measured by ¹H NMR of the liquid products.

^e Molar-average carbon number for all CS₂-soluble hydrocarbons, calculated using **eq A3.21**.

^f $S_{\text{arom}} = S_{\text{ben}} + S_{\text{nap}} + S_{\text{phe}}$. S_{ben} , S_{nap} , and S_{phe} were calculated by solving eqs A3.25-A3.27.

^g Aromatic selectivity was directly quantified by GC-FID. Because of good separation between peaks in this sample, individual peaks were identified by GC-MS (Figures A3.28-A3.29). Using the method described in the footnote j instead gave a value for S_{arom} of 48 mol%.

Table A3.11. Characterization of gas and liquid hydrocarbons formed in the conversion of *norm*-C₃₀H₆₂ catalyzed by physical mixtures of various Pt catalysts and acid catalysts ^a

Pt catalyst	Mass of acid catalyst (mg)		Mass recovery	$\bar{i}$ ^c	H_{arom} $/H_{\text{total}}$	H_{a} $/H_{\text{arom}}$ ^d	aromatic yield (mol%) ^e		
	F-Al ₂ O ₃	Cl-Al ₂ O ₃	<i>m</i> % (wt%) ^b		(%) ^d		<i>n</i> _{ben} $/n_{\text{C30}}$	<i>n</i> _{nap} $/n_{\text{C30}}$	<i>n</i> _{phe} $/n_{\text{C30}}$
Pt/ γ -Al ₂ O ₃	-	-	90.8 (4.0)	28.5 (0.2)	0.3 (0.1)	1.3 (0.1)	5.9 (2.6)	0	0
	5	-	81.8	24.7	0.7	1.3	8.4	1.2	1.5
	25	-	89.3 (2.9)	23.3 (0.5)	0.9 (0.2)	1.6 (0.2)	9.5 (2.5)	2.6 (0.4)	1.6 (0.6)
	50	-	85.1 (1.2)	18.6 (1.0)	1.6 (0.2)	1.7 (0.1)	14.5 (0.5)	4.6 (0.9)	3.8 (0.4)
	100	-	96.8 (1.3)	17.3 (1.8)	2.2 (0.1)	2.0 (0.1)	16.1 (1.1)	5.8 (1.2)	6.3 (0.1)
	-	25	95.1 (5.7)	25.4 (1.3)	0.6 (0.1)	1.3 (0.1)	8.5 (0.7)	1.1 (0.2)	0.9 (0.2)

	-	50	91.6 (3.4)	24.9 (0.2)	0.9 (0.1)	1.5 (0.1)	11.2 (1.2)	2.2 (0.5)	1.5 (0.6)
	-	100	94.9 (9.8)	21.7 (1.3)	1.2 (0.3)	1.6 (0.1)	12.6 (3.6)	3.4 (0.1)	2.2 (0.8)
Pt/SiO ₂			97.5	28.7	0.1	1.1	1.8	0	0
	100	-	90.3	16.8	2.3	2.3	18.1	5.9	6.6
none	100	-	91.5 (4.6)	27.7 (1.1)	n.d.	-	-	-	-
	-	100	100.7 (0.4)	28.5 (0.2)	n.d.	-	-	-	-

^a Reaction conditions: *norm*-C₃₀H₆₂ (0.120 g), Pt/ γ -Al₂O₃ (0.100 g, 1.5 wt% Pt) or Pt/SiO₂ (0.100 g, 1.5 wt% Pt), F-Al₂O₃ (1.3 wt% F) or Cl-Al₂O₃ (1.8 wt% Cl), 12 h at 280°C under Ar.

^b Recovered hydrocarbons from C₁ to C₃₀, measured by GC-FID with yields calculated using **eq A3.20**.

^c Molar-average carbon number for all CS₂-soluble hydrocarbons, calculated using **eq A3.21**.

^d Measured by ¹H NMR.

^e Calculated using molar yields of each type of methyldialkylaromatic (**eq A3.28**). Uncertainties shown in parentheses represent the standard deviation of duplicate experiments.

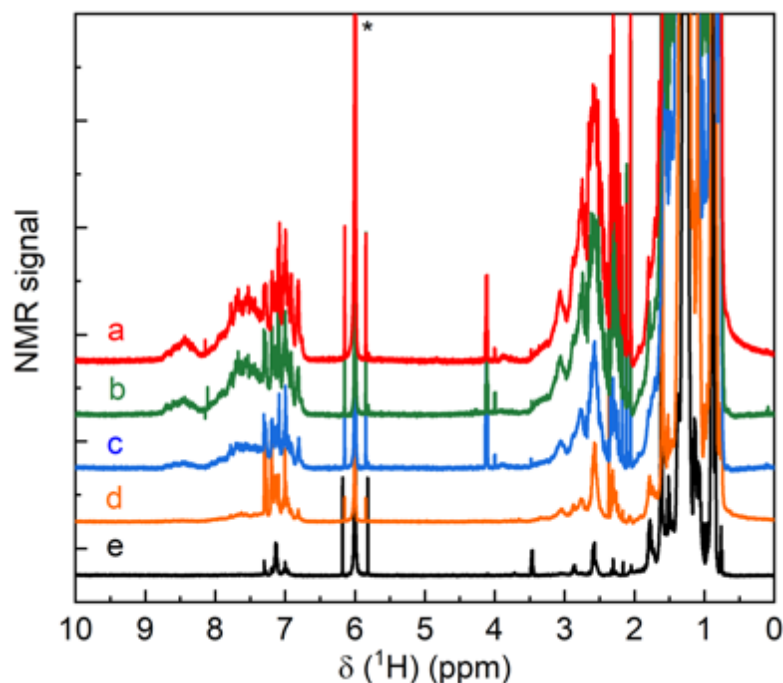


Figure A3.37. ^1H NMR spectrum of liquid hydrocarbons formed during the conversion of *norm*- $\text{C}_{30}\text{H}_{62}$, catalyzed by a physical mixture of $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ (0.100 g, 1.5 wt% Pt) and different amounts of 1.3 wt% $\text{F-Al}_2\text{O}_3$: (a) 0.100 g, (b) 0.050 g, (c) 0.025 g, (d) 0.005 g, (e) 0 g, all after 12 h at 280°C under Ar. * indicates the solvent peak (residual protons of $\text{TCE-}d_2$).

For PE depolymerization, the selectivity for total alkylaromatics (S_{arom}) and each aromatic structure type (S_{ben} , S_{nap} , S_{phe}) in the liquid products were assessed using the same approach (eqs A3.25-A3.27). The individual and total alkylaromatic molar yields were then calculated using eqs A3.30-A3.31. Here, m_{liq} refers to the mass of liquid product after solvent evaporation. The results are summarized in Table A3.12.

$$n_j = (S_j) m_{\text{liq}} / M_n \quad (\text{A3.30})$$

$$n_{\text{arom}} = n_{\text{ben}} + n_{\text{nap}} + n_{\text{phe}} \quad (\text{A3.31})$$

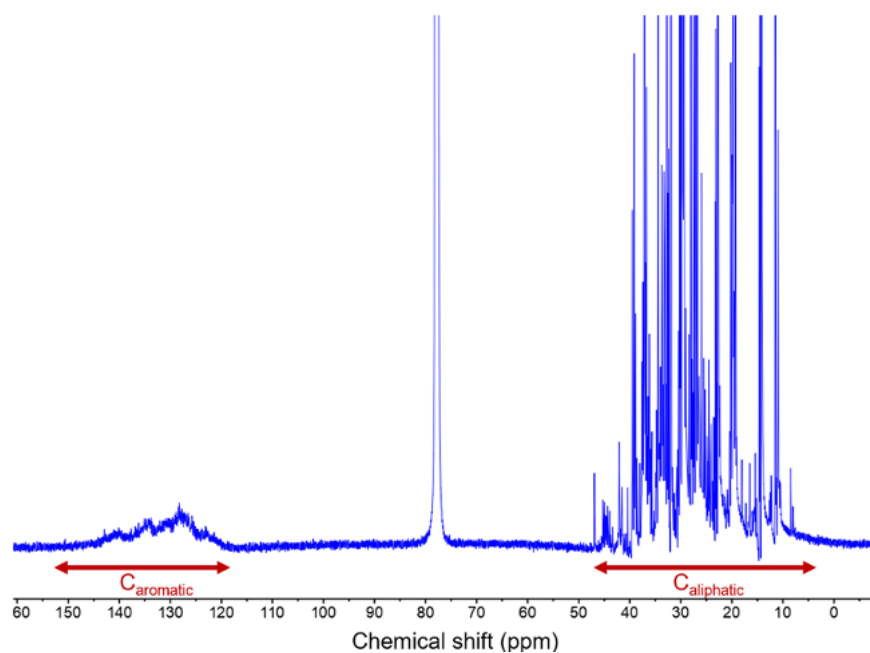


Figure A3.38. Quantitative ^{13}C NMR spectrum of the liquid products obtained from catalytic conversion of *norm*- $\text{C}_{30}\text{H}_{62}$ (0.120 g) using a physical mixture of Pt/ $\gamma\text{-Al}_2\text{O}_3$ (0.100 g, 1.5 wt% Pt) and F- Al_2O_3 (0.100 g, 1.3 wt% F) for 24 h at 280°C.

Table A3.12. Characterization of liquid hydrocarbons recovered from PE conversion ^a

Catalyst Liquid	$\bar{i}$ ^b	H_{arom}	H_{a}	S_{arom}	Aromatic	n_{arom}
Yield	$/H_{\text{total}}$	$/H_{\text{arom}}$ ^c	(mol%)	Yield	(mmol) ^f	
(wt%)	(%) ^c		^d	(wt%)	^e	
		$n_{\text{arom, total}}$	n_{ben}	n_{nap}	n_{phe}	

Pt/ γ - Al_2O_3	44	52	2.9	1.3	82	36	59	48	8	3
Pt/Cl- Al_2O_3	70	25 ^g	6.1	1.5	84	27 ^g	92 ^g	38 ^g	18 ^g	36 ^g
Pt/F- Al_2O_3	64	24	7.1	1.6	56	36	131	45	29	57
Once- recycled Pt/F- Al_2O_3 ^h	61	24	6.3	1.4	49	30	109	35	19	55
Twice- recycled Pt/F- Al_2O_3 ^h	62	24	6.1	1.4	51	31	114	45	21	48
Pt/F- Al_2O_3 ⁱ	59	23	7.5	1.7	59	35	124	40	26	58
Pt/ γ - Al_2O_3 + F- Al_2O_3	61	17	9.2	1.6	48	29	146	68	32	46

^a Reaction conditions: PE (0.120 g, $M_w = 3.5 \times 10^3$ g mol⁻¹, $\bar{D} = 1.9$), Pt catalyst (Pt/ γ - Al_2O_3 , Pt/Cl- Al_2O_3 , or Pt/F- Al_2O_3 , 0.200 g, 1.5 wt%) or a physical mixture of Pt/ γ - Al_2O_3 (0.200, 1.5 wt% Pt) and F- Al_2O_3 (0.100, 1.3 wt% F) after 8 h at 280°C under Ar.

^b Calculated as $M_n/14$.

^c Measured by ^1H NMR.

^d $S_{\text{arom}} = S_{\text{ben}} + S_{\text{nap}} + S_{\text{phe}}$, estimated by eqs A3.25-A3.27.

^e The mass yield of aromatics was estimated as the m_{liq} (wt%) $\times$ S_{arom} (wt%), where S_{arom} (wt%) $\approx S_{\text{arom}}$ (mol%) because GC-MS analysis (Figure A3.35), indicating that aromatics are distributed proportionately across the molecular weight distribution.

^f Molar yields were calculated using eq A3.30.

^g Exceptionally in this experiment, a bimodal molecular weight distribution was observed due to extensive isomerization (and consequently solubilization) of the original polyethylene chains (i.e., with minimal chain cleavage). Results are given for the lower M_n peak of the bimodal distribution, which corresponds to a mass fraction of 45 wt% (Figure A3.23). For the higher M_n peak, corresponding to a mass fraction of 55 wt% and presumably arising from partly depolymerized starting material, $\bar{t} = 67$, and containing 41 mmol and 32 wt% of aromatics. Overall, $\bar{t} = 39$, contains 133 mmol and 59 wt% of aromatics, $n_{\text{ben}} = 55$ mmol, $n_{\text{nap}} = 27$ mmol, and $n_{\text{phe}} = 51$ mmol.

^h Recycled catalyst, recovered from a reaction with PE ($M_w = 3.5 \times 10^3$ g mol⁻¹, $D = 1.9$) at 280°C for 8 h, followed by calcination in flowing O₂ at 500°C and reduction in flowing H₂ (5.0 vol% in Ar) at 280°C.

ⁱ Reaction with PE (0.120 g, $M_w = 2.6 \times 10^4$ g mol⁻¹, $D = 3.9$).

3.8.2.1. UV-vis Measurements

Spectra were recorded using a Shimadzu UV-2401PC spectrophotometer. For reactions of *norm*-C₃₀H₆₂, products extracted by CS₂ were diluted in a 25.00 mL volumetric flask, as described above. An aliquot (0.100 mL) was transferred to a vial by volumetric pipette. Because CS₂ has a long wavelength cut-off (380 nm),³² it was removed in a rotary evaporator

at 30°C and 470 mbar. The sample was then redissolved in HPLC-grade hexanes and diluted in a 3.00 mL volumetric flask. This solution was transferred to a 1-cm square quartz cuvettes for UV-vis measurement, using *norm*-hexane for the background.

A representative UV-vis spectrum is shown in **Figure A3.39a**. Because the product is a complex mixture, the average apparent molar extinction coefficient (ϵ_{app}) was calculated using eq **A3.32**, where A , l , and c denote the absorbance, optical path length (1.0 cm), and the total hydrocarbon concentration (obtained by GC-FID analysis).

$$\epsilon_{app} = A / l c \quad (\text{A3.32})$$

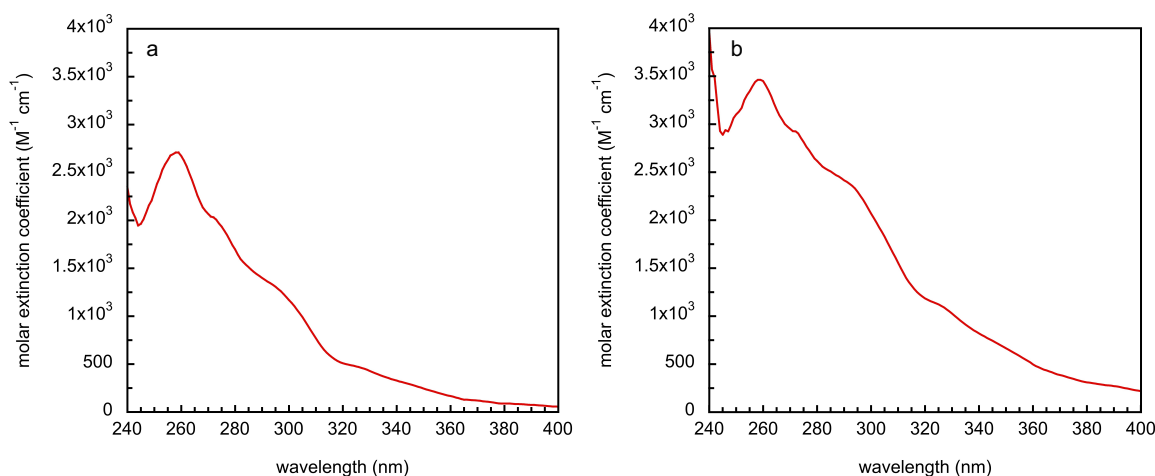


Figure A3.39. Representative UV-vis spectra of liquid hydrocarbons formed during the conversion of (a) *norm*-C₃₀H₆₂ (0.120 g) catalyzed by a physical mixture of Pt/ γ -Al₂O₃ (0.100 g, 1.5 wt% Pt) and F-Al₂O₃ (0.100 g, 1.3 wt% F) in 12 h at 280°C, and (b) PE (0.120 g, $M_w = 3.5 \times 10^3$ g mol⁻¹, $\bar{D} = 1.9$) catalyzed by Pt/F-Al₂O₃ (0.200 g, 1.6 wt% Pt, 0.8 wt% F), in 8 h at 280°C. The total hydrocarbon concentrations are ca. 0.23 and 0.18 mmol/L for the *norm*-C₃₀H₆₂ and PE reactions, respectively. Spectra were recorded in HPLC-grade hexanes.

The absorbance below 320 nm suggests the presence of aromatics (alkylbenzenes,^{33,34} alkylnaphthalenes,^{31,35} and alkylated polyaromatic rings)^{31,36} in the liquids generated from *norm*-C₃₀H₆₂. The nature of the triaromatics was inferred to be predominantly alkylphenanthrenes, since the extinction coefficient of anthracene at 380 nm ($\epsilon = 7.0 \times 10^3$ M⁻¹ cm⁻¹)³¹ is inconsistent with a significant amount of alkylanthracenes (≤ 2.0 mol%, $n_{\text{ant}}/n_{\text{C30}}$, according to **eq A3.28**), while the amount of polyaromatics is ca. 6 mol% (**Table A3.11**). Note that the extinction coefficient of phenanthrene is much smaller at 380 nm ($< 1 \times 10^3$ M⁻¹ cm⁻¹).³¹ We note too that thermodynamic stability favors phenanthrenes over anthracenes.^{37,38}

Finally, the proposed formation mechanism suggests that alkylphenanthrenes are kinetically preferred (**Figure A3.33**).

A similar analysis rules out a major contribution from higher polyaromatics such as chrysenes due to their even higher extinction coefficients (e.g., chrysene, $\epsilon = 1.5 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ at 268 nm).³⁹ Using **eq A3.32** predicts the maximum possible selectivity for alkylchrysenes to be $< 2 \text{ mol}\%$ ($n_{\text{chrysene}}/n_{\text{C30}}$). Since there are many other contributions to the absorbance at this wavelength, larger polyaromatics are clearly very minor components of the product mixture.

Among the liquid products recovered from the reaction of PE ($M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$), a 1.5 mg sample was weighed, dissolved in HPLC-grade *norm*-hexane, and diluted to 25.00 mL in a volumetric flask. An aliquot (3 mL) of this solution was transferred to a 1-cm square quartz cuvette for UV-vis measurement, using the *norm*-hexane for the background spectrum. The spectrum in **Figure A3.39b** resembles that from the *norm*-C₃₀H₆₂ reaction products, but with slightly higher intensity. Nevertheless, a similar analysis shows the maximum possible selectivities to anthracene ($S_{\text{anthracene}}$) and chrysene (S_{chrysene}), calculated using **eqs A3.30** and **A3.32**, are 2.0 and 4.4 mol%, respectively.

3.8.2.2. Characterization of Solid Residue

To assess the nature of hydrocarbon residues post-reaction, catalysts recovered from the reactor after conversion of PE were analyzed by TGA. The measurements were performed in air with a TA Discovery Thermo-Gravimetric Analyzer while heating at $10^\circ\text{C min}^{-1}$ from 50 to 700°C . In the case of Pt/ γ -Al₂O₃, the differential thermogravimetric analysis (**Figure**

A3.40, red) shows a distinct peak at ca. 260°C, corresponding to the oxidation of unreacted PE, and a small peak at ca. 480°C assigned to the oxidation of coke.³³ Two mass-loss events were observed for Pt/Cl-Al₂O₃, although the amount of unreacted PE was much less. For Pt/F-Al₂O₃, almost no unreacted PE was found, but the amount of coke was higher than Pt/Cl-Al₂O₃. The relative amounts of unreacted PE found by TGA are consistent with the relative catalytic activities.

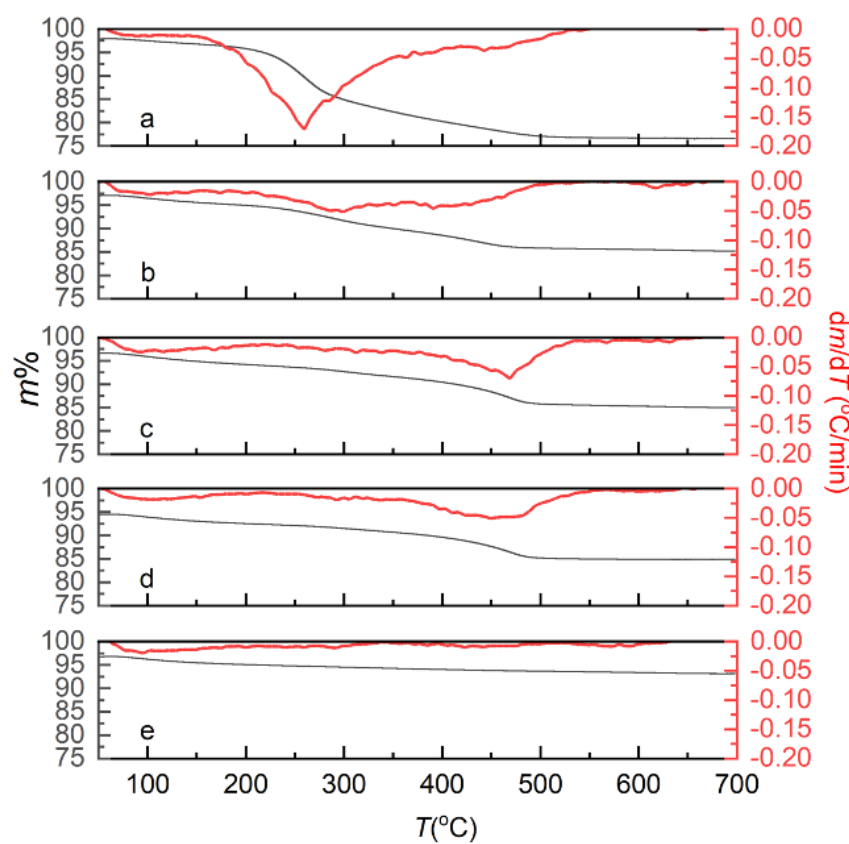


Figure A3.40. TGAs (black) measured in air, and the corresponding DTGAs (red), for the solid residues recovered after the reaction of PE ($M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) catalyzed by (a) Pt/ γ -Al₂O₃ (1.5 wt%), (b) Pt/Cl-Al₂O₃ (1.5 wt% Pt, 1.4 wt% Cl), and (c) Pt/F-Al₂O₃

(1.6 wt% Pt, 0.8 wt% F), all at 280°C for 8 h. (d) Profile recorded after the reaction of PE ($M_w = 2.6 \times 10^4 \text{ g mol}^{-1}$, $D = 3.9$) catalyzed by Pt/F-Al₂O₃ (1.6 wt% Pt, 0.8 wt% F). (e) Profile recorded after the reaction of PE ($M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) catalyzed by Pt/F-Al₂O₃ (1.6 wt% Pt, 0.8 wt% F), followed by calcination in O₂ at 500°C to remove adsorbed carbon.

3.8.2.3. Catalyst Recycling

Freshly reduced Pt/F-Al₂O₃ (0.200 g, 1.6 wt% Pt, 0.8 wt% F) and a low molecular weight PE (0.120 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) were loaded into 90 mL Parr reactors inside an Ar-filled glove-box. Three depolymerization reactions were conducted in parallel at 280°C for 8 h. The catalysts from all three reactors were recovered, combined, and calcined in flowing O₂ (50 mL/min) at 500°C for 2 h to remove organic residue and coke. The removal of hydrocarbons was verified by the complete disappearance of the C-H stretching modes in the IR spectrum (**Figure A3.41**). The calcined catalyst was re-reduced in flowing H₂ (5.0 vol% in Ar, 50 mL/min) at 280°C for 2 h to give the once-recycled catalyst (0.550 g). Two portions of this material (0.200 g each, 1.6 wt% Pt, 0.8 wt% F) were loaded along with portions of low molecular weight PE (0.120 g each, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) into 90 mL Parr reactors inside an Ar-filled glove box. Two depolymerization reactions were conducted at 280°C for 8 h. A similar catalyst recovery/regeneration procedure gave 0.350 g twice-recycled catalyst. This material (0.200 g, 1.6 wt% Pt, 0.8 wt% F) was loaded along with PE (0.120 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) into a 90 mL Parr reactor and the reaction was conducted a third time at 280°C for 8 h. The hydrocarbon product distributions and shown in **Figure A3.42**.

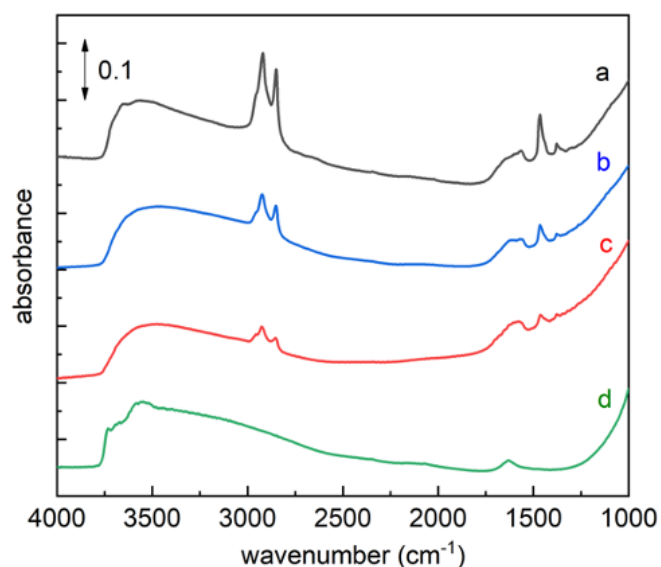


Figure A3.41. IR spectra of solid residues recovered after reaction of PE at 280°C for 8 h, catalyzed by (a) Pt/ γ -Al₂O₃ (1.5 wt%, black), (b) Pt/Cl-Al₂O₃ (1.5 wt% Pt, 1.4 wt% Cl, blue), (c) Pt/F-Al₂O₃ (1.6 wt% Pt, 0.8 wt% F, red), and (d) Pt/F-Al₂O₃ (1.6 wt% Pt, 0.8 wt% F, green, after calcination in O₂ at 500°C). All the samples were diluted with KBr and recorded in Ar-filled glovebox.

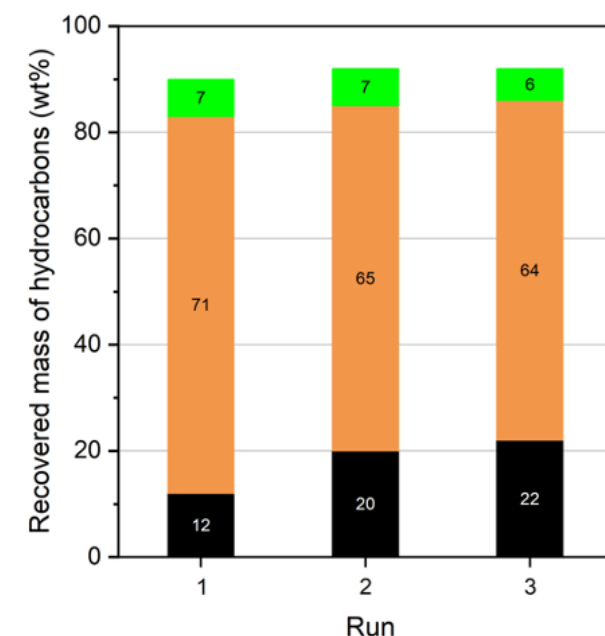


Figure A3.42. Hydrocarbon distributions in three consecutive reactions of PE (0.120 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $\bar{D} = 1.9$), catalyzed by Pt/F-Al₂O₃ (1.6 wt% Pt, 0.8 wt% F) for 8 h at 280°C. Run 1 used 0.200 g fresh catalyst, run 2 used 0.200 g once-recycled catalyst, and run 3 used 0.200 g twice-recycled catalyst. For runs 1 and 2, the yields are averages of triplicate and duplicate experiments, respectively. Mass fractions of hydrocarbons recovered from the batch reactor are shown in: green, for gases; orange, for liquids soluble in hot CH₂Cl₂; black, for organic residues insoluble in hot CH₂Cl₂.

Table A3.13. GPC analyses ^a of liquid hydrocarbons ^b recovered from the conversion of PE catalyzed by Pt/F-Al₂O₃ ^c

Pt/F-Al ₂ O ₃	Liq. Yield (wt%)	M_n	M_w	$\bar{D}$
fresh	64	207	443	2.1

once-recycled	61	203	626	3.1
twice-recycled	62	218	720	3.3

^a Analyzed using polystyrene calibration standards with RI detector (except where noted). M_n , M_w values in g mol^{-1} . $D = M_w / M_n$.

^b Hydrocarbons soluble in hot CH_2Cl_2 , analyzed after solvent removal.

^c Reaction conditions: PE (0.120 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$), Pt catalyst (0.200 g, fresh or recycled) after 8 h at 280°C .

3.8.2.4. Rate of Carbon-Carbon Bond Scission

To quantify the extent of C-C bond breaking, the average rate of C-C bond scission ($r_{\text{C-C}}$) was calculated using **eq A3.33**, where $N(0)$ and $N(t)$ represents the number of chains present at time 0 and time t , respectively. Each C-C scission event generates one additional chain, therefore $N(t)-N(0)$ is the cumulative number of such events, corresponding to the number new chains.

$$r_{\text{C-C}} = dN/dt \approx DN(t)/t = [N(t) - N(0)] / t \quad (\text{A3.33})$$

For the catalytic conversion of *norm*- $\text{C}_{30}\text{H}_{62}$, the number of moles of hydrocarbon (n_i) for each carbon number C_i for $1 \leq i \leq 30$ was obtained by GC-FID, as described above (**Table A3.8**). The total recovered mass varies between experiments, but is typically ca. 90 wt% (**Tables A3.10-A3.11**). To reduce the error caused by incomplete product recovery, the

missing mass in each experiment was assumed to be distributed in the same way as the recovered hydrocarbons. $N(t)$ was calculated using **eq A3.34**:

$$\text{norm-C}_{30}\text{H}_{62} \text{ reactions: } N(t) = \frac{1}{m \%} [\sum_{i=1}^8 n_i(\text{gas}) + \sum_{i=6}^{30} n_i(\text{liq})] \quad (\text{A3.34})$$

where $m \%$ is the mass fraction recovered. $\sum_{i=1}^8 n_i(\text{gas})$, and $\sum_{i=6}^{30} n_i(\text{liq})$ represent the moles of gas and liquid products, respectively. The $r_{\text{C-C}}$ values for reactions of *norm*-C₃₀H₆₂ are summarized in **Table 3.4**, and in **Figures 3.5** and **A3.44-A3.45**.

For PE reactions, $N(t)$ and $N(0)$ were calculated using **eqs A3.35** and **A3.36**, respectively, where $\sum_{i=1}^{11} n_i$ refers to the sum of moles of gas and liquid products recovered in the range C₇₋₁₁ before solvent removal, m_{liq}/M_n represents the moles of liquid products after solvent removal, and m_{PE} refers to the mass of reacted PE (excluding the mass of the insoluble solid residue). These values of $N(t)$ and $N(0)$ were used to obtain $r_{\text{C-C}}$ via **eq A3.33**.

$$\text{PE reactions: } N(t) = \sum_{i=1}^{11} n_i + \frac{m_{\text{liq}}}{M_n} \quad (\text{A3.35})$$

$$N(0) = n_{\text{PE}} = m_{\text{PE}} / M_{\text{n(PE)}} \quad (\text{A3.36})$$

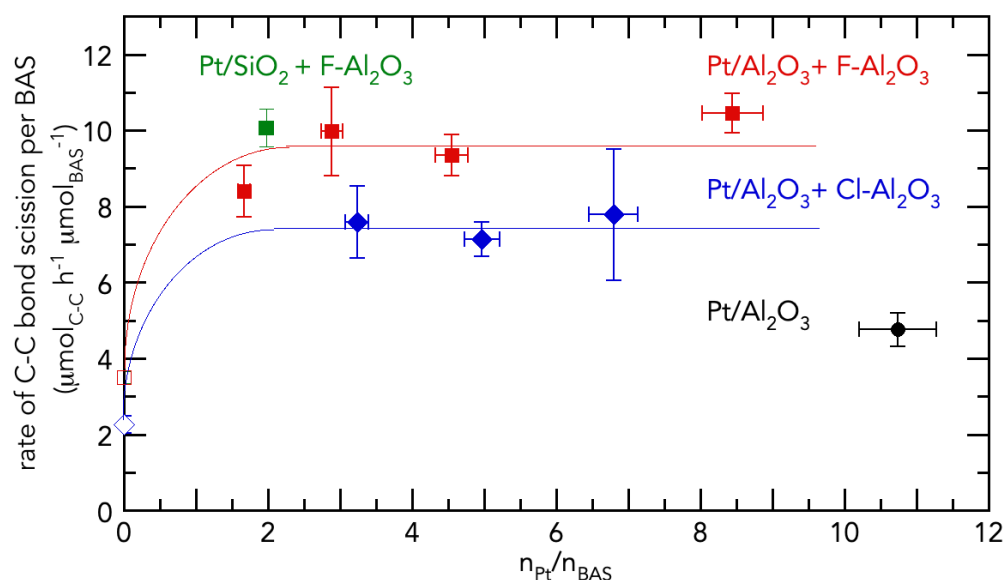


Figure A3.43. Rate of C-C bond scission per strong Brønsted acid sites as a function of $n_{\text{Pt}}/n_{\text{BAS}}$, in the conversion of *norm*-C₃₀H₆₂ (0.120 g), catalyzed by Pt/ γ -Al₂O₃ (0.100 g, 1.5 wt% Pt) with varying amounts of Cl-Al₂O₃ (0.025 – 0.100 g, 1.8 wt% Cl, blue, filled diamonds) or F-Al₂O₃ (0.005 – 0.100 g, 1.3 wt% F, red, filled squares). Results with single-component catalysts Pt/ γ -Al₂O₃ (black, filled circle), F-Al₂O₃ (red, hollow square), and Cl-Al₂O₃ (blue, hollow diamond). Pt/SiO₂ (0.100 g) mixed with F-Al₂O₃ (0.100 g) is represented by the green filled square. Reaction conditions: 12 h, 280°C. The abscissa error bars represent the standard deviation in the number of acid sites contributed by each catalyst support, as measured by IR. The ordinate error bars represent error propagated from the error of rate of C-C scission and number of BAS.

3.8.2.5. Analysis of *norm*- and *iso*-Alkane Yields

According to GC-FID, conversion of *norm*-C₃₀H₆₂ leads to extensive isomerization of *norm*-alkanes to *iso*-alkanes. The yield of *norm*-alkanes relative to the initial charge of *norm*-C₃₀ ($n_{\text{norm-alkane}}/n_{\text{C30}} \times 100\%$) was calculated using **eq A3.37**, for the range C₁₋₃₀. To reduce errors caused by incomplete product recovery, any missing mass was assumed to be distributed in the same way as the recovered hydrocarbons. The results are summarized in **Table 3.4**.

$$\frac{n_{\text{norm-alkane}}}{n_{\text{C30}}}(\text{mol}\%) = \frac{1}{m\%} \cdot \frac{\sum_{i=1}^{30} n_{\text{norm-alkane},i}}{n_{\text{C30}}} \times 100\% \quad (\text{A3.37})$$

The yield of *iso*-alkanes relative to the initial charge of *norm*-C₃₀ ($n_{\text{iso-alkane}}/n_{\text{C30}} \times 100\%$) was calculated using **eq A3.38**, where the yield of *iso*-alkanes was estimated as the difference between yield of non-*norm*-alkanes in the range C₄₋₃₀ and the yield of aromatics in the range C₆₋₃₀ (**eqs A3.28-A3.29**). Since *iso*-alkane and alkylaromatic signals overlap strongly in the GC, the yield of non-*norm*-alkanes was calculated by subtracting the yield of *norm*-alkanes from the total amount of hydrocarbons. A correction factor 1/m% was applied to account for missing mass due to incomplete product recovery. The results are summarized in **Table 3.4** and plotted in **Figures 3.5** and **A3.44-A3.45**.

$$\frac{n_{\text{iso-alkane}}}{n_{\text{C30}}}(\text{mol}\%) = \frac{1}{m\%} \cdot \left(\frac{\sum_{i=4}^{30} n_{\text{non-norm-alkane},i}}{n_{\text{C30}}} - \frac{\sum_{i=6}^{30} n_{\text{arom},i}}{n_{\text{C30}}} \right) \times 100\% \quad (\text{A3.38})$$

3.8.2.6. Apparent Turnover Frequencies (TOFs)

The apparent turnover frequencies for C-C bond scission, isomerization, and aromatization in the catalytic conversion of *norm*-C₃₀H₆₂, were calculated by dividing the number of C-C bond scission events ($n_{\text{C-C scission}}$), the molar yield of iso-alkanes ($n_{\text{iso-alkane}}$), and the molar yield of aromatics (n_{arom}), respectively, by the total number of strong BAS (n_{BAS} , measured by recording the IR of adsorbed DMP) and the reaction time (12 h), according to eqs A3.39-3.41. TOF values in Table 3.4 were obtained by linear regression of data in Figure 3.5.

$$TOF_{\text{C-C bond scission}} = n_{\text{C-C scission}} / (n_{\text{BAS}} t) \quad (\text{A3.39})$$

$$TOF_{\text{isomerization}} = n_{\text{iso-alkane}} / (n_{\text{BAS}} t) \quad (\text{A3.40})$$

$$TOF_{\text{aromatization}} = n_{\text{arom}} / (n_{\text{BAS}} t) \quad (\text{A3.41})$$

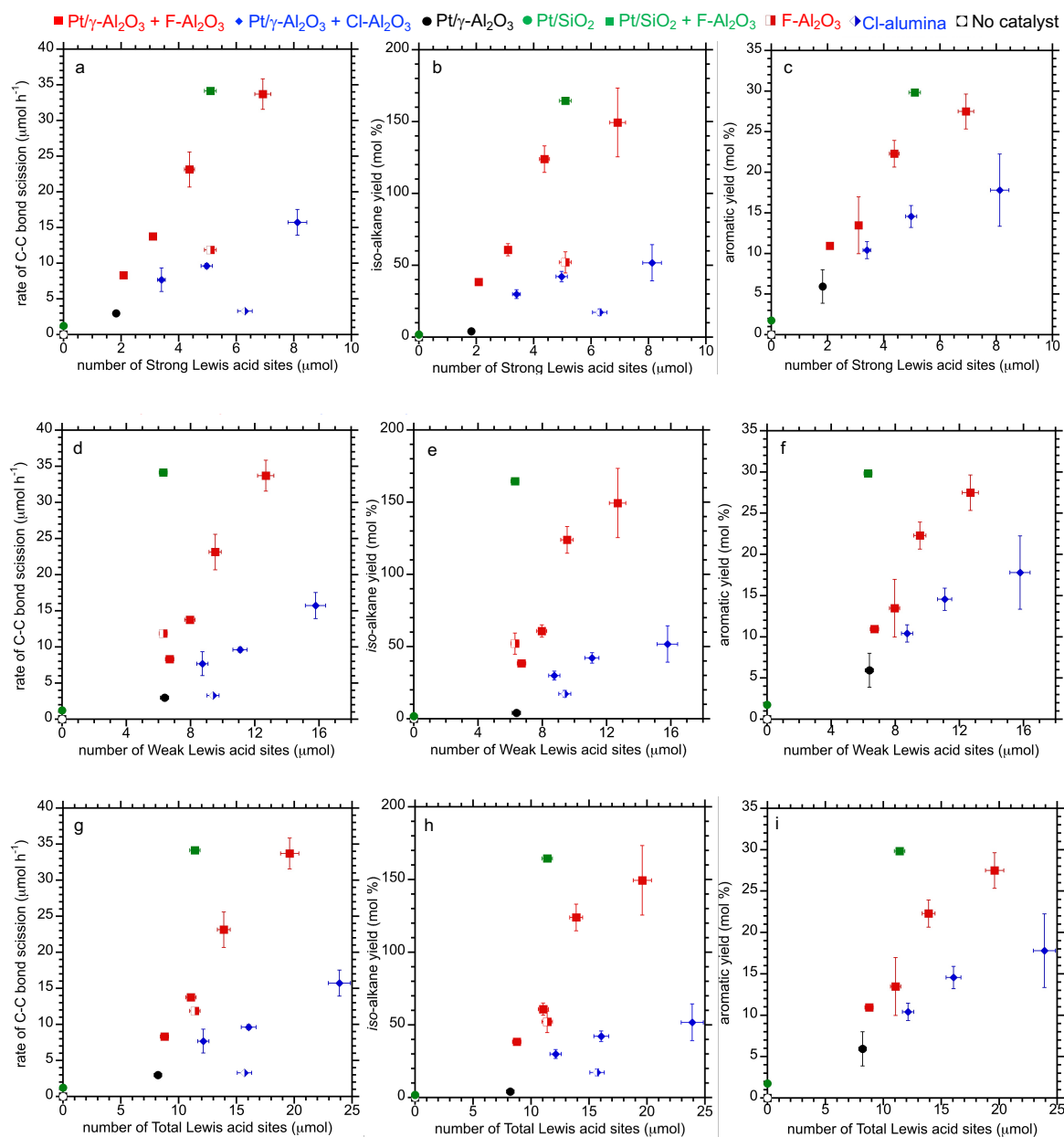


Figure A3.44. Correlation between the rates of C-C bond scission (a, d, g), the *iso*-alkane yield (b, e, h), and the aromatic yield (c, f, i) in the conversion of *norm*-C₃₀H₆₂ (0.120 g) with different types of Lewis acid sites (strong LAS, a, b, c; weak LAS, d, e, f; total LAS, g, h, i), catalyzed by Pt/γ-Al₂O₃ (0.100 g, 1.5 wt% Pt) with varying amounts of Cl-Al₂O₃ (0.025 – 0.100 g, 1.8 wt% Cl, blue, filled diamonds) or F-Al₂O₃ (0.005 – 0.100 g, 1.3 wt% F, red, filled

squares). Results with single component catalysts Pt/ γ -Al₂O₃ (black, filled circle), Pt/SiO₂ (0.100 g, 1.5 wt% Pt, green, filled circle), F-Al₂O₃ (red, half-filled square), and Cl-Al₂O₃ (blue, half-filled diamond), and a control with no catalyst (black, hollow circle), are also shown. Pt/SiO₂ (0.100 g) mixed with F-Al₂O₃ (0.100 g) is represented by the green filled square. Reaction conditions: 12 h, 280°C. The abscissa error bars represent the standard deviation in the number of acid sites contributed by each catalyst support, as measured by IR. The ordinate error bars represent the standard deviations of duplicate experiments.

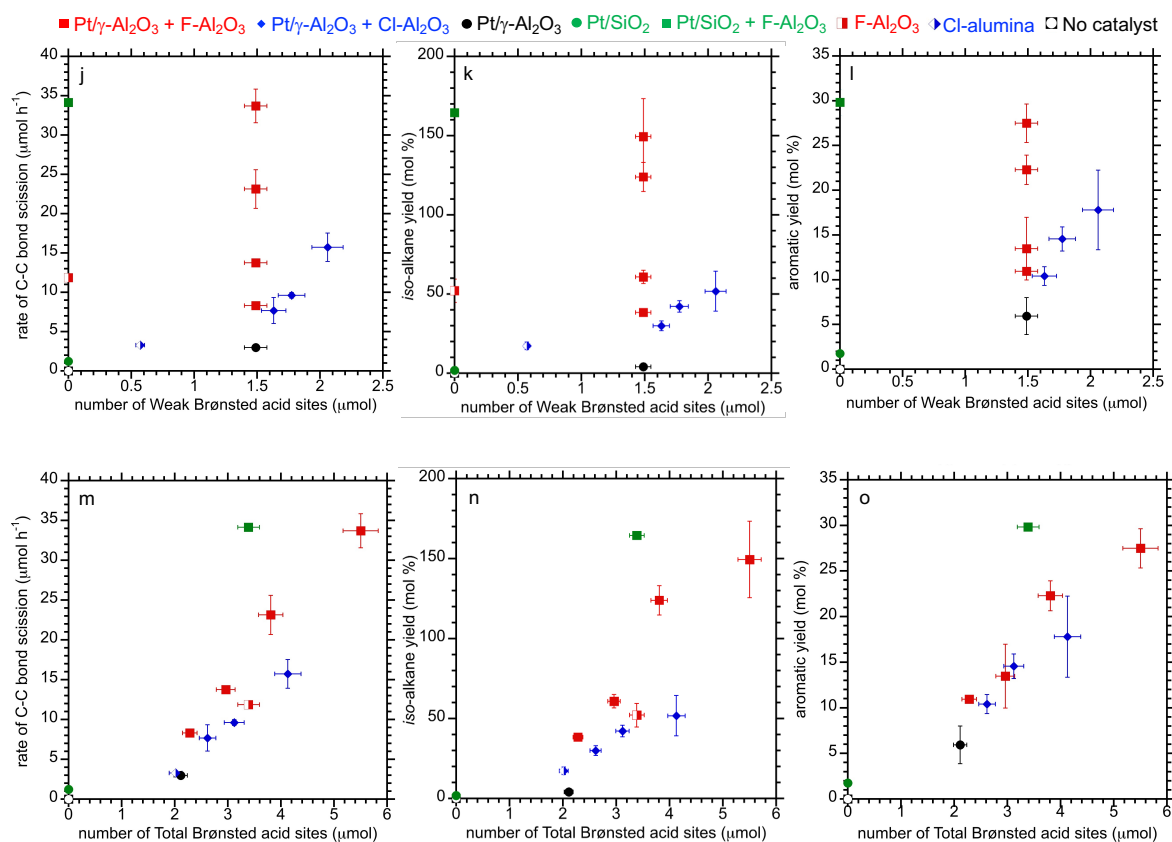


Figure A3.45. Correlation between the rates of C-C bond scission (j, m), the *iso*-alkane yield (k, n), and the aromatic yield (l, o) in the conversion of *norm*-C₃₀H₆₂ (0.120 g) and the number

of weak Brønsted acid sites (j, k, l) and total Brønsted acid sites (m, n, o), catalyzed by Pt/ γ -Al₂O₃ (0.100 g, 1.5 wt% Pt) with varying amounts of Cl-Al₂O₃ (0.025 – 0.100 g, 1.8 wt% Cl, blue, filled diamonds) or F-Al₂O₃ (0.005 – 0.100 g, 1.3 wt% F, red, filled squares). Results with single-component catalysts Pt/ γ -Al₂O₃ (black, filled circle), Pt/SiO₂ (0.100 g, 1.5 wt% Pt, green, filled circle), F-Al₂O₃ (red, half-filled square), and Cl-Al₂O₃ (blue, half-filled diamond), and a control with no catalyst (black, hollow circle), are also shown. Pt/SiO₂ (0.100 g) mixed with F-Al₂O₃ (0.100 g) is represented by the green filled square. Reaction conditions: 12 h, 280°C. The abscissa error bars represent the standard deviation in the number of acid sites contributed by each catalyst support, as measured by IR. The ordinate error bars represent the standard deviations of duplicate experiments.

3.8.2.7. Hydrogen Balance

In the catalytic conversion of *norm*-C₃₀H₆₂, aromatic formation generates H₂, in an amount ($n_{H_2(G)}$) which is the sum of the degrees of unsaturation of benzenes, naphthalenes, and phenanthrenes, **eq A3.42**. At the same time, C-C bond scission consumes H₂, in an amount ($n_{H_2(C)}$) represented by **eq A3.43**, where $N(0)$ and $N(t)$ represent the number of chains initially and after the reaction. The amount of free hydrogen ($n_{H_2(F)}$) was measured by GC-TCD, using Ar as an internal standard. Values are summarized in **Table A3.14**. In most experiments, the value of $n_{H_2(F)}$ corresponds reasonably well to the difference between $n_{H_2(G)}$ and $n_{H_2(C)}$, indicating that the hydrogen balance is well described by these two major processes.

$$n_{H_2(G)} = 4 n_{ben} + 7 n_{nap} + 10 n_{phe} \quad (A3.42)$$

$$n_{\text{H2(C)}} = N(t) - N(0) \quad (\text{A3.43})$$

Table A3.14. H₂ balance (mmol) in catalytic conversion of *norm*-C₃₀H₆₂ by a physical mixture of Pt/ γ -Al₂O₃ (0.100 g, 1.5 wt% Pt) and different amount of F-Al₂O₃ (1.3 wt% F), or Cl-Al₂O₃ (1.8 wt% Cl), after 12 h at 280°C

Mass of acid catalyst (mg)		$n_{\text{H}_2(\text{G})}$ ^a	$n_{\text{H}_2(\text{C})}$ ^b	$n_{\text{H}_2(\text{F})}$ ^c	$n_{\text{H}_2(\text{G})} - n_{\text{H}_2(\text{C})}$
F-Al ₂ O ₃	Cl-Al ₂ O ₃				
0	0	0.07(3)	0.04(1)	0.01	0.03(4)
5	0	0.16	0.10	0.01	0.06
25	0	0.21(5)	0.17(1)	0.02	0.04(6)
50	0	0.36(3)	0.28(3)	0.08	0.08(6)
100	0	0.48(4)	0.40(3)	0.14	0.08(7)
0	25	0.14(2)	0.09(2)	0.02	0.05(4)
0	50	0.21(4)	0.12(1)	0.04	0.09(5)
0	100	0.27(6)	0.19(2)	0.09	0.08(8)

^a Calculated using eq A3.42.

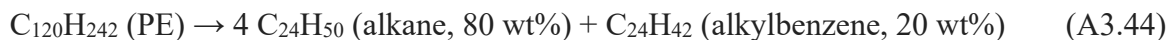
^b Calculated using eq A3.43.

^c Measured by GC-TCD. Uncertainties shown in parentheses represent the standard deviation of duplicate experiments and (for the difference) error propagation.

Note that triacontane has a higher H/C ratio than PE. Consequently, if we start with the same masses of C₁₂₀H₂₄₂ (a model PE) and C₃₀H₆₂, and allow both to undergo similar

amounts of C-C bond scission, the theoretical aromatic yield is lower for triacontane, eq

A3.44-A3.45:



3.8.2.8. Evolution of Number-averaged Molecular Weight

The number-averaged molecular weight (M_n) of a polymer is defined in eq A3.46:

$$M_n = \frac{\sum M_i n_i}{\sum n_i} = \frac{m_{PE}}{\sum n_i} = \frac{m_{PE}}{N(0) + n_{C-C}} \quad (\text{A3.46})$$

where M_i is the molecular weight of an individual polymer chain and n_i is the number of such chains. The mass of polymer, m_{PE} , is equal to $\sum M_i n_i$. During depolymerization over a time interval t , the value of M_n becomes progressively smaller as shorter chains are formed in a zeroth-order reaction. Consider $N(0)$ as the initial number of chains, and n_{C-C} as the number of C-C bond scission events that occurs in this time. Since each scission gives rise to one new chain, the number of chains after time t is $N(0) + n_{C-C}$.

The change in M_n can be calculated using eq A3.46 for equal masses of polymers with different starting molecular weights, as a function of the number of C-C bond scission events (increasing linearly with time). The results are shown in **Figure A3.46** for a low ($M_n = 1.8 \times 10^3$ g/mol, $D = 1.9$) and high ($M_n = 6.6 \times 10^3$ g/mol, $D = 3.9$) molecular-weight PE. The values of M_n converge when the extent of C-C bond scission is large, resulting in similar liquid yields regardless of initial polymer molecular weight.

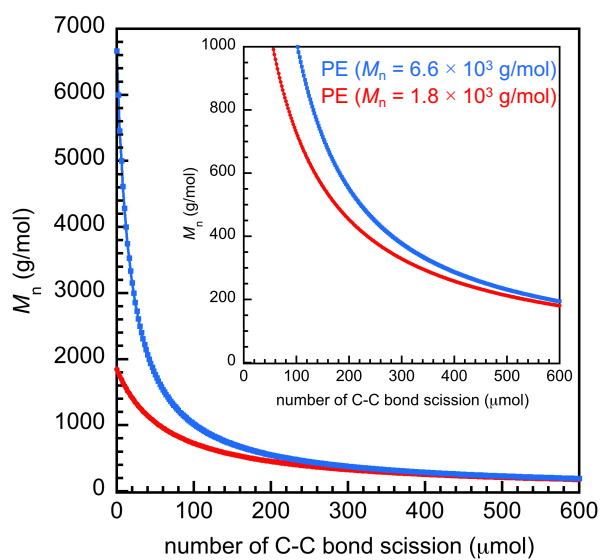


Figure A3.46. Predicted evolution of number-averaged molecular weight (M_n) as a function of the number of C-C bond scission events (or time, for a zeroth-order reaction) for the same mass (0.120 g) of low ($M_n = 1.8 \times 10^3$ g/mol, red) and high ($M_n = 6.6 \times 10^3$ g/mol, blue) molecular-weight PE. The insert shows an expanded view of the low- M_n region.

3.8.3. Additional References

1. Gallo, A., Fong, A., Szeto, K.C., Rieb, J., Delevoye, L., Gauvin, R.M., Taoufik, M., Peters, B., and Scott, S.L. (2016). Ligand exchange-mediated activation and stabilization of a Re-Based olefin metathesis catalyst by chlorinated alumina. *J. Am. Chem. Soc.* *138*, 12935–12947. 10.1021/jacs.6b06953.
2. Yang, E., Jang, E.J., Lee, J.G., Yoon, S., Lee, J., Musselwhite, N., Somorjai, G.A., Kwak, J.H., and An, K. (2018). Acidic effect of porous alumina as supports for Pt nanoparticle catalysts in *n*-hexane reforming. *Catal. Sci. Technol.* *8*, 3295–3303. 10.1039/C8CY00776D.

3. Zhang, F., Zeng, M., Yappert, R.D., Sun, J., Lee, Y.-H., LaPointe, A.M., Peters, B., Abu-Omar, M.M., and Scott, S.L. (2020). Polyethylene upcycling to long-chain alkylaromatics by tandem hydrogenolysis/aromatization. *Science* 370, 437–441. 10.1126/science.abc5441.
4. Oudenhuijzen, M.K., Kooyman, P.J., Tappel, B., van Bokhoven, J.A., and Koningsberger, D.C. (2002). Understanding the influence of the pretreatment procedure on platinum particle size and particle-size distribution for SiO₂ impregnated with [Pt²⁺(NH₃)₄](NO₃⁻)₂: A combination of HRTEM, mass spectrometry, and quick EXAFS. *J. Catal.* 205, 135–146. 10.1006/jcat.2001.3433.
5. Buss, W.C., and Klusdahl, H.E. (1977). Catalytic reforming process and catalyst. U.S. Patent No. 4,012,313. 15 Mar. 1977.
6. Marinho, R.S., Silva, C.N. da, Afonso, J.C., and Cunha, J.W.S.D. da (2011). Recovery of platinum, tin and indium from spent catalysts in chloride medium using strong basic anion exchange resins. *J. Hazard. Mater.* 192, 1155–1160. 10.1016/j.jhazmat.2011.06.021.
7. Jarvis, I., Totland, M.M., and Jarvis, K.E. (1997). Assessment of Dowex 1-X8-based anion-exchange procedures for the separation and determination of Ruthenium, Rhodium, Palladium, Iridium, Platinum and Gold in geological samples by inductively coupled plasma mass spectrometry. *Analyst* 122, 19–26. 10.1039/A606169I.
8. Peru, D.A., and Collins, R.J. (1993). Comparison of cold digestion methods for elemental analysis of a Y-type zeolite by inductively coupled plasma (ICP) spectrometry. *Fresenius' J. Anal. Chem.* 346, 909–913. 10.1007/BF00322749.

9. Job, N., Chatenet, M., Berthon-Fabry, S., Hermans, S., and Maillard, F. (2013). Efficient Pt/carbon electrocatalysts for proton exchange membrane fuel cells: Avoid chloride-based Pt salts! *J. Power Sources* *240*, 294–305. 10.1016/j.jpowsour.2013.03.188.
10. Ismail, I.M.K. (1992). Cross-sectional areas of adsorbed nitrogen, argon, krypton, and oxygen on carbons and fumed silicas at liquid nitrogen temperature. *Langmuir* *8*, 360–365. 10.1021/la00038a006.
11. Morterra, C., and Magnacca, G. (1996). A case study: surface chemistry and surface structure of catalytic aluminas, as studied by vibrational spectroscopy of adsorbed species. *Catal. Today* *27*, 497–532. 10.1016/0920-5861(95)00163-8.
12. Digne, M., Raybaud, P., Sautet, P., Guillaume, D., and Toulhoat, H. (2008). Atomic scale insights on chlorinated γ -alumina surfaces. *J. Am. Chem. Soc.* *130*, 11030–11039. 10.1021/ja8019593.
13. Emeis, C.A. (1993). Determination of integrated molar extinction coefficients for infrared absorption bands of pyridine adsorbed on solid acid catalysts. *J. Catal.* *141*, 347–354. 10.1006/jcat.1993.1145.
14. Tamura, M., Shimizu, K., and Satsuma, A. (2012). Comprehensive IR study on acid/base properties of metal oxides. *Appl. Catal., A* *433–434*, 135–145. 10.1016/j.apcata.2012.05.008.
15. Zhang, F., Szeto, K.C., Taoufik, M., Delevoye, L., Gauvin, R.M., and Scott, S.L. (2018). Enhanced metathesis activity and stability of methyltrioxorhenium on a mostly amorphous alumina: role of the local grafting environment. *J. Am. Chem. Soc.* *140*, 13854–13868. 10.1021/jacs.8b08630.

16. Datka, J. (1992). Acidic properties of supported niobium oxide catalysts: An infrared spectroscopy investigation. *J. Catal.* 135, 186–199. 10.1016/0021-9517(92)90279-Q.
17. Harris, J.W., Cordon, M.J., Di Iorio, J.R., Vega-Vila, J.C., Ribeiro, F.H., and Gounder, R. (2016). Titration and quantification of open and closed Lewis acid sites in Sn-Beta zeolites that catalyze glucose isomerization. *J. Catal.* 335, 141–154. 10.1016/j.jcat.2015.12.024.
18. Healy, M.H., Wieserman, L.F., Arnett, E.M., and Wefers, K. (1989). Infrared spectroscopy and microcalorimetric investigations of d-q and k aluminas using basic probe molecules: acetonitrile, pyridine, 2,6-lutidine, and *n*-butylamine. *Langmuir* 5, 114–123. 10.1021/la00085a021.
19. Onfroy, T., Clet, G., and Houalla, M. (2005). Quantitative IR characterization of the acidity of various oxide catalysts. *Microporous and Mesoporous Mater.* 82, 99–104. 10.1016/j.micromeso.2005.02.020.
20. Hadjiivanov, K. (2014). Identification and characterization of surface hydroxyl groups by infrared spectroscopy. In *Adv. Catal.* (Elsevier), pp. 99–318. 10.1016/B978-0-12-800127-1.00002-3.
21. Oliviero, L., Vimont, A., Lavalley, J.-C., Romero Sarria, F., Gaillard, M., and Maugé, F. (2005). 2,6-Dimethylpyridine as a probe of the strength of Brønsted acid sites: study on zeolites. Application to alumina. *Phys. Chem. Chem. Phys.* 7, 1861–1869. 10.1039/B500689A.
22. Zhang, M., Salje, E.K.H., and Ewing, R.C. (2002). Infrared spectra of Si-O overtones, hydrous species, and U ions in metamict zircon: radiation damage and recrystallization. *J. Phys.: Condens. Matter* 14, 3333–3352. 10.1088/0953-8984/14/12/319.

23. Dietz, W.A. (1967). Response factors for gas chromatographic analyses. *J. Chromatogr. Sci.* **5**, 68–71. 10.1093/chromsci/5.2.68.
24. Ernst, L., and Schulz, P. (1992). ^{13}C and ^1H NMR chemical shift assignments of 1- and 2-alkylnaphthalenes ($\text{R} = \text{Me, Et, } i\text{-Pr, } t\text{-Bu}$) and determination of substituent effects on ^{13}C and ^1H chemical shifts. *Magnetic Resonance in Chemistry* **30**, 73–76. 10.1002/mrc.1260300114.
25. Bartle, K.D., and Smith, J.A.S. (1967). High-resolution nuclear magnetic resonance spectra of phenanthrenes—I Phenanthrene and some alkyl derivatives. *Spectrochim. Acta. Part A* **23**, 1689–1714. 10.1016/0584-8539(67)80053-9.
26. Wakayama, T., and Matsushashi, H. (2005). Reaction of linear, branched, and cyclic alkanes catalyzed by Brönsted and Lewis acids on H-mordenite, H-beta, and sulfated zirconia. *J. Mol. Catal. A: Chem* **239**, 32–40. 10.1016/j.molcata.2005.05.031.
27. Johnson, J.V., Pedder, R.E., and Yost, R.A. (1991). MS-MS parent scans on a quadrupole ion trap mass spectrometer by simultaneous resonant excitation of multiple ions. *Int. J. Mass Spectrom. Ion Processes* **106**, 197–212. 10.1016/0168-1176(91)85019-I.
28. McClennen, W.H., Arnold, N.S., Roberts, K.A., Meuzelaar, H.L.C., Lighty, J.S., and Lindgren, E.R. (1990). Fast, repetitive GC/MS analysis of thermally desorbed polycyclic aromatic hydrocarbons (PAHs) from contaminated soils. *Combust. Sci. Technol.* **74**, 297–309. 10.1080/00102209008951694.
29. Chen, J., Zhang, H., Huang, H., Li, X., Shi, S., Liu, F., and Chen, L. (2013). Impact of anaerobic biodegradation on alkylphenanthrenes in crude oil. *Org. Geochem.* **61**, 6–14. 10.1016/j.orggeochem.2013.05.003.

30. Krauß, S., and Vetter, W. (2018). Phytol and phytol fatty acid esters: occurrence, concentrations, and relevance. *Eur. J. Lipid Sci. Technol.* *120*, 1700387. 10.1002/ejlt.201700387.
31. Tropp, J., Ihde, M.H., Williams, A.K., White, N.J., Eedugurala, N., Bell, N.C., Azoulay, J.D., and Bonizzoni, M. (2019). A sensor array for the discrimination of polycyclic aromatic hydrocarbons using conjugated polymers and the inner filter effect. *Chem. Sci.* *10*, 10247–10255. 10.1039/C9SC03405F.
32. Catalán, J. (2021). Carbon disulfide solvent, helping to clarify the Stokes shift in diphenylpolyenes. *J. Phys. Org. Chem.* *34*, e4147. 10.1002/poc.4147.
33. Chen, Z., Xu, L., and Zhang, X. (2022). Upgrading of polyethylene to hydrocarbon fuels over the Fe-modified Pt/Al₂O₃ catalysts at a mild condition without external H₂. *Chem. Eng. J.*, 136213. 10.1016/j.cej.2022.136213.
34. Romand, J., and Vodar, B. (1951). Absorption spectra of benzene in the vapour state and in condensed (solid) state in the far ultraviolet. *Compt. rend* *233*, 930–932.
35. Ferguson, J., Reeves, L.W., and Schneider, W.G. (1957). Vapor absorption spectra and oscillator strengths of naphthalene, anthracene, and pyrene. *Can. J. Chem.* *35*, 1117–1136. 10.1139/v57-152.
36. Ramart-Lucas, M., Matti, J., and Guilmart, T. (1948). Structure, absorption et comportement chimique dans la serie du phenanthrene. *Bull. Soc. Chim. Fr.* *15*, 1215–1224.

37. Kudchadker, S.A., Kudchadker, A.P., and Zwolinski, B.J. (1979). Chemical thermodynamic properties of anthracene and phenanthrene. *J. Chem. Thermodyn.* *11*, 1051–1059. 10.1016/0021-9614(79)90135-6.
38. Hancock, R.D., and Nikolayenko, I.V. (2012). Do nonbonded H--H interactions in phenanthrene stabilize it relative to anthracene? A possible resolution to this question and its implications for ligands such as 2,2'-bipyridyl. *J. Phys. Chem. A* *116*, 8572–8583. 10.1021/jp300035w.
39. Badger, G.M., Jamieson, N.C., and Lewis, G.E. (1965). Photochemical reactions of azo compounds. IV. Further photochemical cyclodehydrogenations. *Aust. J. Chem.* *18*, 190–198. 10.1071/ch9650190.

Chapter 4. External H₂ Enhances the Tandem Upcycling of Polyethylene to Alkylbenzenes

4.1. Abstract

The catalytic conversion of polyethylene (PE) to value-added alkylbenzenes could motivate better plastic recovery, reduce leakage into the environment, and replace a petrochemical product with one made from recycled carbon. Different from hydrocracking, the process is not conducted under a high pressure of H₂, to allow the formation of aromatic. Indeed, the depolymerization can be performed without adding any external H₂, since it functions by redistributing PE-derived H₂. However, moderate external H₂ pressures (1-8 bar) significantly enhance the depolymerization rate and the alkylbenzene yield (maximum yield at 4 bar H₂). The rate of C-C bond scission is pseudo-zeroth-order in PE. It increases with external $P(\text{H}_2)$ at lower pressures (< 10 bar), then decreases at higher pressures. Modifying the traditional hydrocracking mechanism to include competitive adsorption of aromatics explains the $P(\text{H}_2)$ dependence of the rate. Dynamic control of the reactor atmosphere can further increase the alkylbenzene yield, especially in the desired molecular weight range for anionic surfactants.

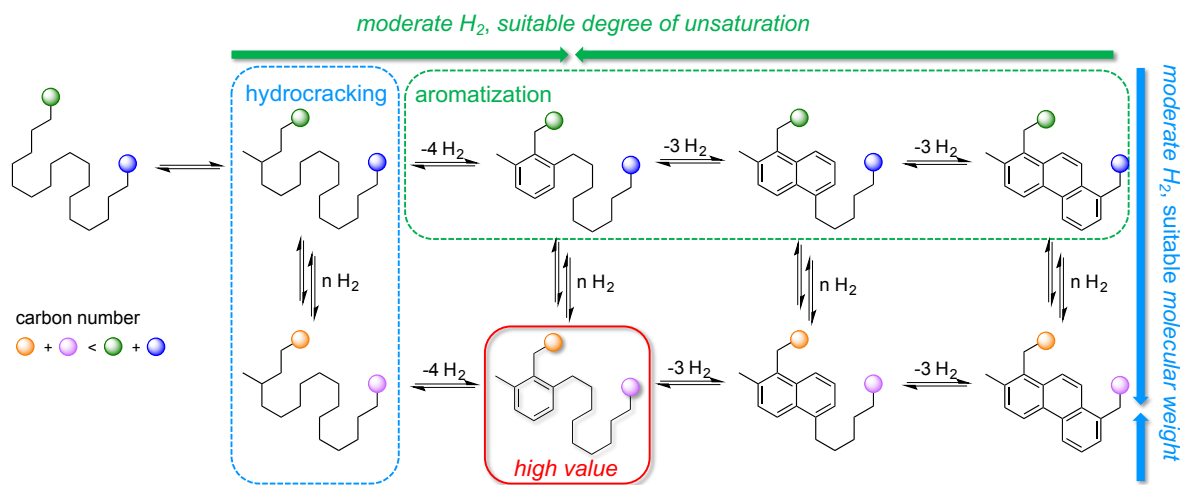
4.2. Introduction

Polyethylene (PE) represents approx. one-third by mass of global plastic production.¹ This commodity plastic is used worldwide for packaging, including bags, containers for liquids, and flexible films. Due to the short lifespan of these products, they generate a large amount of waste. For instance, in 2015, global PE waste represented 84% of total PE production.¹ In

the United States in 2015, only 7% of HDPE and 3% of LDPE were recycled, with the remainder ending up in landfills, being incinerated, or leaking into the natural environment.² The mismanagement of waste plastic is the origin of many current environmental and health concerns, including the impacts of micro- and nano-plastics released by abrasion and disintegration of microplastic pieces.³⁻⁵

Although mechanical recycling is the most energy efficient method for reducing plastic waste, for PE it is invariably accompanied by chain cross-linking which impacts .⁶ Alternatively, chemical (or molecular) recycling converts the plastic waste back into its constituent monomers which can be repolymerized, or other low molecular weight building block chemicals.⁷ If the latter are more valuable than the monomers, the process can be described as upcycling.⁸

One of the most studied PE upcycling reactions is hydrocracking (**Scheme 4.1**), which converts PE to alkanes which can serve as liquid fuels. The process is typically conducted at 250-300°C under a high H₂ pressure (>20 bar).⁹ A bifunctional metal/acid catalyst is required, where the metal catalyzes alkane (de)hydrogenation which the acid catalyzes olefin isomerization and C-C bond scission.¹⁰ However, techno-economic analysis predicts that PE hydrocracking is not viable, due to the low value of the resulting fuel.¹¹



Scheme 4.1. Scheme for polyethylene upcycling catalyzed by a bifunctional metal/acid catalyst, and the effect of H_2 on PE hydrocracking and aromatization.

Alternatively, PE can be upcycled to alkylbenzenes, which can be used as refrigeration fluids¹² or sulfonated to form anionic surfactants,¹³ by conducting the reaction in the absence of external H_2 .¹⁴ The formation of aromatics generates more than enough H_2 to accomplish C-C bond scission, **Scheme 4.1**. Enhancing the Brønsted acidity of the original Pt/ γ - Al_2O_3 catalyst increased the rates of C-C bond scission, alkane isomerization, and aromatization.¹⁵ Strong Brønsted acidity also promotes the formation of fused-ring polyaromatics,^{15,16} which are undesired products.¹⁷ They are also coke precursors, which lead to catalyst deactivation.

To suppress coke formation, the industrial production of BTX (benzene, toluene, and xylenes) from naphtha is conducted under external H_2 pressure (7-68 bar).¹⁸ The aromatics yield is a maximum at intermediate $P(H_2)$ values, since lower $P(H_2)$ favors aromatic formation but also promotes catalyst coking, while higher $P(H_2)$ suppresses both aromatic and coke formation.¹⁹ The choice of $P(H_2)$ will thus influence both the thermodynamics and kinetics of

PE conversion to alkylaromatics. In addition, $P(\text{H}_2)$ is expected to influence the rate of C-C bond scission in PE hydrocracking,^{20,21} which is important for achieving the desired molecular weight in the aromatic products. Consequently, we undertook a study of how $P(\text{H}_2)$ controls the rate and selectivity of alkylaromatic formation from PE, using a bifunctional (metal/acid) catalyst, Pt/SiO₂-Al₂O₃. This catalyst was chosen because of its high reactivity in aromatization and C-C bond scission due to its high acidity.^{15,16}

4.3. Results and Discussion

4.3.1. PE Depolymerization in the Absence of External H₂

Depolymerization was studied initially using a model PE (0.200 g, $M_w = 3.5 \times 10^3$ g mol⁻¹, $\bar{D} = 1.9$) and a strongly acidic catalyst, Pt/SiO₂-Al₂O₃ (0.100 g, 1.7 wt% Pt at 65% dispersion, 7.6 wt % Al, see **Section 4.7.2.2.2: Acidity Analysis**). The yield of light hydrocarbon gases (C₁₋₆) is very small (2 wt%). Prior to reaction, the PE is insoluble in CH₂Cl₂, but during 24 h reaction under Ar (i.e., in the absence of external H₂), most of the hydrocarbons (80 wt%, relative to the initial charge of PE) become soluble in CH₂Cl₂, **Table 4.1** and **Figure 4.1**. This change in solubility is consistent with a significant reduction in molecular weight.

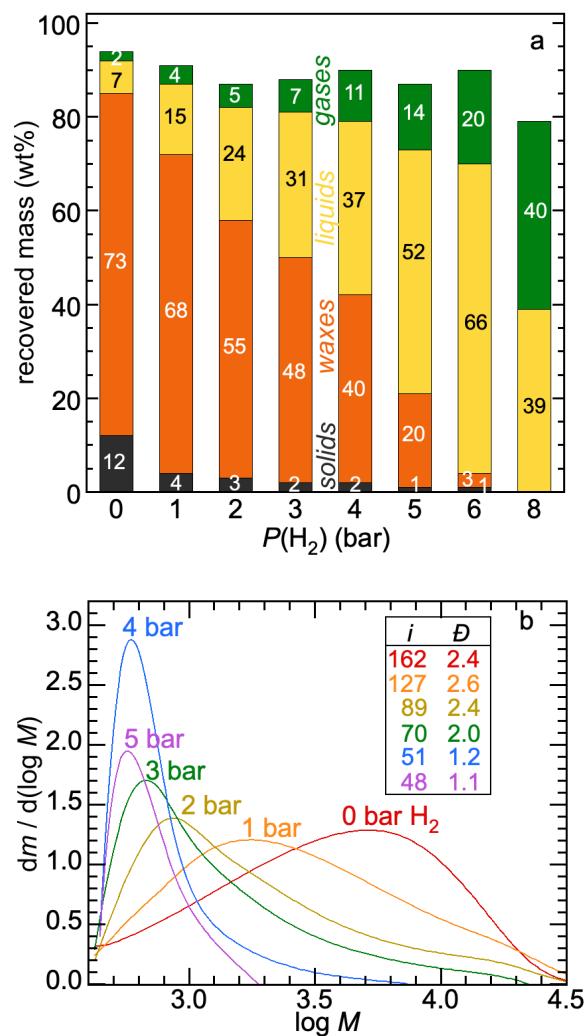
Table 4.1. Effect of $P(\text{H}_2)$ on the distribution of hydrocarbon products generated in catalytic PE depolymerization ^a

$P(\text{H}_2)$ ^b	Masses of hydrocarbon product types	Mass recovery ^c	$\bar{l}_{liq+wax}$ ^d	n_{c-c} scission ^e
(bar)	(wt%)	(wt%)		(mmol)

	Gas ^f	Liquid ^g	Wax ^h	Solid ⁱ			
0	2	7 (12)	73 (162)	12 (6)	94	78	0.15
1.0	4	15 (13)	68 (127)	4 (1)	91	50	0.31
2.0	5	24 (15)	55 (90)	3 (1)	88	35	0.47
3.0	7	31 (14)	48 (70)	2 (1)	88	28	0.61
4.0	11	37 (12)	40 (51)	2 (1)	90	21	0.88
5.0	14	52 (12)	20 (48)	1 (0)	87	15	1.1
6.0	20	66 (11)	3 (31)	1 (0)	90	13	1.4
8.0	40	39 (10)	0	0	79	10	2.1
0 ^j	3	7 (14)	50 (126)	32 (13)	92	64	0.19
4.0 ^j	6	47 (13)	27 (59)	3 (1)	83	18	0.88

^a Reaction conditions: PE (0.200 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$), Pt/SiO₂-Al₂O₃ (0.100 g, 1.7 wt% Pt), magnetically stirred 10 mL Parr reactor, 275 °C, 24 h, except as noted below. The significant numbers indicate the reproducibility, an example of repeat experiment is shown in **Table A4.1**. ^b Measured at room temperature at the start of the experiment. ^c Sum of masses for recovered gas, liquid, wax and solid hydrocarbons. ^d Average carbon number for combined liquid and wax fractions, measured by GC-FID and GPC, respectively, and estimated as $M_n/14$. ^e Number of C-C bond scission events in 24 h, calculated as $N(24)-N(0)$, where $N(24)$ and $N(t)$ represent the total numbers of hydrocarbon chains present initially and after 24 h, respectively. The missing mass (corresponding to a mass balance below 100 %) was assumed to have the same molecular weight distribution as the recovered mass (**Section 4.7.2.5: Analysis of Carbon-Carbon Bond Scission**). ^f C₁-C₆, as measured by GC-FID. ^g C₇-C₃₀, as measured by GC-FID. The value in parentheses is the number-averaged carbon number. ^h C_{>30}, measured by GPC-RI and calibrated using PS standards. The value in

parentheses is the number-averaged carbon number, estimated as $M_n/14$, where M_n was calculated using **eq A4.2**. ⁱ Measured by TGA, except where noted. The value in parentheses is the relative amount of unreacted PE, considered to be the carbon that is fully oxidized in air below 350 °C. ^j A higher molecular weight PE (0.200 g, $M_w = 2.6 \times 10^4$ g mol⁻¹, $\bar{D} = 3.9$) was used in this experiment.



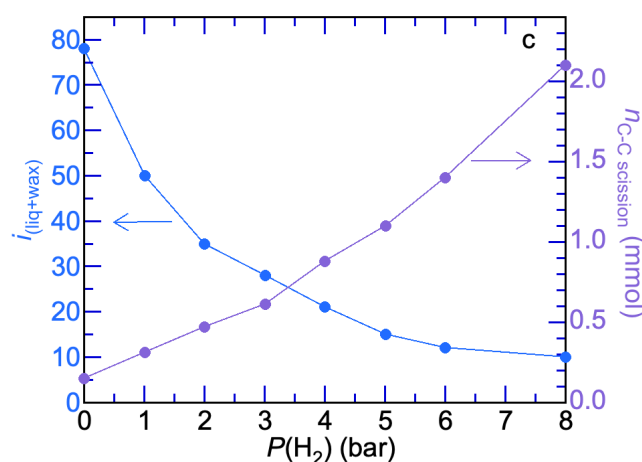
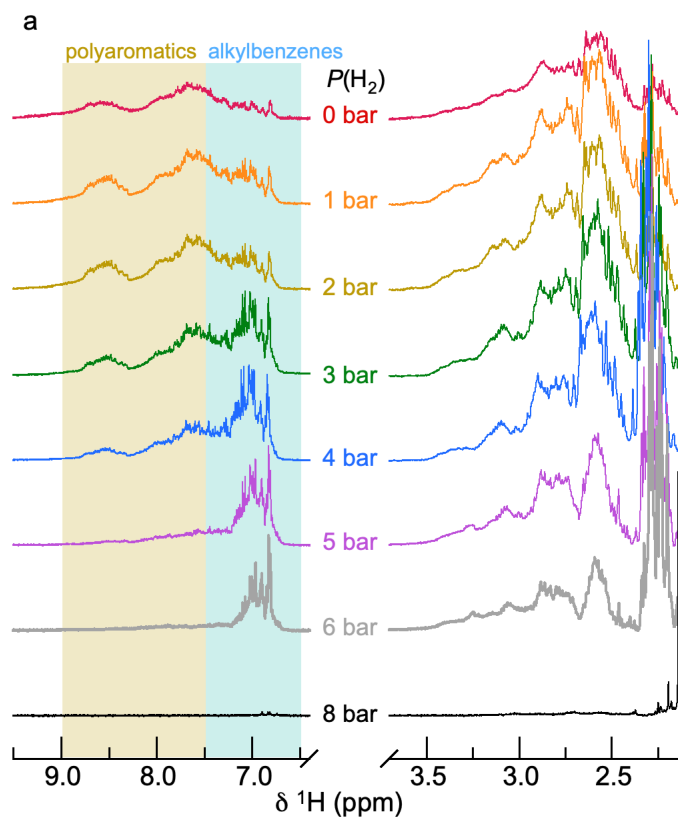


Figure 4.1. Effect of external $P(\text{H}_2)$ on (a) the mass fractions of various hydrocarbon types (green, gases (C_{1-6}); yellow, liquids (C_{7-30}) soluble in CH_2Cl_2 ; orange, waxes ($\text{C}_{>30}$) soluble in CH_2Cl_2 ; black, organic residues insoluble in CH_2Cl_2), (b) molecular weight distributions for the wax products, measured by GPC-RI (note that waxes are only formed in appreciable amounts for $P(\text{H}_2) < 6$ bar), and (c) the average carbon number in the combined liquid + wax fractions, and the total number of C-C bond scission events. Batch reaction conditions: 0.200 g PE ($M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$), Pt/SiO₂-Al₂O₃ (0.100 g), 275 °C, 24 h.

The brown color of the liquid indicates aromatic formation, including fused-ring aromatics that absorb in the visible.^{22,23} *Iso*-alkanes are the major paraffinic products in the liquid phase (**Figure A4.3**), consistent with C-C bond scission by an acid-catalyzed carbenium ion mechanism.¹⁰ In addition, the reactor headspace contains 1.2 bar H₂ (0.5 mmol, compared to 7.1 mmol ethylene monomer content in the PE, see **Section 4.7.2.6: Analysis of H₂ Balance**, and **Table A4.5**). Based on the aromatic yield (**Table 4.2**), the amount of H₂ formed by aromatization is 0.5 mmol. Therefore depolymerization proceeds via tandem

hydrocracking/aromatization, with 30 % of the H_2 generated by aromatization being consumed by C-C bond scission reactions.²⁴

In the 1H NMR spectrum of the combined liquid and wax products (**Figure 4.2a**), signals from 6.5 to 7.4 ppm are assigned to alkylbenzenes (H_{benz}), while signals from 7.4 to 9.0 ppm are assigned to polyaromatics (H_{poly}), where $H_{\text{arom}} = H_{\text{benz}} + H_{\text{poly}}$. The 1H NMR-derived ratio $H_{\text{benz}}/H_{\text{arom}}$ is 0.31. The molar selectivity for alkylbenzenes relative to all alkylaromatics (include alkylnaphthalenes and alkylphenanthrenes) is therefore moderate. It resembles that reported for H_2 -free PE depolymerization catalyzed by metal-free $SiO_2-Al_2O_3$ at 280°C for 24 h,¹⁶ consistent with high catalyst acidity promoting polyaromatic formation.²⁵



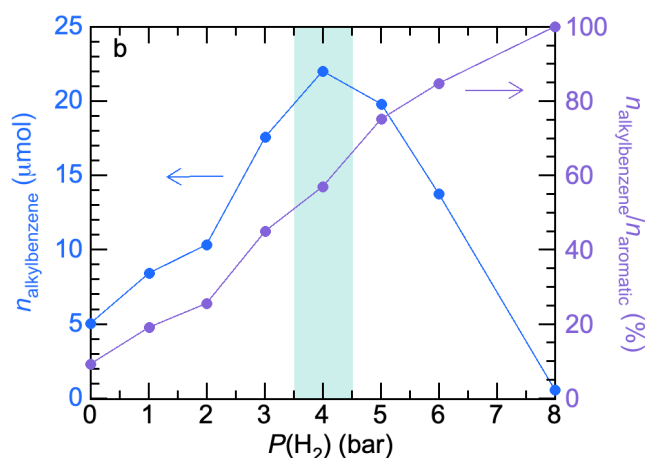


Figure 4.2. Effect of external $P(\text{H}_2)$ on (a) ^1H NMR spectra, recorded in CD_2Cl_2 , of the combined liquid/wax products recovered from the catalytic conversion of PE, and (b) the molar yield of alkylbenzenes and the alkylbenzene selectivity relative to all aromatics. Batch reaction conditions: 0.200 g PE ($M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$), Pt/SiO₂-Al₂O₃ (0.100 g), 275 °C, 24 h.

4.3.2. Effect of External H₂ on PE Chain Scission

When PE depolymerization was conducted under 8 bar external $P(\text{H}_2)$ (corresponding to 3.2 mmol H₂, **Table A4.5**), the CH₂Cl₂-soluble products were colorless and formed in a smaller amount (39 wt%). Instead, the reaction generated a large amount of light hydrocarbon gases (40 wt%), amounting to nearly 14× more C-C bond scission events in the same reaction time. Over half of the external H₂ was consumed, leaving 1.4 mmol H₂ present at the end of the reaction. This result suggests that PE hydrocracking to saturated alkanes becomes the dominant reaction when enough H₂ is present.

To probe the influence of H₂ pressure on C-C bond scission and alkane aromatization, reactions were also conducted with external $P(\text{H}_2)$ values from 1-7 bar. As $P(\text{H}_2)$ increased, the total number of C-C bond scission events increased, the average carbon number in the hydrocarbon products decreased, and the major product type shifted from waxes to liquids, then to gases. The overall average carbon number for the combined liquid and wax products ($\bar{n}_{\text{liq}+\text{wax}}$) decreased gradually (**Figure 4.1c**), suggesting random chain scission instead of end-of-chain scission.^{10,26,27} Regardless of whether the depolymerization is conducted with or without H₂, little CH₄ was formed (<3 wt% of total gas).

4.3.3. Effect of External H₂ on PE Aromatization

Moderate external $P(\text{H}_2)$ significantly improves the selectivity for alkylbenzenes relative to polyaromatics, according to **Figure 4.2a** and **Table A4.2**. GC-MS analysis also confirmed that the characteristic ions of the aromatic products shift from polyaromatic to alkylbenzene as $P(\text{H}_2)$ increases, **Figure A4.10b**. Thus the alkylbenzene selectivity increases from 10 to 100 mol% as $P(\text{H}_2)$ increases from 0 to 8 bar, **Figure 4.2b**. Further quantitative analysis by GC-FID and ¹H NMR (see **Section 4.7.2.4.2: Analysis on Selectivity and Yield of Aromatics**) showed that the alkylbenzene yield increases with $P(\text{H}_2)$ from 0 to ca. 4 bar, then decreases as $P(\text{H}_2)$ increases further (**Figure 4.2b** and **Table 4.2**). At ca. 4 bar, the alkylbenzene yield is a maximum, at ca. 4× the yield obtained without external H₂. A maximum in the yield of alkyl-naphthalenes was observed at ca. 3 bar, but the yield of alkylphenanthrenes decreased monotonically with increasing $P(\text{H}_2)$, **Table 4.2**.

Table 4.2. Effect of $P(\text{H}_2)$ on the liquid/wax products of PE depolymerization ^a

$P(\text{H}_2)^b$	$P(\text{H}_2)^c$	n_{alk}^d	n_{benz}^d	n_{naph}^d	n_{phen}^d	n_{arom}^e	$n_{\text{arom rings}}^f$	$n_{\text{benz}}/n_{\text{arom}}^g$	$n_{\text{arom}}/n_{\text{total}}^h$
(bar)	(bar)	(μmol)	(μmol)	(μmol)	(μmol)	(μmol)	(μmol)	(%)	(%)
0	1.2	30	5	8	41	54	145	9	65
1.0	1.4	118	8	4	32	44	112	19	27
2.0	1.8	203	10	6	24	40	94	27	17
3.0	2.3	275	18	11	11	39	71	44	12
4.0	2.6	383	22	10	7	38	62	56	9
5.0	3.0	578	20	4	2	26	35	70	5
6.0	3.1	722	14	1	1	16	20	90	2
8.0	3.4	549	<1	0	0	<1	<1	100	<1
0 ⁱ	1.2	22	10	8	32	50	120	20	69
4.0 ⁱ	3.0	485	30	5	6	41	58	73	8

^a Reaction conditions: PE (0.200 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$), Pt/SiO₂-Al₂O₃ (0.100 g, 1.7 wt% Pt), 275 °C, 24 h, 10 mL, in a stirred Parr reactor. The reproducibility of the product distribution is reported in **Table A4.1** as an example. ^b H₂ pressure measured before the reaction at room temperature.

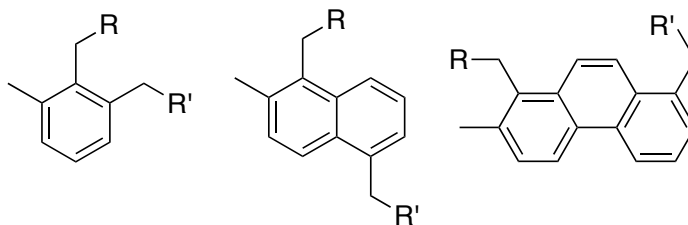
^c H₂ pressure measured after the reaction at room temperature, see **Section 4.7.2.6: Analysis of H₂**

Balance. ^d Yields of alkanes (n_{alk}), alkylbenzenes (n_{benz}), alkylnaphthalenes (n_{naph}), and alkylphenanthrenes (n_{phen}), estimated by combining the integrated ¹H NMR intensity and the GC-FID product distribution (**Section 4.7.2.4.2: Analysis on Selectivity and Yield of Aromatics**). ^e Total yield of alkylaromatics, calculated as $n_{\text{arom}} = n_{\text{benz}} + n_{\text{naph}} + n_{\text{phen}}$. ^f Yield of six-member aromatic rings, calculated as $n_{\text{arom rings}} = n_{\text{benz}} + 2n_{\text{naph}} + 3n_{\text{phen}}$. Here, each naphthalene and phenanthrene contains 2 and

3 aromatic rings, respectively. ^g Molar selectivity of alkylbenzene relative to total aromatics. ^h Molar selectivity of alkylaromatics relative to total hydrocarbons (n_{total}), where $n_{\text{total}} = n_{\text{alk}} + n_{\text{benz}} + n_{\text{naph}} + n_{\text{phen}}$. ⁱ A higher molecular weight PE (0.200 g, $M_w = 2.6 \times 10^4 \text{ g mol}^{-1}$, $\bar{D} = 3.9$) was used in this experiment.

GC-MS analysis further revealed that the yields of alkyltetralins and alkyldecalins (i.e., alkyltetrahydronaphthalenes and alkyldecahydronaphthalenes, respectively) increased initially with $P(\text{H}_2)$, then decreased (**Figure A4.10a**). These maxima could arise due to the conversion of alkanes to alkylbenzenes becoming thermodynamically more favored relative to polyaromatics as $P(\text{H}_2)$ increases, and when $P(\text{H}_2)$ become even higher, the formation of alkylbenzenes also become unfavorable (**Figure A4.16**). The thermodynamic yields of alkylbenzenes and alkyltetralins are predicted to increase with $P(\text{H}_2)$ then decrease (See **Section 4.7.2.9: Thermodynamic Assessment** and **Figure A4.17**), a trend that is consistent with the experimental observation.

The aromatic substitution pattern for the products of H_2 -free depolymerization catalyzed by acidic Pt/F- Al_2O_3 are primarily a mixture of methyl and longer alkyl chains unbranched at C_α , indicated by ^1H NMR signals at 2.0-2.5 ppm ($\text{C}_\alpha\text{H}_3$) and 2.5-3.1 ppm ($\text{C}_\alpha\text{H}_2$).¹⁵ The alkyl substituents on the aromatic rings. As $P(\text{H}_2)$ increased from 0 to 6 bar, the fraction of methyl substituents on the aromatic rings increased from 20 to 46 %, while the fraction of longer alkyl substituents decreased from 70 to 37 %, potentially due to more C-C bond scission at higher $P(\text{H}_2)$ (see **Section 4.7.2.4.1: Analysis of Alkyl Substituents of Aromatics**). On average, the aromatic products are dialkylmethyl-substituted (**Scheme 4.2** and **Table A4.3**).



Scheme 4.2. Proposed structures for PE-derived dialkylmethylbenzenes, -naphthalenes, -and phenanthrenes.

The molecular weight distribution of the aromatic products was analyzed by GPC with UV detection. When the reaction is conducted without external H_2 , the distribution is bimodal after 24 h at 275 °C (**Figure A4.8a**). Most aromatics are present in the liquid phase (C_7 - C_{30} , 71 % peak area) with a smaller fraction in the wax ($C_{>30}$, 29 % peak area). With external $P(H_2) \geq 2$ bar, the UV absorption of the wax decreased further (**Figure A4.8b**), such that aromatic products are present only in the liquid phase, which could be due to more C-C scission with higher $P(\text{initial } H_2)$. The overall average carbon number of the aromatics was ca. C_{15} without the addition of external H_2 , decreasing to C_{10} as $P(H_2)$ increased to 6 bar (**Figure A4.11**). In contrast, the overall average carbon number decreased much more, from C_{77} to C_{12} , as external $P(H_2)$ increased from 0 to 6 bar. This result suggests much faster C-C bond scission rate for the alkylaromatics relative to alkanes with the same carbon number, and faster chain scission for longer alkyl chains.²⁸ GC-MS further reveals that aromatics are distributed similarly to alkanes in the liquid fraction, **Figure A4.9**. Therefore, the average carbon number of the aromatic fractions is the same as the average for all liquid hydrocarbons.

4.3.4. Behavior of a Higher Molecular Weight PE

Depolymerization of a higher molecular weight PE ($M_w = 2.6 \times 10^4 \text{ g mol}^{-1}$, $D = 3.9$, closer to closer commercial grade PE) was tested with Pt/SiO₂-Al₂O₃ at 280 °C for 24 h. Similar to the behavior of the model low molecular weight PE, more C-C bond scission occurs under 4 bar H₂ compared to 2 bar Ar, **Table 4.1**. In addition, the alkylbenzene yield under 4 bar H₂ is three times higher than under Ar (30 vs. 10 μmol), **Table 4.2**.

4.3.5. Kinetics of Aromatization

To understand how $P(\text{H}_2)$ influences the yield and molecular weight distribution of alkylbenzenes, the kinetics of C-C bond scission and aromatization were studied. Because H₂ is generated and consumed at different rates, $P(\text{H}_2)$ varies over the course of a depolymerization reaction (**Table 4.2** and **Figure A4.15a**). To obtain kinetic information at pseudo-constant $P(\text{H}_2)$, the reactor was refilled periodically with H₂ (or simply evacuated, in the case of the experiment starting with no H₂), **Figure A4.15b**. $P(\text{H}_2)$ was measured prior to each refill, and the average value (initial and final values prior to refill) are reported. The yield of aromatic rings (defined as $n_{\text{arom}} = n_{\text{benz}} + 2 n_{\text{naph}} + 3 n_{\text{phen}}$) was also evaluated prior to each H₂ refill, using a combination of ¹H NMR and GC-FID.

For each average $P(\text{H}_2)$ value from 0.2 to 7.3 bar, the aromatic yield rises to a plateau within the first 4 h (**Figure 4.3a** and **Table A4.6**). No aromatics were detected with 16 or 24 bar H₂, **Table A4.6**. The location of the plateau decreases as $P(\text{H}_2)$ increases, consistent with the expected thermodynamic trend which disfavors aromatics at the reaction temperature

when H_2 is present. Thus the total aromatic yield is ca. $6\times$ lower under ca. 4 bar H_2 , relative to the experiment with 0.2 bar H_2 . When present in measurable quantities, aromatics are mostly in the liquid fraction, and their average carbon number decreased slightly at longer reaction times according to GPC-UV (shown for 2 bar H_2 in **Figure A4.12**).

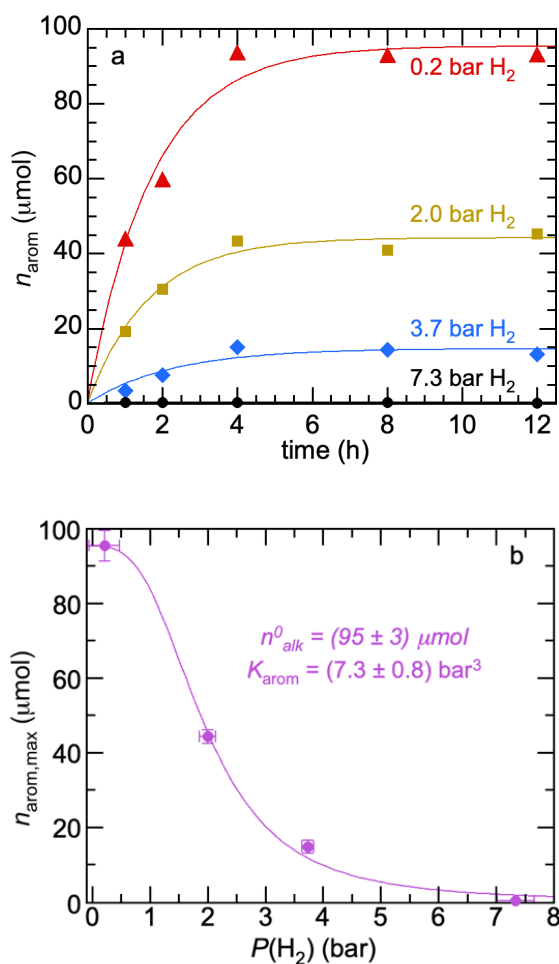
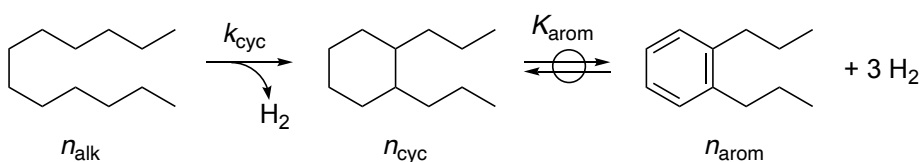


Figure 4.3. Effect of average reactor $P(H_2)$ on (a) the total yield of aromatic rings, defined as $n_{\text{arom}} = n_{\text{benz}} + 2 n_{\text{naph}} + 3 n_{\text{phen}}$, as a function of reaction time (lines represent non-linear least-squares curvefits of **eq 4.1**), and (b) the maximum yield of aromatic rings (line represents non-linear least-squares curvefit of **eq 4.2**; abscissa and ordinate error bars represent the variation

in $P(\text{H}_2)$ over the course of each experiment, and the standard deviation of $n_{\text{arom,max}}$ obtained from the curvefits in part a, respectively). Batch reaction conditions: 0.200 g PE ($M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$), Pt/SiO₂-Al₂O₃ (0.100 g), 275 °C. In part (a), the reactor was evacuated and refilled with the appropriate amount of H₂ after each measurement; for the lowest $P(\text{H}_2)$ reported, the reactor was simply evacuated after each measurement.

To describe these kinetic profiles quantitatively, we adapted the accepted alkane aromatization mechanism for naphtha catalytic reforming.¹⁸ In this mechanism, dehydrocyclization is considered irreversible and rate-determining, and subsequent cycloalkane aromatization is quasi-equilibrated (**Scheme 4.3**). The resulting expressions for the time evolution of aromatic rings and their maximum yield are given by **eq 4.1-4.2** (for derivations, see the **Section 4.7.2.7: Simplified Microkinetic Model for Aromatization**).



Scheme 4.3. Simplified alkane aromatization mechanism, where k_{cyc} is the apparent rate constant for rate-determining alkane dehydrocyclization, and K_{arom} is the equilibrium constant for cycloalkane aromatization.

$$n_{\text{arom}} = n_{\text{arom,max}}(1 - e^{-k_{\text{cyc}}t}) \quad (4.1)$$

$$n_{\text{arom,max}} = K_{\text{arom}}n_{\text{alk}}^0/(K_{\text{arom}} + P_{\text{H}_2}^3) \quad (4.2)$$

Based on the curvefits of **eq 4.1** shown in **Figure 4.3a**, the weighted mean value of k_{cyc} is $(0.57 \pm 0.10) \text{ h}^{-1}$ (note that k_{cyc} is not an elementary rate constant; its numerical value presumably includes the number of acid sites). Consistent with the assumption that dehydrocyclization is irreversible, k_{cyc} is independent of average $P(\text{H}_2)$ for values from 0.2 to 3.7 bar. From the curvefit of **eq 4.2** in **Figure 4.3b**, the value of K_{arom} is $(7.3 \pm 0.8) \text{ bar}^3$ at 275 °C. This value is the same order of magnitude as a value reported for the equilibrium between 1,2-dimethylcyclohexane and *o*-xylene, 32 bar³ at 300 °C.²⁹ It will be used in the next section to describe the accelerating effect of $P(\text{H}_2)$ on the rate of C-C bond scission, for low-to-moderate values of $P(\text{H}_2)$. At very low $P(\text{H}_2)$, $n_{\text{arom,max}}$ tends to n_{alk}^0 . This condition appears to be met at the lowest average $P(\text{H}_2)$ value in our experiments, 0.2 bar, with $n_{\text{arom,max}} = n_{\text{alk}}^0 = (95 \pm 3) \mu\text{mol}$. It agrees remarkably well with the estimated number of PE chains, $m_{\text{PE}}/M_{\text{n}} = 0.200 \text{ g} / 1850 \text{ g}\cdot\text{mol}^{-1} = 108 \mu\text{mol}$, further validating the simple mechanistic model in **Scheme 4.3**.

4.3.6. Kinetics of C-C Bond Scission

In the same series of experiments, the number of C-C bond scission events ($n_{\text{C-C scission}}$) was measured as a function of reaction time. For each average value of $P(\text{H}_2)$, $n_{\text{C-C scission}}$ increases linearly with time, **Figure 4.4a** and **Table A4.6**. This result indicates that the reaction is pseudo-zeroth-order with respect to the number of C-C bonds. Since the initial charge of PE, 0.200 g, contains 14 mmol C-C bonds, and <10% are cleaved during the reaction

(according to **Figure 4.4a**), their number is both large and relatively constant, consistent with the pseudo-zeroth-order behavior. For a given $P(\text{H}_2)$, the rate ($r_{\text{C-C scission}}$) is the slope of a plot of $n_{\text{C-C scission}}$ vs. time. The value of $r_{\text{C-C scission}}$ clearly increases with $P(\text{H}_2)$, up to 7.3 bar.

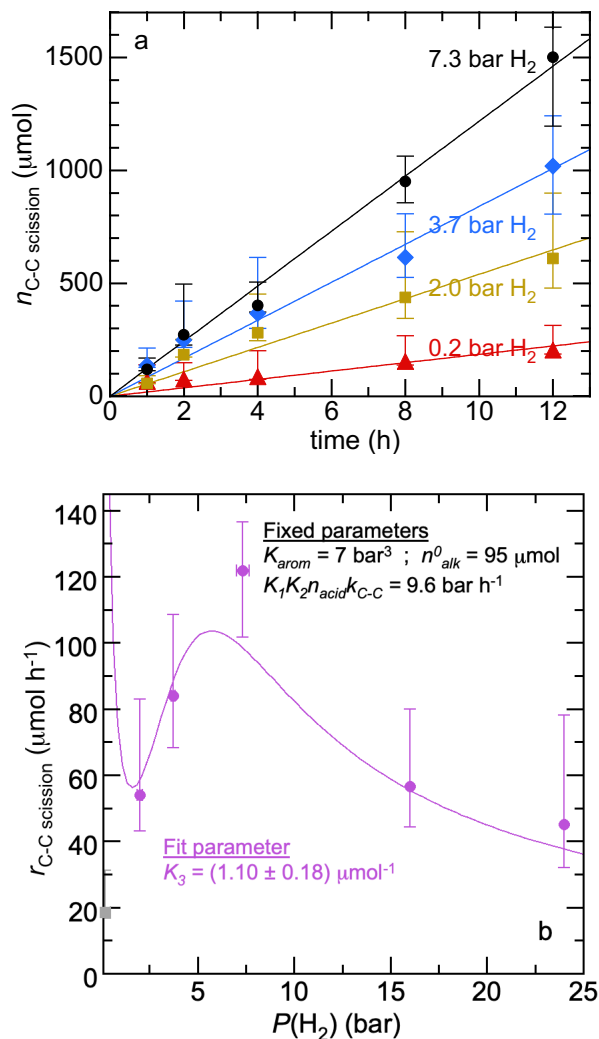


Figure 4.4. Effect of $P(\text{H}_2)$ on (a) the number of C-C bond scissions with time (lines are linear curvefits; ordinate error bars represent lower and upper bounds for $n_{\text{C-C scission}}$, due to the incomplete collection of mass), and (b) variation of the rate of C-C bond scission for all values

of $P(\text{H}_2)$, showing curvefit of **eq 4.6** (excluding the grey data point at $P(\text{H}_2) = 0.2$ bar; ordinate error bars arise from the linear fits to the lower and upper bounds for $n_{\text{C-C scission}}$ as a function of time. Batch reaction conditions: 0.200 g PE ($M_w = 3.5 \times 10^3$ g mol⁻¹, $D = 1.9$), Pt/SiO₂-Al₂O₃ (0.100 g), 275 °C. In part (a), the reactor was evacuated and refilled with the appropriate amount of H₂ after each measurement; for the lowest $P(\text{H}_2)$ reported, the reactor was simply evacuated after each measurement.

When $P(\text{H}_2)$ increases even further, the rate of C-C bond scission decreases (**Figure 4.4b** and **Table A4.9**), as suggested by other studies of PE hydrocracking.^{20,30} This change is expected based on the accepted mechanism of bifunctional hydrocracking for small alkanes, in which quasi-equilibrated alkane dehydrogenation catalyzed by metal sites is followed by rate-determining C-C bond cleavage catalyzed by Brønsted acid sites.³¹ The rate of C-C bond cleavage therefore depends on the equilibrium yield of olefin, which decreases as $P(\text{H}_2)$ increases, **eq 4.3**.

$$r_{\text{C-C scission}} = K_1 K_2 k_{\text{C-C}} n_{\text{acid}} n_{\text{alk}}^0 / (K_1 K_2 n_{\text{alk}}^0 + P_{\text{H}_2}) \quad (4.3)$$

where K_1 is the equilibrium constant for alkane dehydrogenation, K_2 is the equilibrium constant for olefin protonation, n_{acid} is the number of strong Brønsted acid sites, n_{alk}^0 is the initial number of alkane chains, and $k_{\text{C-C}}$ is the rate constant for C-C scission (for derivation, see the **Section 4.7.2.8: Microkinetic Model for C-C Bond Scission**). The denominator simplifies for large values of $P(\text{H}_2)$, giving **eq 4.4**.

$$r_{C-C \text{ scission}} \approx K_1 K_2 k_{C-C} n_{acid} n_{alk}^0 / P_{H_2} \quad (4.4)$$

Because few aromatics are formed for values of $P(H_2) \geq 7.3$ bar, the dominant reaction under these conditions is hydrocracking. Fitting **eq 4.4** to the dependence of the three values of $r_{C-C \text{ scission}}$ on $P(H_2)$ at $P(H_2) > 7$ bar, while fixing the value of n_{acid} at its known value of 4 μmol and n_{alk}^0 at 95 μmol (see the previous section), gives the product $K_1 K_2 k_{C-C} = (2.39 \pm 0.09) \text{ bar} \cdot \mu\text{mol}^{-1} \cdot \text{h}^{-1}$ as the sole fit parameter, **Figure A4.18**.

Eq 4.3 clearly does not describe the observed dependence of $r_{C-C \text{ scission}}$ on $P(H_2)$ for relatively low H_2 pressures. To explain the non-monotonic behavior, we postulate the formation of aromatics at low $P(H_2)$ poisons acid sites where aromatics adsorb more strongly than olefins.³³ The modified rate equation in **eq 4.5** accounts for this effect, by including K_3 as an equilibrium constant for aromatic adsorption onto the acid sites.

$$r_{C-C \text{ scission}} = K_1 K_2 k_{C-C} n_{acid} n_{alk}^0 / [P_{H_2} (1 + K_3 n_{arom})] \quad (4.5)$$

Finally, since according to **Figure 4.3a** the yield of aromatics stabilizes at a plateau early in the course of the reaction relative to PE chain cleavage, the expression for $n_{arom, \text{max}}$ in **eq 4.2** replaces n_{arom} , giving the final form of the kinetic equation shown in **eq 4.6**:

$$r_{C-C \text{ scission}} = K_1 K_2 k_{C-C} n_{acid} n_{alk}^0 / [P_{H_2} (1 + K_3 K_{arom} n_{alk}^0 / (K_{arom} + P_{H_2}^3))] \quad (4.6)$$

Values for n_{acid} , n_{alk}^0 , K_{arom} , and the product $K_1K_2k_{\text{C-C}}$ are already known from the analyses described above. Consequently, **eq 4.6** requires a single fit parameter: K_3 . The curvefit is shown in **Figure 4.4b**. The predicted trend matches the non-monotonic experimental behavior for $2 \text{ bar} \leq P(\text{H}_2) \leq 24 \text{ bar}$ with a fitted value of $K_3 = 1.1 \times 10^6 \text{ mol}^{-1}$. **Eq 4.6** becomes indeterminate when $P(\text{H}_2)$ becomes very small, justifying the exclusion of the $r_{\text{C-C scission}}$ value measured without added H_2 (average $P(\text{H}_2) = 0.2 \text{ bar}$) from the fit.

To probe the hypothesis that aromatics, especially polyaromatics, adsorb strongly and poison acid sites,³² phenanthrene was intentionally introduced into the reactor with PE and catalyst at the beginning of a depolymerization experiment conducted under 4 bar H_2 . The addition of 11 μmol phenanthrene (3 equivalent of n_{acid}) led to a 25% reduction in the number of C-C bond scissions after 12 h, **Table A4.6**. No phenanthrene was detected in the depolymerization products, likely due to its hydrogenation and/or hydrocracking. Increasing the amount of phenanthrene to 110 μmol completely shut down C-C bond scission, and 5 μmol phenanthrene, as well as its hydrogenated forms (10 μmol), remained in the PE depolymerization products, **Figures A4.19-A4.20**. These results indicate that the catalyst $\text{Pt/SiO}_2\text{-Al}_2\text{O}_3$ tolerates only small amounts of polyaromatics and becomes deactivated when they are formed in appreciable amounts.

4.3.7. Optimizing Reactor H_2 to Maximize Alkylbenzene Production

The results above show that moderate H_2 pressure (e.g., 8 bar) is effective in rapidly decreasing the PE molecular weight, but completely suppresses the aromatic yield, while the absence of external H_2 results in a slower depolymerization which maximizes the aromatic

yield but at the expense of alkylbenzene selectivity. Some of the tradeoffs inherent in choosing a single reactor atmosphere may be overcome by varying the headspace gas over the course of a single experiment. For example, the average hydrocarbon molecular weight (and viscosity) would decrease rapidly if the reaction were initiated under moderate $P(\text{H}_2)$, then the aromatic yield could be maximized by removing the H_2 from the reactor atmosphere. Alternatively, a high rate of aromatization could be achieved by starting the reaction under Ar, then introducing moderate $P(\text{H}_2)$ to convert polyaromatics and higher molecular weight alkylbenzenes to the desired surfactant-range alkylbenzenes.

The potential for dynamic control of the reactor atmosphere was explored in a series of preliminary experiments involving depolymerization of a model PE catalyzed by Pt/SiO₂-Al₂O₃ at 275 °C for two consecutive 4 h periods. After the first 4 h period, conducted starting under either 2 bar Ar or 8 bar H₂, the reactor was cooled to room temperature and gases were removed from the reactor headspace for analysis by GC-FID. Next, the same reactor was charged with either 2 bar Ar or 8 bar H₂ for a second 4 h period under the same reaction conditions. When both 4-h reaction stages were conducted under Ar, the average carbon number in the liquid/wax hydrocarbon products was high ($\bar{\tau} = 60$) and the yield of alkylbenzenes, 12 μmol , was low, representing only 29 mol% of the aromatics produced (**Table 4.3**). As expected, when both 4-h reaction stages were conducted under 8 bar H₂, the average carbon number in the liquid/wax hydrocarbon products was much lower ($\bar{\tau} = 21$) but the yield of alkylbenzenes was negligible.

Table 4.3. Effect of changing the reactor headspace gas during PE depolymerization

Reaction conditions ^a		$n_{\text{C-C scission}}^{\text{c}}$	$\bar{t}^{\text{d}}$	$n_{\text{benz}}^{\text{e}}$	$n_{\text{benz}}/n_{\text{arom}}^{\text{e}}$	$n_{\text{arom}}/n_{\text{total}}$
First stage ^b	Second stage ^b	(μmol)		(μmol)	(mol%)	(mol%)
Ar (2 bar)	Ar (2 bar)	150	60	12	29	53
H ₂ (8 bar)	H ₂ (8 bar)	942	21	<1	-	<1
Ar (8 bar)	H ₂ (8 bar)	216	39	25	69	21
H ₂ (8 bar)	Ar (2 bar)	530	28	28	49	19

^a Reaction conditions: PE (0.200 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$), Pt/SiO₂-Al₂O₃ (0.100 g, 1.7 wt% Pt), 275 °C, 10 mL, stirred Parr reactor. ^b Pressure measured at room temperature. The duration of each reaction stage was 4 h. ^c Total number of C-C bond scission events, calculated as $N(t)-N(0)$, where $N(0)$ and $N(t)$ represent the total number of chains present at time 0 and time t , respectively. Any missing mass was assumed to have the same distribution as the recovered mass (see **Section 4.7.2.5 Analysis of Carbon-Carbon Bond Scission**). ^d Average carbon number in the combined liquid and wax products. ^e Estimated from ¹H NMR peak areas and the average carbon number.

Conducting the first reaction stage under Ar, followed by a second stage under 8 bar H₂, yielded liquid/wax with an intermediate average carbon number of 39, consistent with the shorter time in the fast hydrogenolysis conditions. However, the yield of alkylbenzenes, 25 μmol , doubled relative to the yield under Ar alone. An even better result was obtained when the first reaction stage was conducted under 8 bar H₂, followed by a second stage under Ar. For this experiment, the average carbon number was lower (28) and the alkylbenzene yield was even higher (28 μmol). Presumably the initial reduction in molecular weight under H₂

without polyaromatic formation reduces catalyst poisoning while accelerating the subsequent aromatization of the lower molecular weight alkanes.

The effectiveness of this strategy for alkylbenzene production was tested with a higher PE: catalyst ratio (0.400 g PE, 0.100 g Pt/SiO₂-Al₂O₃) in a larger-volume reactor (100 mL) at 280 °C. The reaction was conducted initially under 4 bar H₂ for 4 h, followed by 4 h under 2 bar Ar. The experiment yielded 91 μmol alkylbenzenes with an average carbon number C₁₇, representing an alkylbenzene selectivity of 56 mol% relative to all aromatics. For comparison, the reaction of the same PE (0.200 g) catalyzed by Pt/F-Al₂O₃ (0.200 g, 1.6 wt% Pt) under 2 bar Ar for 8 h was reported to give 45 μmol alkylbenzenes with an average carbon number of C₂₃, representing a lower selectivity for alkylbenzenes of 34 mol% relative to all aromatics.¹⁵ The average rate of alkylbenzene formation for the process catalyzed by Pt/SiO₂-Al₂O₃, 114 μmol h⁻¹ (g_{catalyst})⁻¹, is four times higher than that of Pt/F-Al₂O₃, 28 μmol h⁻¹ (g_{catalyst})⁻¹.

4.4. Conclusion

$P(\text{H}_2)$ is a critical parameter in the bifunctional catalytic depolymerization of polyethylene to alkylaromatics. H₂ is required for C-C bond scission, reducing the molecular weight of hydrocarbons through hydrocracking, while also affecting the selectivity to alkylbenzenes relative to polyaromatics. Consistent with thermodynamic predictions, the highest yields of alkylbenzenes are obtained at moderate $P(\text{H}_2)$ values, 3-5 bar, while the highest selectivities for alkylbenzenes relative to polyaromatics requires 6-7 bar $P(\text{H}_2)$.

This study also provides insight into the kinetics of C-C bond scission and aromatization. The rate of C-C bond scission is pseudo-zeroth-order with respect to the number of alkane chains. The order with respect to H_2 is positive at low pressures and negative at high pressure. The non-monotonic behavior is consistent with a traditional hydrocracking mechanism combined with competitive adsorption of aromatics. The formation of aromatics is pseudo-first-order and the total aromatic yield decreases with increasing $P(H_2)$, as expected. The formation of polyaromatics at low $P(H_2)$ deactivates the catalyst. These findings can potentially guide catalyst design and the optimization of reaction conditions for selective conversion of polyethylene to surfactant-range alkylaromatics.

4.5. Simplified Experimental Procedures

4.5.1. Catalyst Synthesis

$SiO_2-Al_2O_3$ (1.50 g) was calcined in air in a temperature-controlled muffle furnace at 500 °C for 4 h, then dehydrated at ca. 10^{-2} Torr and 400 °C for 8 h. Pt/ $SiO_2-Al_2O_3$ was prepared by chemical vapor deposition of $CpPtMe_3$ (42 mg) onto dehydrated $SiO_2-Al_2O_3$ (1.5 g), followed by heating in flowing H_2 (5.0 vol% in Ar) to 280 °C at 2 °C min^{-1} , then holding for 2 h.

4.5.2. Polyethylene Depolymerization

PE and a H_2 -reduced Pt/SA catalyst were loaded into a stainless steel autoclave (10 or 100 mL) inside an Ar-filled glove-box. The reactor was sealed and removed from glovebox, which was then connected onto the vacuum line to remove initial gas. The reactor was then filled with target pressure of desired gas, and was placed onto heating system. The contents were

magnetically stirred at $(275 \pm 5)^{\circ}\text{C}$ for the desired reaction time, then the reaction was quenched under a jet of flowing air.

PE, catalyst, and a magnetic stir bar were loaded into a stainless steel autoclave inside an Ar-filled glove-box. The reactor was sealed and removed from glovebox, then evacuated, back-filled with the desired pressure of gas, and placed onto heating system. The contents were stirred at $(275 \pm 5)^{\circ}\text{C}$ for the desired reaction time, then the reaction was quenched by cooling the reactor with a jet of compressed air.

For reactions at pseudo-constant $P(\text{H}_2)$, the reaction was conducted as described above for 4 h, then the reaction was quenched and the gas products were analyzed. The reactor was then evacuated, repressurized with the same initial pressure of H_2 , and heated for a further 4 h. The procedure was repeated twice more, then gas, liquid, wax, and insoluble hydrocarbon products were analyzed as described below. The amounts of gases formed in each step were combined to give the total gas products.

4.5.3. Depolymerization Products Analysis

Volatile hydrocarbon products sampled from the reactor headspace via gas-tight syringe were characterized by GC-FID, using propene added as an internal standard. Liquid and wax products were extracted from the reactor using CD_2Cl_2 (3 mL). An aliquot of the supernatant (1 mL) was analyzed by ^1H NMR. The suspension, consisting of dissolved hydrocarbons and insoluble solids, was vacuum-filtered through a fine funnel (4.0-5.5 mm). More CH_2Cl_2 was added to the reactor to ensure complete transfer of the suspension into the funnel. Insoluble material remaining on the frit, including the catalyst and insoluble hydrocarbons, was

recovered and weighed. In some cases, the solid was characterized by thermogravimetric analysis to give information on unreacted PE and carbon residue.

The filtrate was transferred to a 25.00 mL volumetric flask. C₇₋₃₀ hydrocarbons in the filtrate were quantified by GC-FID, using an external standard. After solvent removal under reduced pressure (0.1 Torr, 1 h), a portion of the liquid/wax (6-7 mg) was dissolved in CHCl₃ containing 0.25 vol% triethylamine (1.5 mL) for GPC analysis. Another portion (6-7 mg) was dissolved in CH₂Cl₂ (0.2 mL) for GC-MS analysis.

4.6. References

1. Geyer, R., Jambeck, J.R., and Law, K.L. (2017). Production, use, and fate of all plastics ever made. *Sci. Adv.* 3, e1700782. 10.1126/sciadv.1700782.
2. Di, J., Reck, B.K., Miatto, A., and Graedel, T.E. (2021). United States plastics: Large flows, short lifetimes, and negligible recycling. *Resour. Conserv. Recycl.* 167, 105440. 10.1016/j.resconrec.2021.105440.
3. Eriksson, O., and Finnveden, G. (2009). Plastic waste as a fuel - CO₂-neutral or not? *Energy Environ. Sci.* 2, 907–914. 10.1039/b908135f.
4. Rochman, C.M., Browne, M.A., Halpern, B.S., Hentschel, B.T., Hoh, E., Karapanagioti, H.K., Rios-Mendoza, L.M., Takada, H., Teh, S., and Thompson, R.C. (2013). Classify plastic waste as hazardous. *Nature* 494, 169–171. 10.1038/494169a.
5. Bouwmeester, H., Hollman, P.C.H., and Peters, R.J.B. (2015). Potential health impact of environmentally released micro- and nanoplastics in the human food production chain:

- experiences from nanotoxicology. *Environ. Sci. Technol.* **49**, 8932–8947. 10.1021/acs.est.5b01090.
6. Yin, S., Tuladhar, R., Shi, F., Shanks, R.A., Combe, M., and Collister, T. (2015). Mechanical reprocessing of polyolefin waste: A review. *Polym. Eng. Sci.* **55**, 2899–2909. 10.1002/pen.24182.
7. Vollmer, I., Jenks, M.J.F., Roelands, M.C.P., White, R.J., van Harmelen, T., de Wild, P., van der Laan, G.P., Meirer, F., Keurentjes, J.T.F., and Weckhuysen, B.M. (2020). Beyond Mechanical Recycling: Giving New Life to Plastic Waste. *Angew. Chem. Int. Ed.* **59**, 15402–15423. 10.1002/anie.201915651.
8. Jehanno, C., Alty, J.W., Roosen, M., De Meester, S., Dove, A.P., Chen, E.Y.-X., Leibfarth, F.A., and Sardon, H. (2022). Critical advances and future opportunities in upcycling commodity polymers. *Nature* **603**, 803–814. 10.1038/s41586-021-04350-0.
9. Kots, P.A., Vance, B.C., and Vlachos, D.G. (2022). Polyolefin plastic waste hydroconversion to fuels, lubricants, and waxes: a comparative study. *React. Chem. Eng.* **7**, 41–54. 10.1039/D1RE00447F.
10. Weitkamp, J. (2012). Catalytic hydrocracking—mechanisms and versatility of the Process. *ChemCatChem* **4**, 292–306. <https://doi.org/10.1002/cctc.201100315>.
11. Hernández, B., Kots, P., Selvam, E., Vlachos, D.G., and Ierapetritou, M.G. (2023). Techno-Economic and Life Cycle Analyses of Thermochemical Upcycling Technologies of Low-Density Polyethylene Waste. *ACS Sustain. Chem. Eng.* **11**, 7170–7181. 10.1021/acssuschemeng.3c00636.

12. Rudnick, L.R., and Shubkin, R.L. (1999). *Synthetic Lubricants And High- Performance Functional Fluids, Revised And Expanded* (CRC Press).
13. Holmberg, K. (2019). Surfactants. In *Ullmann's Encyclopedia of Industrial Chemistry* (John Wiley & Sons, Ltd), pp. 1–56. 10.1002/14356007.a25_747.pub2.
14. Rudnick, L.R. (2020). *Synthetics, Mineral Oils, and Bio-Based Lubricants: Chemistry and Technology* (CRC Press).
15. Sun, J., Lee, Y.-H., Yappert, R.D., LaPointe, A.M., Coates, G.W., Peters, B., Abu-Omar, M.M., and Scott, S.L. (2023). Bifunctional tandem catalytic upcycling of polyethylene to surfactant-range alkylaromatics. *Chem.* 9, 2318–2336. 10.1016/j.chempr.2023.05.017.
16. Pennel, M.L., Maurya, A.K., Ebrahim, A.M., Tassone, C.J., and Cargnello, M. (2023). Activity of Silica-Alumina for the Conversion of Polyethylene into Tunable Aromatics Below Pyrolytic Temperatures. *ACS Sustain. Chem. Eng.* 11, 12623–12630. 10.1021/acssuschemeng.3c02295.
17. Abdel-Shafy, H.I., and Mansour, M.S.M. (2016). A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation. *Egypt. J. Pet.* 25, 107–123. 10.1016/j.ejpe.2015.03.011.
18. le Goff, P.-Y., Kostka, W., and Ross, J. (2017). Catalytic Reforming. In *Springer Handbook of Petroleum Technology*, C. S. Hsu and P. R. Robinson, eds. (Springer International Publishing), pp. 589–616. 10.1007/978-3-319-49347-3_18.
19. Dufresne, P., Bigeard, P.H., and Billon, A. (1987). New developments in hydrocracking: low pressure high-conversion hydrocracking. *Catal. Today* 1, 367–384. 10.1016/0920-5861(87)80005-6.

20. Liu, S., Kots, P.A., Vance, B.C., Danielson, A., and Vlachos, D.G. (2021). Plastic waste to fuels by hydrocracking at mild conditions. *Sci. Adv.* 7, eabf8283. 10.1126/sciadv.abf8283.
21. Li, L., Luo, H., Shao, Z., Zhou, H., Lu, J., Chen, J., Huang, C., Zhang, S., Liu, X., Xia, L., et al. (2023). Converting Plastic Wastes to Naphtha for Closing the Plastic Loop. *J. Am. Chem. Soc.* 145, 1847–1854. 10.1021/jacs.2c11407.
22. Watson, M.D., Fechtenkötter, A., and Müllen, K. (2001). Big Is Beautiful—“Aromaticity” Revisited from the Viewpoint of Macromolecular and Supramolecular Benzene Chemistry. *Chem. Rev.* 101, 1267–1300. 10.1021/cr990322p.
23. Chanyshv, A.D., Litasov, K.D., Furukawa, Y., Kokh, K.A., and Shatskiy, A.F. (2017). Temperature-induced oligomerization of polycyclic aromatic hydrocarbons at ambient and high pressures. *Sci. Rep.* 7, 7889. 10.1038/s41598-017-08529-2.
24. Zhang, F., Zeng, M., Yappert, R.D., Sun, J., Lee, Y.-H., LaPointe, A.M., Peters, B., Abu-Omar, M.M., and Scott, S.L. (2020). Polyethylene upcycling to long-chain alkylaromatics by tandem hydrogenolysis/aromatization. *Science* 370, 437–441. 10.1126/science.abc5441.
25. Serrano, D.P., Aguado, J., and Escola, J.M. (2012). Developing advanced catalysts for the conversion of polyolefinic waste plastics into fuels and chemicals. *ACS Catal.* 2, 1924–1941. 10.1021/cs3003403.
26. Celik, G., Kennedy, R.M., Hackler, R.A., Ferrandon, M., Tennakoon, A., Patnaik, S., LaPointe, A.M., Ammal, S.C., Heyden, A., Perras, F.A., et al. (2019). Upcycling Single-

- Use Polyethylene into High-Quality Liquid Products. ACS Cent. Sci. 5, 1795–1803. 10.1021/acscentsci.9b00722.
27. Yappert, R., and Peters, B. (2022). Population balance models for polymer upcycling: signatures of the mechanism in the molecular weight evolution. J. Mater. Chem. A 10, 24084–24095. 10.1039/D2TA04628H.
28. Smith, G.C. (1993). Catalytic Cracking of *n*-Alkanes and *n*-Alkylbenzenes over H-ZSM-5 Zeolite.
29. Ali, S.A. (2007). Thermodynamic Aspects of Aromatic Hydrogenation. Pet. Sci. Technol. 25, 1293–1304. 10.1080/10916460500528607.
30. Qiu, Z., Lin, S., Chen, Z., Chen, A., Zhou, Y., Cao, X., Wang, Y., and Lin, B.-L. (2023). A reusable, impurity-tolerant and noble metal-free catalyst for hydrocracking of waste polyolefins. Sci. Adv. 9, eadg5332. 10.1126/sciadv.adg5332.
31. Rossetti, I., Gambaro, C., and Calemme, V. (2009). Hydrocracking of long chain linear paraffins. Chem. Eng. J. 154, 295–301. 10.1016/j.cej.2009.03.018.
32. Snyder, L.R. (1963). Adsorption from Solution. I. Fused Aromatic Hydrocarbons on Alumina. J. Phys. Chem. 67, 234–240. 10.1021/j100796a007.

4.7. Appendix III

4.7.1. Materials

Trimethyl(cyclopentadienyl)platinum (CpPtMe₃, 99%) was purchased from Strem. Silica–alumina (SiO₂–Al₂O₃, Davicat 3113, 7.6 wt % Al, B.E.T. surface area 573 m² g^{−1}, pore volume 0.76 cm³ g^{−1}) was obtained from Grace-Davison.

A standard Pt solution containing (976 ± 2) mg Pt/kg in 5% w/w HCl, pyridine (anhydrous, 99.8%), and polyethylene of two different molecular weights (Lots SKU 427772 and SKU 427799) were purchased from Sigma-Aldrich. Nitric acid (68.0-70.0 wt%), hydrochloric acid (36.5-38.0 wt%), and chloroform (HPLC grade, OmniSolv®, CX1054-6) were obtained from EMD Millipore Corp. HPLC-grade water, HPLC-grade triethylamine were purchased from Fisher Chemicals. CH_2Cl_2 - d_2 (D, 99.8%) was purchased from Cambridge Isotope Laboratories.

H_2 (5.048 vol% in Ar, Airgas Certified Standard) was purified by passing through 13X molecular sieves and BTS catalyst (Sigma Aldrich) before its use for Pt reduction. Ar (UHP, Airgas) and H_2 (UHP, Airgas) were used in the study of H_2 effect. Propene (99.8%) was obtained from PRAXAir. Carbon monoxide (9.890 vol% in He, Airgas Certified Standard) was used in pulsed CO chemisorption.

4.7.2. Experimental Procedures and Data Analyses

4.7.2.1. Catalyst Synthesis

Prior to Pt deposition, $\text{SiO}_2\text{-Al}_2\text{O}_3$ (1.50 g) was first calcined in static air in a temperature-controlled muffle furnace (Thermo Scientific Lindberg/Blue M BF51848C) at 500 °C for 4 h. The calcined $\text{SiO}_2\text{-Al}_2\text{O}_3$ was then dehydrated at ca. 10^{-2} Torr and 400 °C for 8 h.

Pt/ $\text{SiO}_2\text{-Al}_2\text{O}_3$ (denoted as Pt/SA) was prepared by chemical vapor deposition of CpPtMe_3 (42 mg) onto dehydrated $\text{SiO}_2\text{-Al}_2\text{O}_3$ (1.5 g), followed by reduction by heating to 280 °C at a rate of 2 °C min^{-1} in flowing H_2 (5.0 vol% in Ar), then holding for 2 h.

4.7.2.2. Catalyst Characterization

4.7.2.2.1. Metal Analysis

Pt analysis was performed using Inductively-Coupled Plasma (ICP) – Optical Emission Spectrometry (ICP-OES), on a Thermo iCAP 6300. The calibration curve was constructed using a standard Pt solution, prepared by diluting the commercial Pt standard with homemade aqua regia (5 vol%) in HPLC-grade water. Pt was extracted from catalyst samples following a literature procedure,¹ involving stirring in aqua regia at 75 °C for 30 min. To ensure complete digestion of Pt, the extraction method was modified by allowing the suspensions to stand at room temperature for an additional 12 h. The suspensions were then filtered through a syringe filter (pore size 0.2 µm). The solid residues were washed three times with HPLC-grade H₂O. The filtrate and washings were combined and diluted with aqua regia (5 vol % in water), then analyzed by ICP-OES. Pt loadings was measured to be 1.7 wt% in the Pt/SiO₂-Al₂O₃.

Accessible Pt surface areas in the fresh catalysts were measured by CO chemisorption, using a Micrometrics Autochem ii 2920. The catalyst (ca. 40 mg) was placed on a plug of glass wool in a U-shaped quartz reactor. A thermocouple was attached to the outside of the reactor, at the level of the middle of the bed. Complete reduction of the catalyst was ensured activated by heating in flowing H₂ (5.0 mol% in He) at a rate of 5°C min⁻¹ to 200°C, then held for 1 h before switching to He flow then cooling to room temperature. The catalyst was subjected to 30 pulses of CO (9.9 vol% in He, 124 µL each at 110°C). The amount of CO not adsorbed in each pulse was measured using a TCD detector. The Pt dispersion (*D*, %), were calculated to 65%.

TEM images of catalysts were obtained using a ThermoFisher Talos F200X. Pt particle sizes were estimated by analysis of the high angle annular dark field (HAADF) images, **Figure A4.1**. Pt/SA contain particles with average sizes of (1.0 ± 0.2) nm, which is smaller than the Pt particles size measured by CO chemisorption (1.5 nm).

4.7.2.2.2. Acidity Analysis

Lewis and Brønsted acidity were measured by pyridine adsorption. The IR calibration curve reported in the literature² was also used here.

A sample of dried material (ca. 80 mg) was transferred to a Schlenk tube inside an Ar-filled glovebox. The Schlenk tube was sealed, removed from the glovebox, and connected to a high vacuum line (base pressure 30 mTorr). The tube was evacuated at 400 °C for 2 h, then cooled to room temperature. Excess dry, air-free pyridine vapor was introduced at room temperature and allowed to equilibrate for 15 min. The tube was then evacuated at ca. 30 mTorr for 30 min while heating at 150 °C to remove physisorbed pyridine. The tube was then transferred into an Ar-filled glovebox, where ca. 10 mg (precisely weighed) was pressed into a self-supporting pellet of diameter 5.0 mm using an ICL hand press. The spectrum of glovebox atmosphere was used as the background.

IR spectra were recorded using a Bruker Alpha FTIR spectrometer over the range 4000–400 cm^{-1} at a resolution of 2 cm^{-1} , accumulating 64 scans. The absorbance was normalized by the precise sample mass. The areas of the peaks at 1455 and 1545 cm^{-1} , corresponding to pyridine interacting with LAS and BAS, respectively, were used for quantification.

The numbers of Brønsted acid sites (BAS) and Lewis acid sites (LAS) on Pt/SA, measured by IR of adsorbed pyridine (**Figure A4.2**), are 42 and 120 $\mu\text{mol/g}$, respectively.

4.7.2.3. Catalytic Reactions and Products analysis

4.7.2.3.1. Polyethylene Depolymerization Reaction

A high pressure Parr reactors (10 mL, Parr 2550, Parr 4590 or Parr Series 5000 Multiple Reactor System, internal volume ca. 100 mL, stainless steel) equipped with a pressure gauge and type J thermocouple was loaded with PE and a freshly-reduced Pt/SiO₂-Al₂O₃ catalyst inside an Ar-filled glove-box. The reactor was sealed and removed from glovebox, which was then connected onto the vacuum line to remove initial gas. The reactor was then filled with target pressure of desired gas, and was placed onto heating system. The contents were stirred magnetically at ca. 100 rpm, using a Pyrex-encapsulated stir bar. Timing of the reaction began when the internal temperature reached the desired temperature, 275°C, after ca. 30 min.

After the reaction, the reactor was removed from the heater and cooled under a jet of flowing air to room temperature. To characterize volatile products, the reactor and a Schlenk flask capped with a white rubber septum were connected to a glass vacuum line equipped with a pressure gauge and a gas sampling port. The Schlenk flask and vacuum lines were evacuated (10^{-2} Torr), then isolated from the pumping system. The gases in the autoclave were expanded into the line and Schlenk flask. The pressure reading are recorded before (P_0) and after (P_0) the gas expansion.

H₂ analysis by GC-TCD was achieved by removing an aliquot of gas (400 μL) via the gas sampling port using a gas-tight syringe. If Ar is present in the autoclave at the start of the

reaction, it is used as the internal standard for quantification of H₂ remaining in the reactor after reaction. If Ar is not present in the reactor, the amount of H₂ is estimated by pressure, please see **Section 4.7.2.6: Analysis of H₂ Balance**. The hydrocarbon gas (mostly C₁ to C₆, $m_{\text{gas}} = m_{\text{C1-C6}}$) was sample for GC-FID analysis. Propene (400 μL , 200-600 mbar) was injected into the Schlenk tube for use as an internal standard prior to removing a gas aliquot (200 μL) for GC-FID analysis (**Figure A4.3** for an example).

After the gas analysis, ca. 3.0 ml of deuterated CH₂Cl₂-d₂ was added into the reactor through the vent hose upon opening it. The CH₂Cl₂-d₂ and post-reaction mixture were stirred under magnetitic stirring at ca. 100 rpm, using the Pyrex-encapsulated stir bar in the reactor for 5 mins to ensure a good mixing. The mixture was then allowed to stand for 3 mins for the catalyst particles to precipitate. ca. 1 ml of supernatant was used for ¹H NMR analysis.

To separate out CH₂Cl₂-soluble hydrocarbon, the suspension consisting of the hydrocarbons dissolved in CH₂Cl₂, solid hydrocarbons, and solid catalyst, was filtered through a fine funnel (4.0-5.5 μm) by vacuum filtration. The extracted CH₂Cl₂-soluble hydrocarbons, including the supernatant for ¹H NMR measurement, were transferred into a 25.00 mL volumetric flask. Two aliquots of this mixture were used for GC-MS (**Figure A4.9** for an example) and GC-FID (**Figure A4.6** for an example) analysis for qualitative and quantitative analysis of liquid hydrocarbon (C₇ to C₃₀, $m_{\text{liquid}} = m_{\text{C7-C30}}$), respectively. The CH₂Cl₂ in the hydrocarbon was removed under reduced pressure (0.1 Torr, 2h), accompanied with the loss of light liquid (C₇-C₁₁, $m_{\text{light liquid}} = m_{\text{C7-C11}}$).³ The resulting product contain hydrocarbons larger than C₁₂ including heavy liquid (C₁₂-C₃₀, $m_{\text{heavy liquid}} = m_{\text{C12-C30}}$) and wax (C_{>30}, $m_{\text{wax}} = m_{>30}$), which were weighed (m_{total}) to obtain the mass of wax using a mass balance (**eq A4.1**).

$$m_{\text{wax}} = m_{\text{total}} - m_{\text{heavy liquid}} \quad (\text{A4.1})$$

To obtain molecular weight distribution on wax products, ca. 5 mg of heavy liquid and wax product was dissolved in 1 mL CHCl₃ containing 0.25 vol% triethylamine for GPC analysis. Typically, a bimodal distribution was observed in the GPC results, with a lower molecular weight peak centered at smaller than ca. 200 g/mol (**Figure A4.8** for an example). The molecular weight distribution of lower molecular weight peak (heavy liquid) has been described more accurately by GC-FID, as mentioned above. This is because the refractive index is dependent on molecular weight when the molecular is small, thus giving inaccurate quantities in GPC measurements.⁴ The higher molecular weight peak mostly contain molecules larger than C₃₀, (squalane, a C₃₀ *iso*-alkane, is measured to have 560 g/mol, with 30% error). The number- and mass-average molecular of wax is calculated using **eq A4.2** and **eq A4.3**, respectively. The number-average molecular of combined liquid and wax fraction is calculated using **eq A4.4**.

$$M_n = \frac{\sum_i f_i}{\sum_i (\frac{f_i}{M_i})}, M_i > 420 \text{ g/mol} \quad (\text{A4.2})$$

$$M_w = \frac{\sum_i f_i M_i}{\sum_i f_i}, M_i > 420 \text{ g/mol} \quad (\text{A4.3})$$

$$M_{n,\text{liquid/wax}} = \frac{m_{\text{liquid}} + m_{\text{wax}}}{n_{\text{liquid}} + \frac{m_{\text{wax}}}{M_{n,\text{wax}}}} \quad (\text{A4.4})$$

Where f_i is the response of detector in GPC measurement, and M_i is derived from the retention time in GPC measurement, based on its calibration curve. m_{liquid} and n_{liquid} are obtained from GC-FID analysis.

The insoluble material remaining on the frit, including the catalyst and insoluble hydrocarbons, was recovered and weighed. The mass of insoluble hydrocarbons was calculated by subtracting the initial mass of the catalyst. In some cases, the post-extraction solid was characterized by thermogravimetric analysis (TGA, **Figure A4.13**), giving information on unreacted PE (insoluble in CH_2Cl_2 but fully oxidized in air to CO_2 and H_2O below 350°C) and carbon residue (insoluble in CH_2Cl_2 and completely oxidized above 350°C in air).

4.7.2.3.2. Pseudo-Constant $P(\text{H}_2)$ Depolymerization

This set of reactions involves conducting multiple short-duration periods, typically 4 h each, of reactions. Between these periods, the target gas is refilled before the next stage of the reaction, which keeps the $P(\text{H}_2)$ relative constant. The first stage of reaction follow the same procedure for packing the reactor, conducting the reaction, and analyzing gas products as described in **Section 4.7.2.3.1: Polyethylene Depolymerization Reaction**.

After gas analysis, the reactor is then connected to a vacuum line to remove volatile hydrocarbons until pressure indicated by the pressure gauge stabilizes. Subsequently, the reactor is pressurized to the desired pressure with the specific type of gas, and then heated for another round of reaction. This procedure can be repeated multiple times. In the final run,

after the analysis of gas products, liquid, wax, and insoluble hydrocarbon are analyzed as described in **Section 4.7.2.3.1: Polyethylene Depolymerization Reaction**. The gas analyzed at each stage is combined to form the total gas products.

4.7.2.3.3. H₂ and Hydrocarbon Analysis

H₂ analysis by GC-TCD. H₂ was quantified on a Shimadzu GC-8AIT gas chromatograph equipped with a packed column (ShinCarbon ST 80/100, 2 m x 2 mm) and a thermal conductivity detector (TCD). The column, injector and detector temperatures were all 130°C. The TCD current was 70 mA and the head pressure was 300 kPa (N₂). Ar present in the reactor was used as the internal standard. The linear responses of the TCD signal to the injected volumes of H₂ and Ar were confirmed using standard H₂/Ar gas mixtures. The response factors were obtained as described previously.⁵

Gas hydrocarbon analysis by GC-FID. Hydrocarbons in the gas fraction (C₁₋₈) were analyzed qualitatively and quantitatively on a Shimadzu GC-2010 gas chromatograph equipped with a capillary column (Supelco Alumina Sulfate plot, 30 m x 0.32 mm) and a flame ionization detector (FID). The injector and detector temperatures were both 200 °C. The temperature program was: 90 °C (hold 3 min), ramp 20 °C/min to 180 °C (hold 20 min). The yields of each hydrocarbon were calculated assuming all have the same relative carbon response factor.

Liquid hydrocarbon analysis by GC-FID. The hydrocarbons were quantified on an Agilent 6890N Network gas chromatograph equipped with an Agilent DB-5 capillary column (fused silica, 30 m x 0.25 mm x 0.25 µm) and an FID detector. The inlet and detector temperatures

were 300 and 280°C, respectively. The temperature ramp program was: 40°C (hold 3 min), ramp 25°C /min to 320°C (hold 10 min). The flow rate was 1.0 mL/min (He) with a 5:1 split ratio. The same relative carbon response factor (*f*) was assumed for all hydrocarbons. *norm*-Octadecane in CS₂ was used as an external standard. Peak areas were measured by injection of several *n*-octadecane solutions of different concentrations, giving the calibration curve in **Figure A4.5**.

GC-MS Analysis. An aliquot of the liquid products dissolved in CH₂Cl₂ (2 mL) was transferred to a vial for solvent removal in a rotary evaporator (30°C, 350 Torr), then analyzed on a Shimadzu GC-2010 gas chromatograph equipped with an Agilent DB-5 MS capillary column ((5%-phenyl)-methylpolysiloxane, 30 m x 0.25 mm x 0.25 µm) coupled to a QP2010 Mass Spectrometer. The injector and detector temperatures were 250°C. The temperature ramp program was: 60°C (hold 2 min), ramp 15°C per min to 270°C, hold 50 min.

NMR spectroscopic analysis. ¹H NMR spectra of liquid products recovered from the reactions of PE were recorded on a Varian Unity Inova AS600 spectrometer, and analyzed by MestReNova (v11.0.1, Mestrelab Research S. L.).

Gel permeation chromatography analysis. Molecular weight distributions of hydrocarbon and aromatic chromophores were analyzed by GPC with RI and UV detection, respectively. Analyses were conducted on a Waters 2690 HPLC equipped with two Agilent Columns (PLgel, 5 µm MiniMIX-D, 250×4.6 mm) and a guard column (*M_w* linear range 200 - 400,000 g mol⁻¹), a Waters 2410 refractive index (RI) detector and a Waters 2998 photodiode array detector (PDA). Chloroform containing 0.25 vol% triethylamine was used as the mobile phase at room temperature and 0.35 mL min⁻¹. Calibration was achieved using polystyrene standards

(Agilent EasiVial kit, linear response for molecular weights in the range 200 - 400,000 g mol⁻¹).

Thermogravimetric analysis. To assess the nature of hydrocarbon residues post-reaction, catalysts recovered from the reactor after conversion of PE were analyzed by TGA. The measurements were performed in air with a TA Discovery Thermo- Gravimetric Analyzer while heating at 10°C min⁻¹ from 50 to 700°C. the differential thermogravimetric analysis shows a distinct peak at ca. 250-300°C, corresponding to the oxidation of unreacted PE, and the peak at ca. 550°C assigned to the oxidation of coke, (**Figure A4.13**).

4.7.2.4. Analysis of Aromatic

4.7.2.4.1. Analysis of Alkyl Substituents of Aromatics

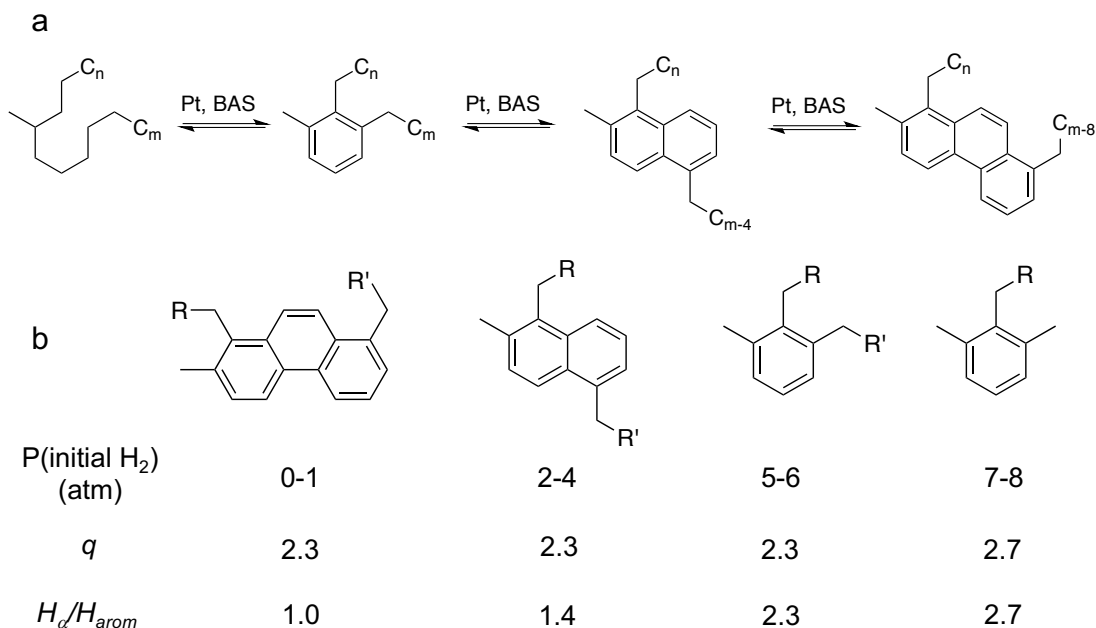
To understand the type of substituents on the aromatics, ¹H NMR signals at 2.0-3.5 ppm (H_α) arise due to alkyl substituents on the aromatic rings, are further subdivided into 2.0-2.5 ppm ($H_{\alpha\text{-methyl}}$), 2.5-3.1 ppm ($H_{\alpha\text{-methylene}}$), and 3.1-3.5 ppm ($H_{\alpha\text{-methine}}$).⁶ The average number of H_α per alkyl substituent, q , was calculated using **eq A4.5**.

$$q = (H_{\alpha,\text{methyl}} + H_{\alpha,\text{methylene}} + H_{\alpha,\text{methine}})/(H_{\alpha,\text{methyl}}/3 + H_{\alpha,\text{methylene}}/2 + H_{\alpha,\text{methine}}) \quad (\text{A4.5})$$

As $P(\text{initial H}_2)$ rises from 0 to 6 bar, the value of q increases slightly from 1.9 to 2.2 (**Table A4.3**). This result indicates that there are, on average, two H_α per alkyl substituent (i.e., -CH₂R). When $P(\text{initial H}_2)$ increased further to 8 bar, the value of q rose to 2.7, corresponding to a mixture of -CH₂R and -CH₃ substituents. The increase in q at high P_{H_2}

could result from preferential C_{sp3}-C_{sp3} bond scission instead of C_{sp3}-C_{sp2} bond scission in the alkylaromatics, due to the higher C_{sp2}-C_{sp3} bond energy.⁷ As a result, methyl-substituted aromatics become the major aromatic products under more C-C scission caused by H₂.

To estimate the average number of substituents per aromatic ring, the ratio $H_{\alpha}/H_{\text{arom}}$ (H_{arom} , aromatic protons, ¹H NMR signals at 6.5-9.0 ppm) was evaluated (**Table A4.3**). When $P(\text{initial H}_2)$ was ≤ 1 bar, the yield of phenanthrenes is high. In addition, the $H_{\alpha}/H_{\text{arom}}$ in both products are close to 1.2, indicating the major products are trialkyl-substituted phenanthrenes. Based on a plausible mechanism to make alkylaromatics using the bifunctional catalyst (**Scheme A4.1a**), one -CH₃ and two -CH₂R substituents are proposed (**Scheme A4.1b**), where the -CH₃ group originates from acid-catalyzed skeletal isomerization of the polymer which installs methyl branches.² The $H_{\alpha}/H_{\text{arom}}$ ratio increased further, from 1.3 to 1.7, as $P(\text{initial H}_2)$ increased from 2 to 4 bar, indicating that the major products shifted to trialkyl-substituted naphthalenes. The $H_{\alpha}/H_{\text{arom}}$ further increased above 2 for $P(\text{initial H}_2)$ values between 5 to 8 bar, corresponding to trialkyl-substituted benzenes. Therefore, trialkyl-substituted benzenes, naphthalenes, and phenanthrenes are the major aromatic products under low, middle, and high $P(\text{initial H}_2)$, respectively.



Scheme A4.1. (a) Proposed bifunctional mechanism for methyldialkylaromatics formation from long-chain methyl-branched alkanes.² (b) Major structures of the alkylaromatic products (trialkyl-substituted phenanthrenes, naphthalenes, and benzenes) formed in the depolymerization of PE (0.200 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) catalyzed by Pt/SA (0.100 g) at 275 °C for 24 h under the presence of $P(\text{initial } H_2)$ from 0 to 8 bar, along with their corresponding predicted q and H_α/H_{arom} ratios.

4.7.2.4.2. Analysis on Selectivity and Yield of Aromatics

Trialkyl-substituted alkylbenzene, alkyl-naphthalene and alkylphenanthrene (as described in **Section 4.7.2.4.1**), each contribute 3, 5, and 7 aromatic protons, respectively. Besides aromatics, alkanes are also present in the products. The ratio of aromatic proton to the total protons can be calculated using **eq A4.6**, as adapted from the literature.³

$$\frac{H_{arom}}{H_{total}} = \frac{3 \sum_i n_{ben,i} + 5 \sum_i n_{nap,i} + 7 \sum_i n_{phe,i}}{(2\bar{i}_{ben} - 6) \sum_i n_{ben,i} + (2\bar{i}_{nap} - 12) \sum_i n_{nap,i} + (2\bar{i}_{phe} - 18) \sum_i n_{phe,i} + (2\bar{i}_{alk} + 2) \sum_i n_{alk,i}} \quad (A4.6)$$

Where ben, nap, phe, and alk represent for alkylbenzene, alkylnaphthalene, alkylphenanthrene, and alkanes respectively. $\sum_i n_i$, and $\bar{i}$ represent the total number and average carbon number of each species.

Since alkylbenzene, alkylnaphthalene, and alkylphenanthrene are mostly present in the liquid range (C₇-C₃₀, **Figure A4.8**, **Figure A4.11** and **Figure A4.12**), and their distributions are similar to that of total liquid products (**Figure A4.9**). On the other hand, alkanes are present in both the liquid and wax fractions.

Therefore, the contributions of the liquid and wax fraction to the total protons in **eq A4.6** are separately accounted for and rewritten into **eq A4.7**.

$$\frac{H_{arom}}{H_{total}} = \frac{3 \sum_{i,liq} n_{ben,i} + 5 \sum_{i,liq} n_{nap,i} + 7 \sum_{i,liq} n_{phe,i}}{(2\bar{i}_{ben,liq} - 6) \sum_{i,liq} n_{ben,i} + (2\bar{i}_{nap,liq} - 12) \sum_{i,liq} n_{nap,i} + (2\bar{i}_{phe,liq} - 18) \sum_{i,liq} n_{phe,i} + (2\bar{i}_{alk,liq} + 2) \sum_{i,liq} n_{alk,i} + (2\bar{i}_{alk,wax} + 2) \sum_{i,wax} n_{alk,i}} \quad (A4.7)$$

Where $\sum_{i,wax} n_{alk,i} = \sum_{i,wax} n_i$, because all of the species in the wax correspond to alkanes.

The molar selectivity to alkylbenzenes in the liquid fraction ($S_{ben,liq}$) is defined in **eq A4.8** (molar selectivities for other components are defined similarly):

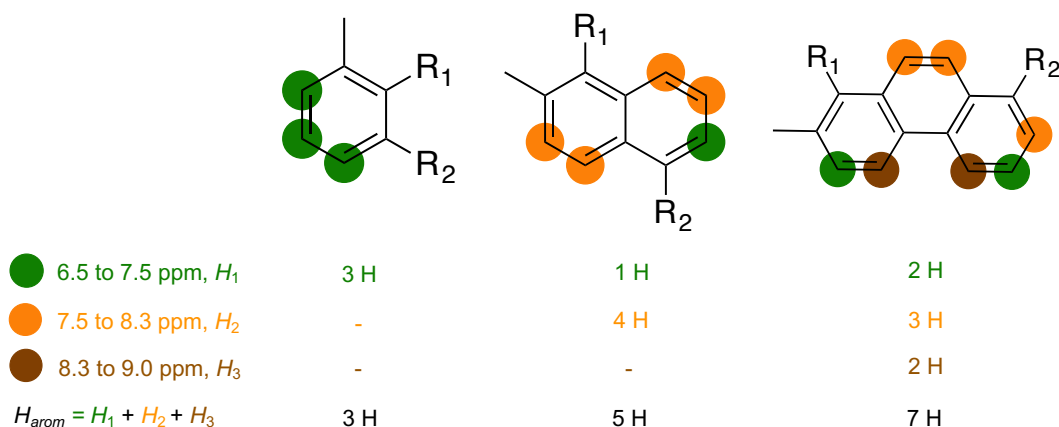
$$S_{ben,liq} = \frac{\sum_{i,liq} n_{ben,i}}{\sum_{i,liq} n_{ben,i} + \sum_{i,liq} n_{nap,i} + \sum_{i,liq} n_{phe,i} + \sum_{i,liq} n_{alk,i}} \quad (A4.8)$$

Where $\sum_{i,liq} n_{ben,i} + \sum_{i,liq} n_{nap,i} + \sum_{i,liq} n_{phe,i} + \sum_{i,liq} n_{alk,i} = \sum_{i,liq} n_i$

Therefore **eq A4.9** is obtained by combining **eqs A4.7-4.8**.

$$\frac{H_{arom}}{H_{total}} = \frac{3S_{ben,liq} + 5S_{nap,liq} + 7S_{phe,liq}}{(2\overline{i_{ben,liq}} - 6)S_{ben,liq} + (2\overline{i_{nap,liq}} - 12)S_{nap,liq} + (2\overline{i_{phe,liq}} - 18)S_{phe,liq} + (2\overline{i_{alk,liq}} + 2)S_{alk,liq} + (2\overline{i_{alk,wax}} + 2)\frac{\sum_{i,wax} n_i}{\sum_{i,liq} n_i}} \quad (A4.9)$$

To obtain the selectivity of each species, the potential contributions of methylalkyl-substituted aromatics to the ^1H NMR signals in the aromatic region are summarized in **Scheme A4.2**, as reproduced from ref 2.



Scheme A4.2. Predicted chemical shifts for aromatic protons in methylalkyl-substituted benzenes, -naphthalenes, and -phenanthrenes, showing the assignments of the expected ^1H signals for each structure type to one of the three aromatic regions (H_1 , green; H_2 , orange; H_3 , brown), and the relative contributions of each type of aromatic proton to each structure type. Reproduced from ref 2.

The experimental ratios $H_1 : H_2 : H_3$ were obtained by integrating the relevant aromatic regions in the ^1H NMR spectrum. These values were related to the molar amounts (n_j) for each aromatic structure type to estimate the relative molar selectivities, **eq A4.10**, as reported in ref 2.

$$S_{\text{phe}} : S_{\text{nap}} : S_{\text{ben}} = n_{\text{phe}} : n_{\text{nap}} : n_{\text{ben}} = 1/2 H_3 : 1/4 (H_2 - 3/2 H_3) : 1/3 H_1 - 1/12 H_2 - 5/24 H_3 \quad (\text{A4.10})$$

The average carbon number of alkylbenzenes, alkyl naphthalenes, alkylphenanthrenes, and alkanes is assumed to be similar in the liquid range, **eq A4.11 (assumption 1)**.

$$\overline{i_{ben,liq}} = \overline{i_{nap,liq}} = \overline{i_{phe,liq}} = \overline{i_{alk,liq}} \quad (\text{A4.11})$$

The selectivity of each species can be obtained by combining **eqs A4.9-A4.11**. Alternatively, since alkylbenzene, alkylnaphthalene, and alkylphenanthrene contain at least 6 carbons, 10 carbons, and 14 carbons, respectively. The average carbon number of alkylbenzenes, alkylnaphthalenes, and alkylphenanthrenes are assumed to equal to the average carbon number of alkanes within the range of C₆₋₃₀, C₁₀₋₃₀, and C₁₄₋₃₀, respectively, **eqs A4.12-14 (assumption 2)**.

$$\overline{i_{ben,liq}} = \overline{i_{alk,C6-30}} \quad (\text{A4.12})$$

$$\overline{i_{naphthalene,liq}} = \overline{i_{alk,C10-30}} \quad (\text{A4.13})$$

$$\overline{i_{phenanthrene,liq}} = \overline{i_{alk,C14-30}} \quad (\text{A4.14})$$

The impact of different assumptions is small, as compared in **Table A4.4**. For simplicity, the reported selectivities are calculated using **assumption 1** unless otherwise stated.

The yield of each type of product is calculated using **eq A4.8** after obtaining the selectivity as mentioned above, and the total liquid fraction products, $\sum_{i,liq} n_i$, is measured by GC-FID.

4.7.2.5. Analysis of Carbon-Carbon Bond Scission

The number of C-C bond scission ($n_{\text{C-C scission, measured}}$) is calculated by counting the change in the number of chains before ($N(0)$) and after the reaction ($N(t)$), **eqs A4.15-4.17**.³

$$n_{\text{C-C scission, measured}} = N(t) - N(0) \quad (\text{A4.15})$$

$$N(t) = n_{\text{gas}} + n_{\text{liquid}} + n_{\text{wax}} + n_{\text{solid}} \quad (\text{A4.16})$$

$$N(0) = n_{\text{PE}} \quad (\text{A4.17})$$

Where the number of solid hydrocarbon chains (n_{solid}) and initial number of PE chains are estimated as $m_{\text{solid}}/M_{n,\text{PE}}$ and $m_{\text{PE}}/M_{n,\text{PE}}$, respectively. Here, m_{solid} and m_{PE} refer to the mass of solid residue and PE, respectively, while $M_{n,\text{PE}}$ represents the initial number-averaged molecular weight of PE.

Due to an incomplete collection of mass, the missing mass ($200 \text{ mg} - m_{\text{total}}$) is assumed to have the same fraction as the detected mass. Consequently, the total mass-corrected number of C-C bond scissions is calculated as shown in **eq A4.18**.

$$n_{\text{C-C scission, Ctotal}} = n_{\text{C-C scission, measured}} + (200 - m_{\text{total}})/m_{\text{total}} * N(t) \quad (\text{A4.18})$$

Alternatively, the missing mass can be attributed to incomplete collections of gas ($\text{C}_1\text{-C}_6$), light liquid ($\text{C}_7\text{-C}_{11}$), heavy liquid ($\text{C}_{12}\text{-C}_{30}$), wax ($\text{C}_{>30}$), and solid ($\text{C}_{\text{insoluble}}$), respectively. Because C_6 alkanes overlaps with solvent peak in GC-FID analysis, the missing mass is

assumed to come from underestimation of C_6 . The mass-corrected C-C bond scission is shown in **eq A4.19**, assuming the missing mass only came from C_6 .

$$n_{\text{C-C scission, C6}} = n_{\text{C-C scission, measured}} + (200 - m_{\text{total}})/m_{\text{C6}} * n_{\text{C6}} \quad (\text{A4.19})$$

Therefore, the measured C-C bond scission and the calculation assuming missing mass from C_6 represent the lower and upper limits of C-C bond scission, respectively, **Figure A4.14**.

4.7.2.6. Analysis of H_2 Balance

When the parr reactor (with volume of $V_r = 10$ mL) was filled initially with Ar (P_{Ar}), the amount of H_2 after reaction was measured by GC-TCD using Ar as the internal standard, through measuring the peak areas of H_2 (A_{H_2}) and Ar signals (A_{Ar}), **eq A4.20**. The response factor for H_2 and Ar reported in the literature were used here.⁵

$$\frac{n_{H_2}}{n_{Ar}} = \frac{V_{H_2}}{V_{Ar}} = \frac{A_{H_2}/f_{H_2}}{A_{Ar}/f_{H_2}} \quad (\text{A4.20})$$

When Ar was not present initially, the amount of H_2 after reaction is estimated by measuring the gas pressure in the reactor. After reaction, the reactor was connected to the pre-evacuated vacuum line and a Schlenk flask (with volume V_{vs}), initially at pressure reading P_0 . The gases in the reactor were then allowed to expand into the vacuum line and Schlenk flask,

resulting in a pressure reading P_1 . The amount of gaseous molecules is calculated using the ideal gas law, **eq A4.21**.

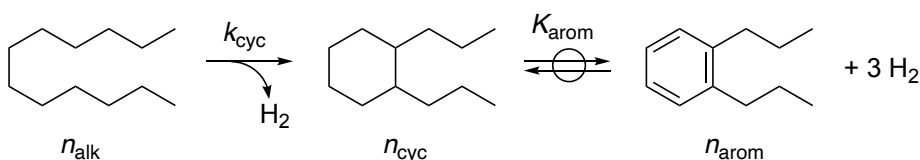
$$n_{total\ gas} = \frac{P_1(V_{vs}+V_r)-P_0V_{vs}}{RT} \quad (\text{A4.21})$$

The number of remaining H_2 is determined by calculating the total number of total molecules and subtract the gaseous hydrocarbon ($n_{gas\ hydrocarbon}$) measured by GC-FID, **eq A4.22**.

$$n_{H_2} = n_{total\ gas} - n_{gas\ hydrocarbon} \quad (\text{A4.22})$$

4.7.2.7. Microkinetic Model for Aromatization

To analyze the kinetic profiles reported for aromatic ring formation (**Figure 4.3a**), the simplified mechanism used in naphtha catalytic reforming is considered, where dehydrocyclization is irreversible and rate-determining, and aromatization is quasi-equilibrated, **Scheme A4.3**.⁸



Scheme A4.3. Standard alkane aromatization mechanism.

At all reaction times, the yield of aromatics is given by **eq A4.23**:

$$n_{arom} = K_{arom} n_{cyc} / P_{H_2}^3 \quad (A4.23)$$

Substituting n_{cyc} from the site balance in **eq A4.24** gives the expression for the aromatic yield in **eq A4.25**:

$$n_{cyc} = n_{alk}^0 - n_{alk} - n_{arom} \quad (A4.24)$$

$$n_{arom} = K_{arom} (n_{alk}^0 - n_{alk}) / (K_{arom} + P_{H_2}^3) \quad (A4.25)$$

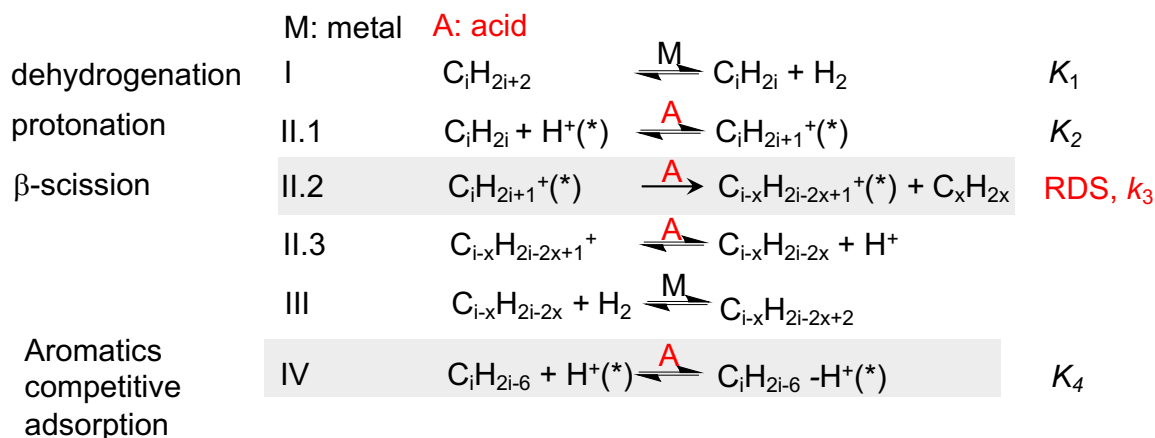
Finally, using the first-order rate expression in **eq A4.26** allows us to convert **eq A4.25** into the form of **eq 4.1** fitted to the time profiles in **Figure 4.3a**:

$$n_{alk} = n_{alk}^0 e^{-k_{cyc} t} \quad (A4.26)$$

$$n_{arom} = K_{arom} n_{alk}^0 (1 - e^{-k_{cyc} t}) / (K_{arom} + P_{H_2}^3) \quad (4.1)$$

In this formulation, the number of active sites that catalyze alkane cyclization is included in the numerical value of k_{cyc} .

4.7.2.8. Microkinetic Model for C-C Bond Scission



Scheme A4.4. Proposed reaction mechanism of C-C bond scission. M and A standard for metal and acid sites, respectively.

The reaction mechanism for catalytic C-C bond scission proceeds via initial rapid, quasi-equilibrated steps involving dehydrogenation of an alkane (*alk*) to an olefin (*ole*) on a metal site (K_1) and olefin protonation to a carbenium ion (RH^+) on an acid site (K_2), followed by rate-determining C-C bond scission in the carbenium ion leading to a new olefin and a new carbenium ion (k_{C-C}). Following the rate-determining step, deprotonation of the carbenium ion regenerates the acid site and produces a new olefin. Olefins are rapidly rehydrogenated on metal sites. The equilibrium constants, the rate law for the rate-determining step, and the site balance for that step involving the catalyst's acid sites, are shown in eqs A4.27-30:

$$K_1 = \frac{n_{ole} P_{H_2}}{n_{alk}} \quad (A4.27)$$

$$K_2 = \frac{n_{RH^+}}{n_{ole} n_{H^+}} \quad (A4.28)$$

$$r_{C-C} = k_{C-C} n_{RH^+} \quad (A4.29)$$

$$n_{acid} = n_{H+} + n_{RH+} \quad (A4.30)$$

By combining these equations, the amount of carbenium ion can be written as a function of experimental observables, with the result given in **eq A4.31**. Using this expression in **eq A4.29** gives the rate law expression in **eq A4.32**. Note that it predicts the rate of C-C bond scission to be zeroth-order in H_2 at low $P(H_2)$, and inverse-first-order in H_2 at high $P(H_2)$; at no time does it predict the rate should increase with $P(H_2)$.

$$n_{RH+} = \frac{K_1 K_2 n_{alk} n_{acid}}{K_1 K_2 n_{alk} + P_{H_2}} \quad (A4.31)$$

$$r_{C-C} = k_{C-C} \left\{ \frac{K_1 K_2 n_{alk} n_{acid}}{K_1 K_2 n_{alk} + P_{H_2}} \right\} \quad (A4.32)$$

Next, we consider the quasi-equilibrated adsorption of aromatics on the acid sites (K_3) and modify the acid site balance appropriately, eqs **A4.33-4.34**. The revised expressions for n_{RH+} and r_{C-C} are shown in **eqs A4.35-36**.

$$K_3 = \frac{n_{ArH+}}{n_{arom} n_{H+}} \quad (A4.33)$$

$$n_{acid} = n_{H+} + n_{RH+} + n_{ArH+} \quad (A4.34)$$

$$n_{RH+} = \frac{K_1 K_2 n_{alk} n_{acid}}{K_1 K_2 n_{alk} + P_{H_2} (1 + K_3 n_{arom})} \quad (A4.35)$$

$$r_{C-C} = k_{C-C} \left\{ \frac{K_1 K_2 n_{alk} n_{acid}}{K_1 K_2 n_{alk} + P_{H_2} (1 + K_3 n_{arom})} \right\} \quad (A4.36)$$

After 4 h at 275 °C, the value of n_{arom} does not change further, and can be represented by $n_{\text{arom,max}}$ (eq A4.37). Its use in eq A4.36 gives eq A4.38, whose denominator simplifies for large values of $P(\text{H}_2)$, leading to the version of the rate equation used in curvefitting, eq 4.6:

$$n_{\text{arom,max}} = \frac{K_{\text{arom}} n_{\text{alk}}^0}{K_{\text{arom}} + P_{\text{H}_2}^3} \quad (\text{A4.37})$$

$$r_{\text{C-C}} = k_{\text{C-C}} \left\{ \frac{K_1 K_2 n_{\text{alk}} n_{\text{acid}}}{K_1 K_2 n_{\text{alk}} + P_{\text{H}_2} (1 + K_3 \frac{K_{\text{arom}} n_{\text{alk}}^0}{K_{\text{arom}} + P_{\text{H}_2}^3})} \right\} \quad (\text{A4.38})$$

$$r_{\text{C-C}} = k_{\text{C-C}} \left\{ \frac{K_1 K_2 n_{\text{alk}} n_{\text{acid}}}{P_{\text{H}_2} (1 + K_3 \frac{K_{\text{arom}} n_{\text{alk}}^0}{K_{\text{arom}} + P_{\text{H}_2}^3})} \right\} \quad (\text{A4.6})$$

4.7.2.9. Thermodynamic Assessment

4.7.2.9.1. DFT Calculation Setup

Ab initio calculations of the reaction free energies were performed using non-periodic density functional theory (DFT) as implemented in the TURBOMOLE 7.5 program package.⁸⁻¹⁰ For each gas phase species, free energy computations involved a geometry optimization of the molecule, followed by the estimation of the enthalpic and entropic contributions to the free energy.

The electronic wavefunction/electron density of the gas phase molecules was computed using the quadruple- ζ with two sets of polarizing functions (def2-QZVPP) valence adaptation of the Karlsruhe basis set for all electrons. ω -B97M-V which is a state-of-the-art, hybrid, meta-GGA functional,¹¹ was utilized for the optimization of all species. We used a Gauss-

Chebyshev type spherical grid, m5, for the numerical integration and a self-consistent field energy convergence criterion of 1.0×10^{-8} Ha.

Frequency calculations were performed using the Perdew-Burke-Ernzerhof (PBE) functional¹² (a generalized gradient approximation (GGA) functional) coupled with the D3 dispersion correction technique¹³ as we observed small imaginary frequencies for the ω -B97M-V functional for large molecules even after tightening our convergence criterion and distorting the structures along the imaginary mode.

4.7.2.9.2. Free Energy Calculations

The free energy of species at 280 °C was calculated using classical partition functions within the harmonic approximation, **eq A4.39**.

$$G_i(T = 280^{\circ}C) = E_o + ZPE + R \cdot T \cdot \ln(Q(T = 280^{\circ}C)) \quad (\text{A4.39})$$

where E_o is the temperature-independent optimized electronic energy, ZPE is the zero-point-corrected energy, R is the universal gas constant, Q is the total partition function of the molecule without electronic contributions.

The zero-point-corrected energy (ZPE) was calculated using **eq A4.40**.

$$ZPE = \sum_{i=1}^N \frac{h \cdot c \cdot \nu_i}{2} \quad (\text{A4.40})$$

where h is Planck's constant, c is the speed of light, and ν_i is the wave number of vibrational mode, i , of the molecule.

The total partition function is decoupled into the translational, rotational, and vibrational contributions, **eq A4.41**.

$$Q(T = 280^{\circ}\text{C}) = q_{trans} \cdot q_{rot} \cdot q_{vib} \quad (\text{A4.41})$$

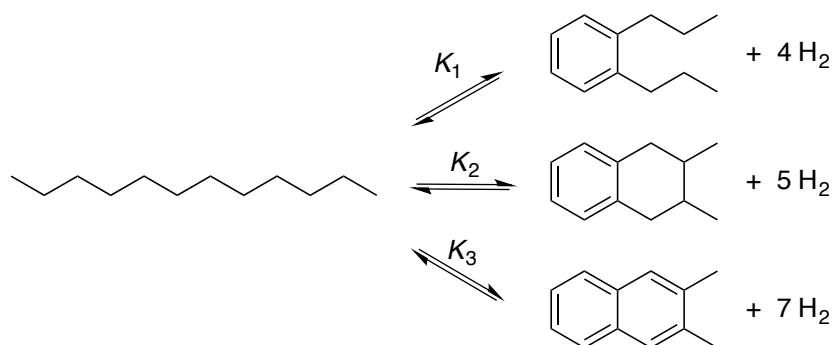
For each reaction, the Gibbs free energy of reaction is calculated using the algebraic sum of the free energies of the reactants and products, **eq A4.42**.

$$\Delta G_{rxn,i}(T = 280^{\circ}\text{C}) = \sum_{j=1}^N n_{ij} \cdot G_j(T = 280^{\circ}\text{C}) \quad (\text{A4.42})$$

where n_{ij} represents the stoichiometric coefficient of species j in reaction i .

4.7.2.9.3. Thermodynamic Yield Assessment

To assess the thermodynamic yield of aromatics from PE, the conversion of n -dodecane to 1,2-dipropylbenzene, 2,3-dimethyltetralin, 2,3-dimethylnapthalene are considered as model reactions (**Scheme A4.5**).



Scheme A4.5. Conversion of *n*-dodecane to 1,2-dipropylbenzene, 2,3-dimethyltetralin, and 2,3-dimethylnaphthalene, respectively.

The equilibrium concentrations of *n*-dodecane, 1,2-dipropylbenzene, 2,3-dimethyltetralin, 2,3-dimethylnaphthalene are denoted as [D], [B], [T], and [N], respectively. The equilibrium constants for the conversion of *n*-dodecane to 1,2-dipropylbenzene, 2,3-dimethyltetralin, and 2,3-dimethylnaphthalene, each generating H₂ as by products, are denoted as K_1 , K_2 , and K_3 , respectively, **eq A4.43**. Assuming all three reactions reach thermodynamic equilibrium simultaneously, **eq A4.44** is obtained.

$$K_1 = \frac{[B]P_{H_2}^4}{[D]} ; K_2 = \frac{[T]P_{H_2}^5}{[D]} ; K_3 = \frac{[N]P_{H_2}^7}{[D]} \quad (\text{A4.43})$$

$$[D] : [B] : [T] : [N] = 1 : \frac{K_1}{P^4(H_2)} : \frac{K_2}{P^5(H_2)} : \frac{K_3}{P^7(H_2)} \quad (\text{A4.44})$$

The relative fraction of each component, using [B] as an example, can be calculated as shown in **eq A4.45**.

$$\frac{[B]}{[D]+[B]+[T]+[N]} (\%) = \frac{\frac{K_1}{P^4(H_2)}}{1 + \frac{K_1}{P^4(H_2)} + \frac{K_2}{P^5(H_2)} + \frac{K_3}{P^7(H_2)}} (\%) \quad (\text{A4.45})$$

The equilibrium constants of K_1 , K_2 and K_3 are computed using DFT calculation (**Section 4.7.2.9.1** and **Section 4.7.2.9.2**). The obtained equilibrium constants are $K_1 = 1.25$, $K_2 = 4.46$, $K_3 = 111$. The equilibrium concentration of [B] and [T] vs $P(H_2)$ are plotted in **Figure A4.17**, predicted to first increase with increasing $P(H_2)$ and then decrease.

4.7.3. Supplemental Figures

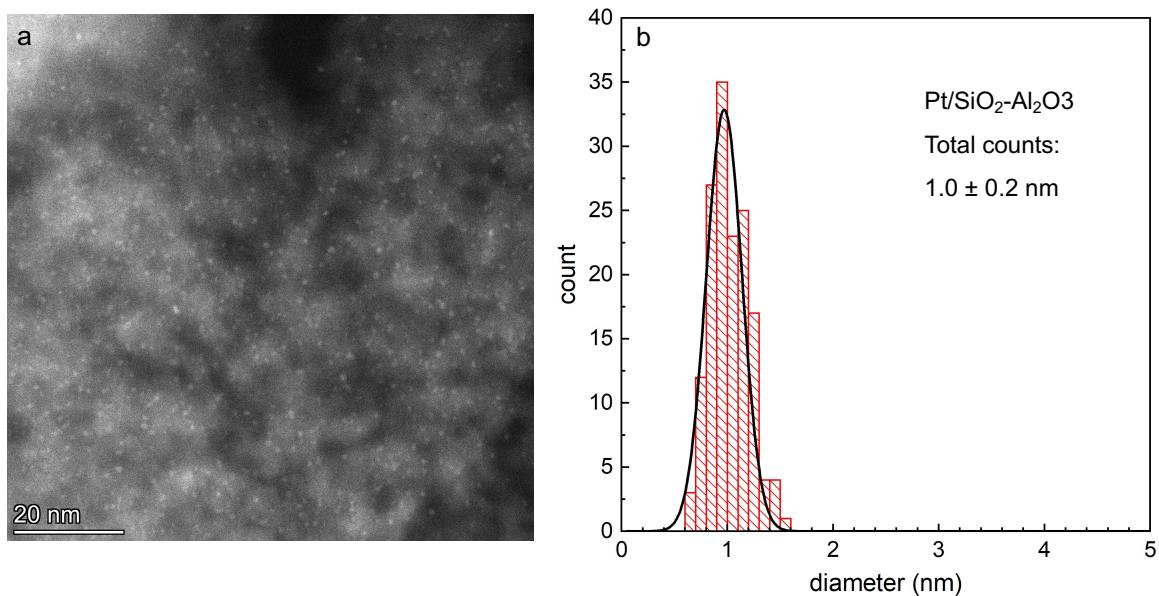


Figure A4.1. (a) HAADF-STEM image, and (b) Pt particle size histogram, for fresh, reduced Pt/SiO₂-Al₂O₃ (1.7 wt% Pt). The average nanoparticle size, obtained by fitting a Gaussian function to the distribution, is (1.0 ± 0.2) nm.

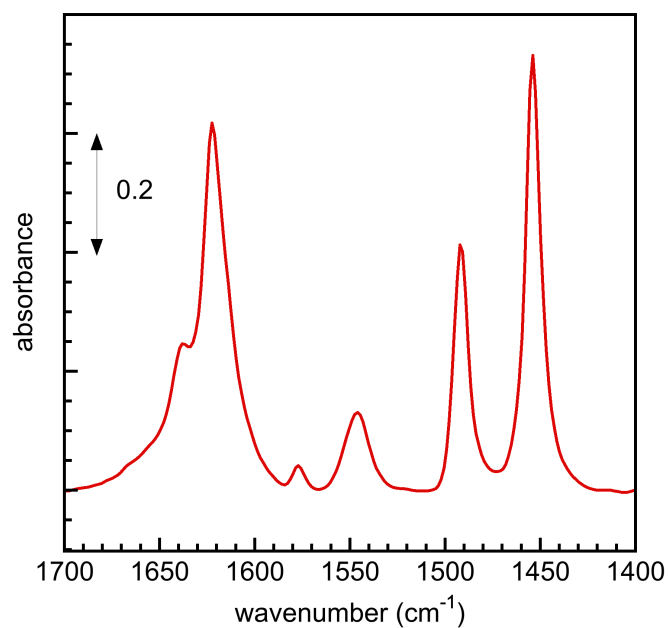


Figure A4.2. IR spectra of Pt/SiO₂-Al₂O₃ (10.0 mg) recorded after adsorption of excess pyridine at room temperature, followed by desorption at 150 °C and ca. 30 mTorr for 30 min. The areas of the peaks at 1455 and 1545 cm⁻¹, corresponding to pyridine interacting with LAS and BAS, respectively, were used for quantification.

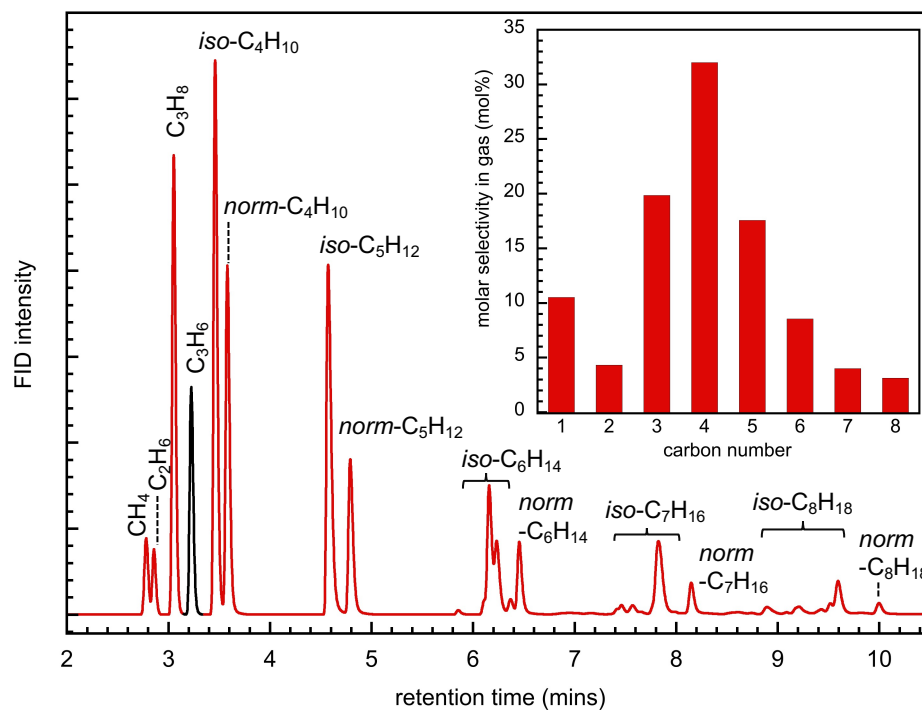


Figure A4.3. GC-FID of gas products and their molar distribution (inserted), recovered from the catalytic conversion of PE (0.200 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) using Pt/SiO₂-Al₂O₃ (0.100 g) for 24 h at 275 °C under $P(\text{initial H}_2) = 0$ bar. Propene (black peak) was used as internal standard.

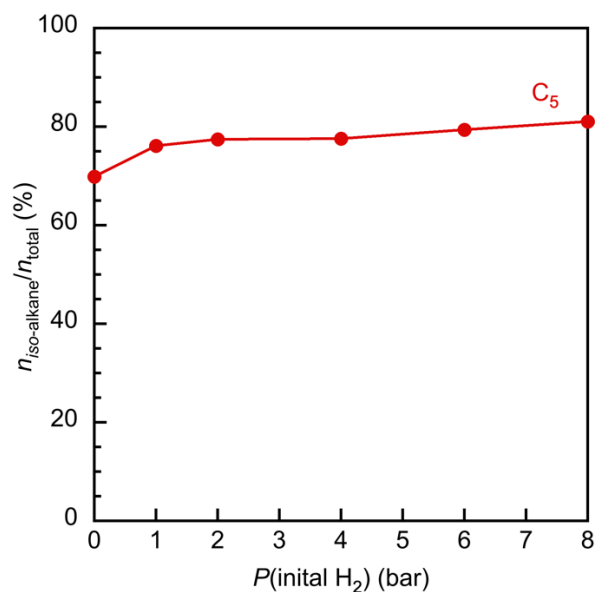


Figure A4.4. Molar ratio of *iso*-pentane to pentanes (*iso*- and *norm*-) (red), recovered from the catalytic conversion of PE (0.200 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) using Pt/SiO₂-Al₂O₃ (0.100 g) for 24 h at 275 °C under different $P(\text{initial H}_2)$ from 0 to 8 bar.

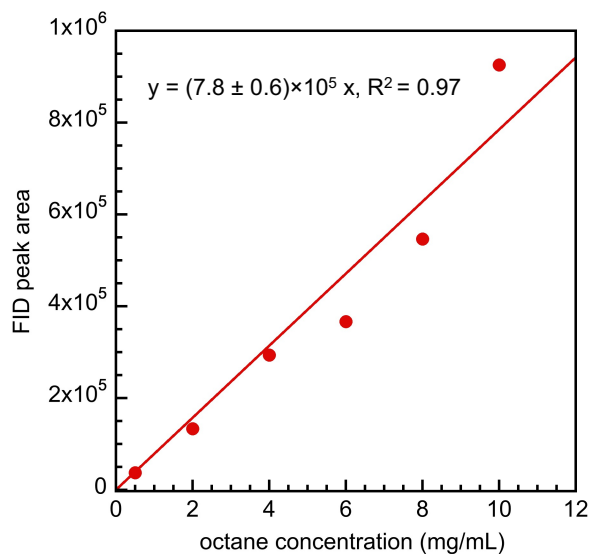


Figure A4.5. Calibration curve for the *n*-octane response of the flame ionization detector. The line is a least-squares fit of the equation $y = mx$ to the data.

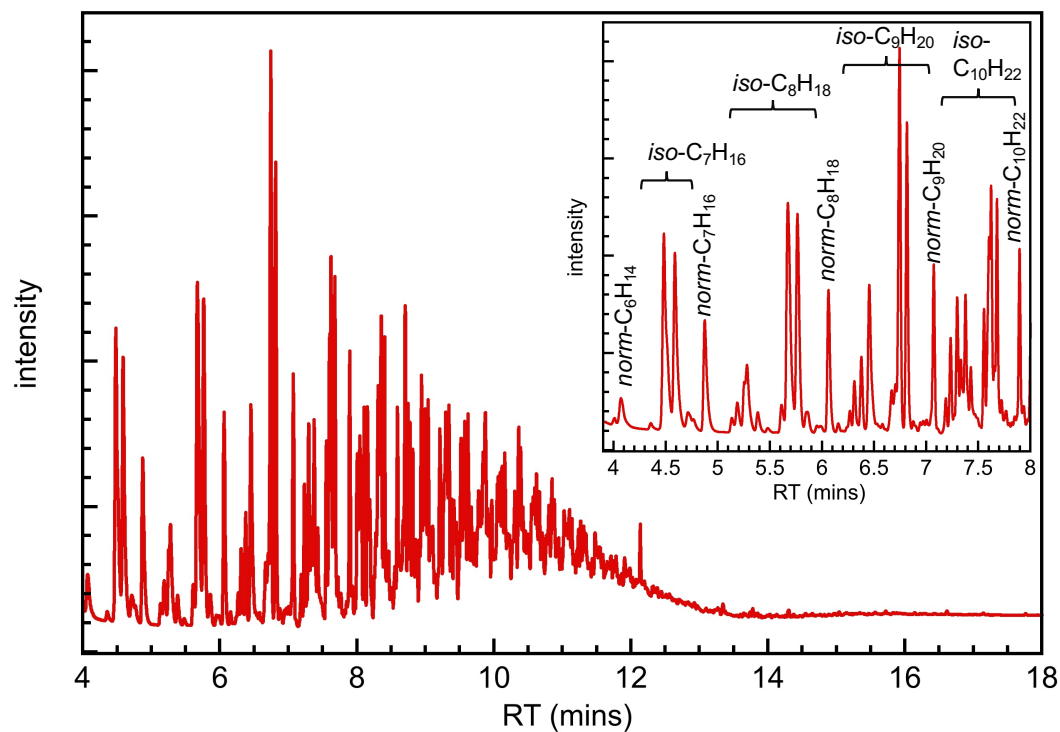


Figure A4.6. Distribution of liquid products obtained from Pt/SA (0.100 g) reacting with PE (0.200 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) after 24 h reaction at 275 °C under $P(\text{initial H}_2) = 0$ bar. The inserted figure is a zoom-in of the small-molecular weight peak, along with the corresponding assignment of major peaks.

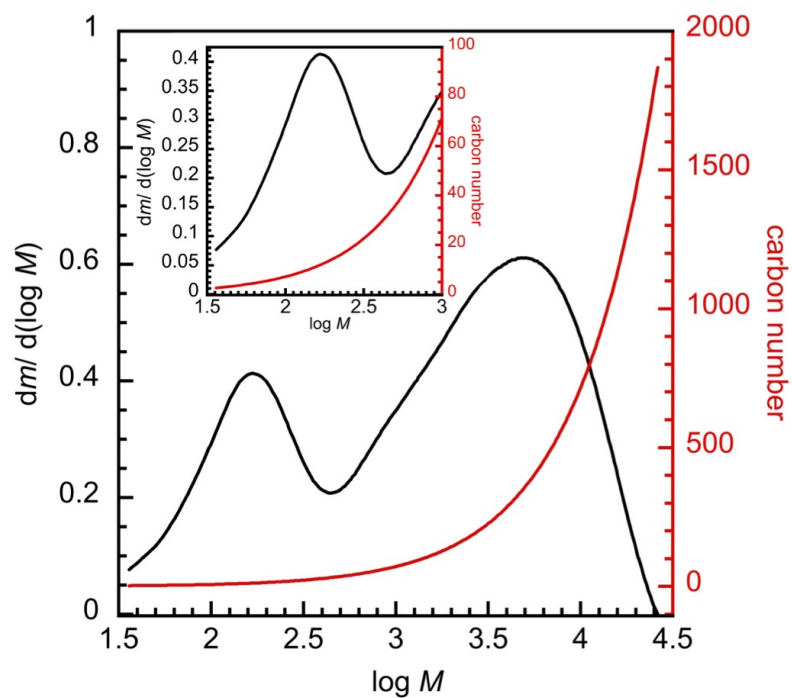


Figure A4.7. Products distribution (black) and corresponding carbon number (red) of products from Pt/SA (0.100 g) reacting with PE (0.200 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) after 24 h reaction at 275 °C under $P(\text{initial H}_2) = 0$ bar. The inserted figure is a zoom-in for the small-molecular weight peak. $C_{>30}$ is used for the analysis of wax product.

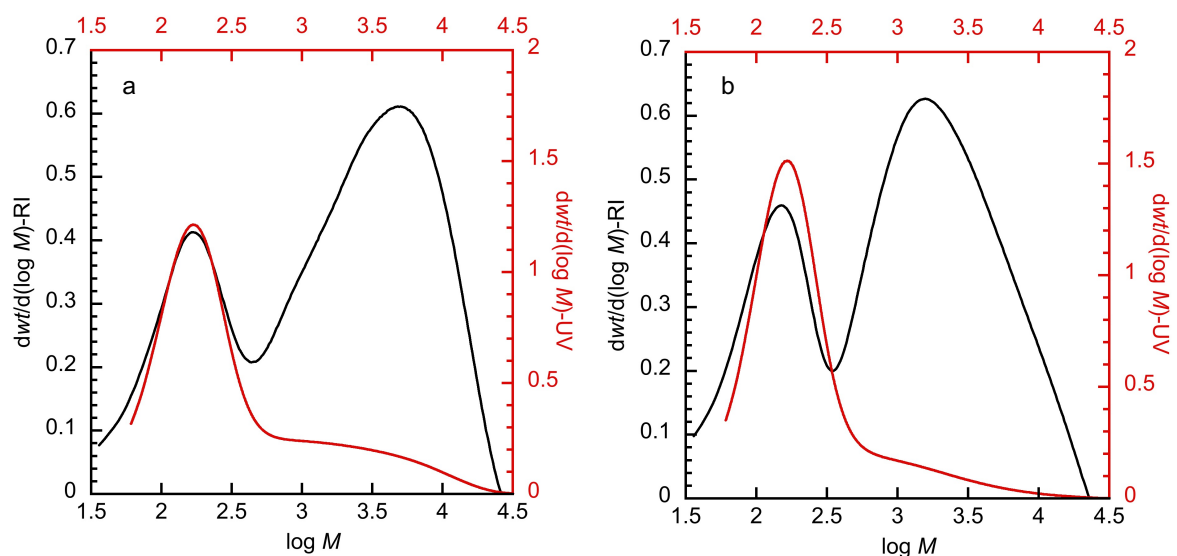


Figure A4.8. GPC-RI (black) and UV (red) chromatogram of liquid hydrocarbons recovered from the catalytic conversion of PE (0.200 g , $M_w = 3.5 \times 10^3\text{ g mol}^{-1}$, $\bar{D} = 1.9$) using Pt/SA (0.100 g) for 24 h under $P(\text{initial H}_2) = 0\text{ bar}$ (a) and 1 bar (b), respectively.

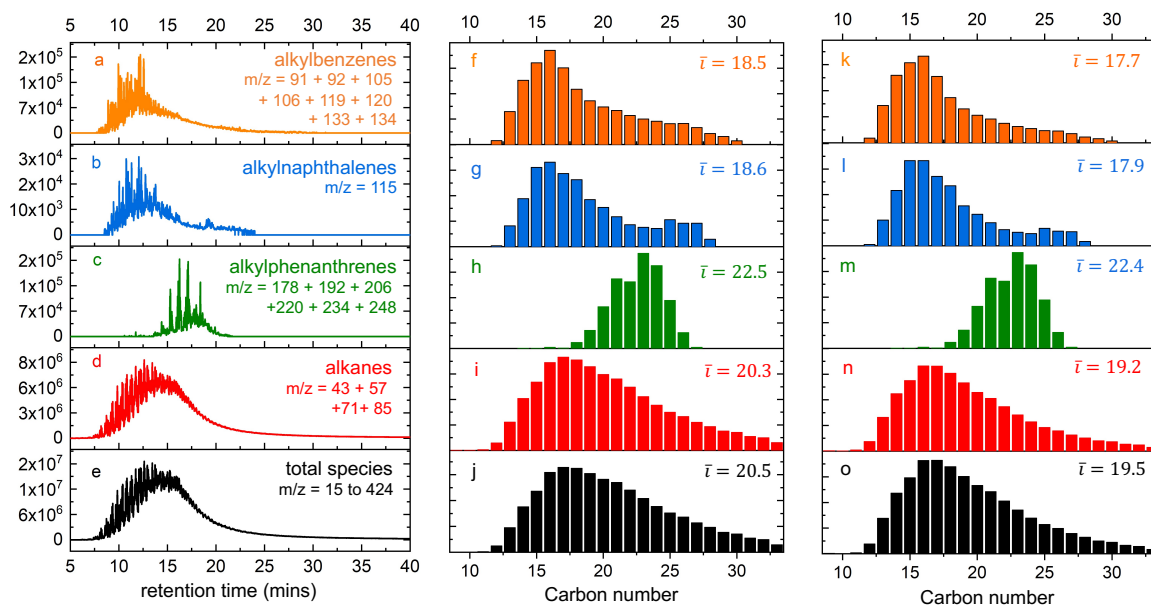


Figure A4.9. GC-MS ion chromatography plot (a-e), molar distribution (assuming MS response factor depends only on the type of hydrocarbon, f-j), and molar distribution (assuming MS response factor depends on each type and molecular weight of hydrocarbon, i-l) of alkylbenzenes (orange, a, f, k), alkylnaphthalene (blue, b, g, l), alkylphenanthrene (green, c, h, m), alkanes (d, i, n), and total species (black, d, h, l) in the liquid products, obtained from the reaction of PE (0.200 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) catalyzed by Pt/SiO₂-Al₂O₃ (0.100 g) after 24 h at 275 °C under $P(\text{initial H}_2) = 4 \text{ bar}$.

Since low-molecular weight hydrocarbons in the liquid fraction are close to the GPC mass detection limit (200 g/mol), the liquid was also analyzed by GC-MS (**Figure A4.7**). Low molecular weight alkanes, alkylbenzenes, and alkylnaphthalenes all have molecular weight distributions close to that of the total hydrocarbon distribution in the liquid component. The alkylphenanthrene distribution is shifted towards higher carbon numbers (as expected, since the phenanthrene ring itself contains 14 carbons).

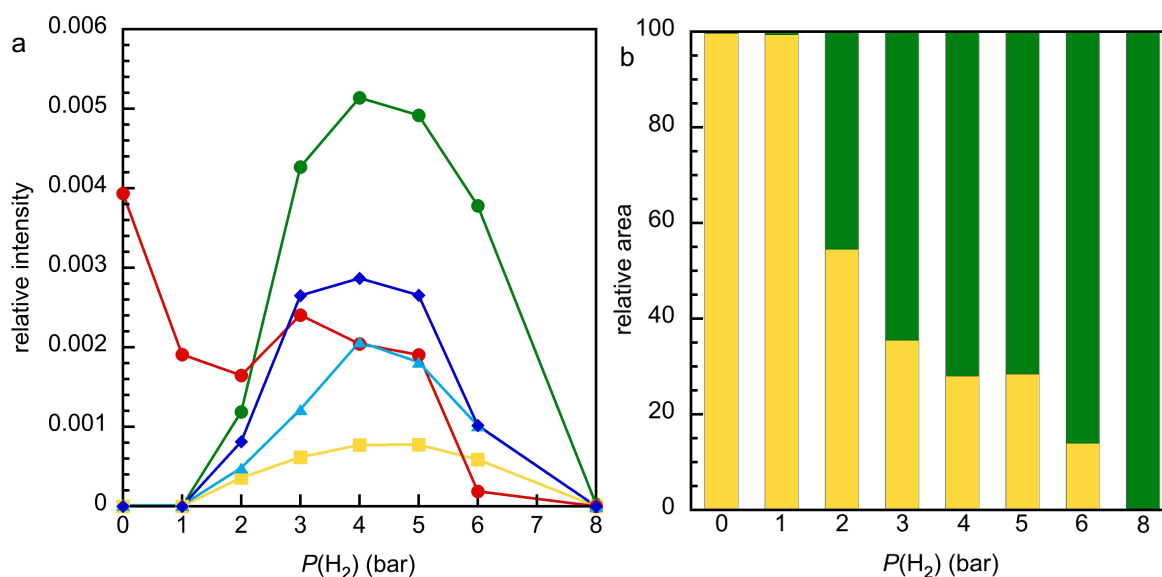


Figure A4.10. (a) Intensity of characteristic ions of benzene rings ($m/z = 91+92+105+106+119+120+133+134$, green), decalin ($m/z = 138+152+166+180+194$, blue), tetralin ($m/z = 132+146+160+174+188+202+216+230$, light blue), naphthalene ($m/z = 115$, yellow), and phenanthrene ($m/z = 178+192+206+220+234+248$, red) relative to the total ion counts, respectively, and (b) Intensity of the characteristic ions of polyaromatics (including naphthalene and phenanthrene, yellow) and monoaromatics (benzene and decalin, green) relative to the total aromatics (sum of monoaromatics and polyaromatics), measured by GC-MS of the liquid products, obtained from the reaction of PE (0.200 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) catalyzed by Pt/SiO₂-Al₂O₃ (0.100 g) after 24 h at 275 °C under $P(\text{initial H}_2) = 0$ -8 bar.

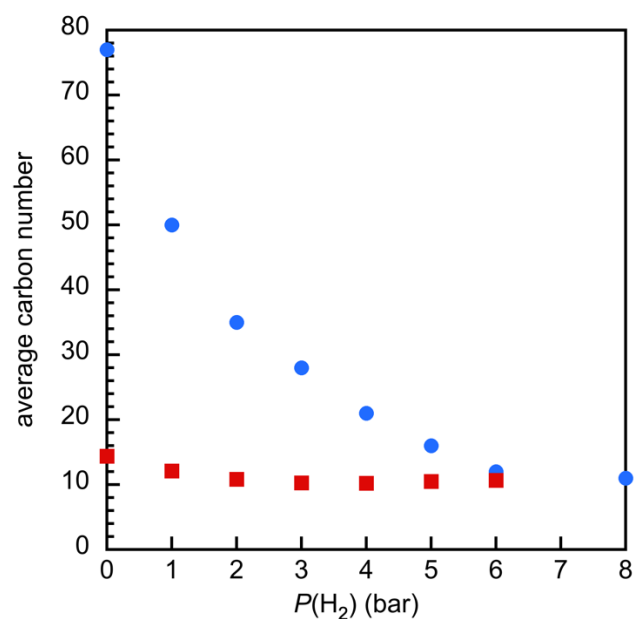


Figure A4.11. Average carbon number of alkylaromatics (red) and total hydrocarbons (blue) in the liquid and wax fraction obtained from the reaction of PE (0.200 g, $M_w = 3.5 \times 10^3$ g mol⁻¹, $D = 1.9$) catalyzed by Pt/SiO₂-Al₂O₃ (0.100 g, 1.7 wt%) after 24 h at 275 °C under $P(\text{initial H}_2) = 0\text{-}8$ bar, measured by GPC-UV and -RI detection, respectively.

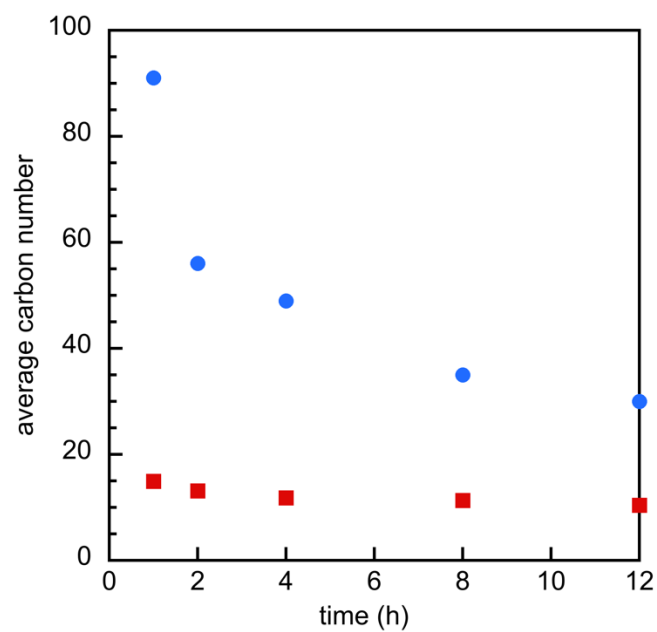


Figure A4.12. Average carbon number of aromatics (red) and total hydrocarbons (blue) in the liquid and wax fraction, obtained from the reaction of PE ($M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) catalyzed by Pt/SiO₂-Al₂O₃ (0.100 g) for 0-12 h at 275 °C under $P(\text{H}_2) = 2$ bar, measured by GPC-UV and -RI detection, respectively.

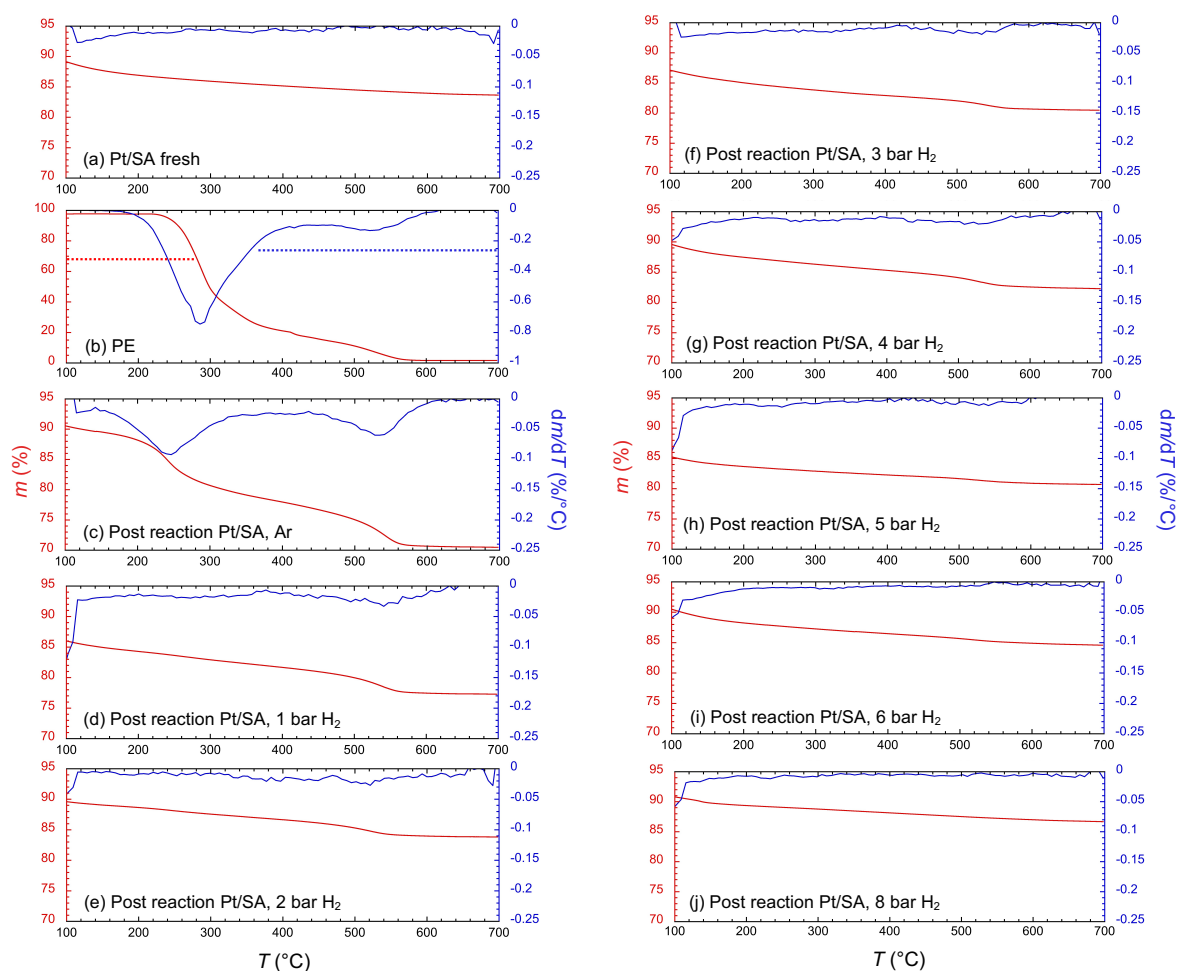


Figure A4.13. TGAs (red) measured in air, and the corresponding DTGAs (blue), for (a) fresh Pt/SiO₂-Al₂O₃, (b) PE ($M_w = 3.5 \times 10^3$ g mol⁻¹, $\bar{D} = 1.9$), and the solid residues, recovered by CH₂Cl₂ extraction, after the reaction of PE (0.200, $M_w = 3.5 \times 10^3$ g mol⁻¹, $\bar{D} = 1.9$) catalyzed by Pt/SiO₂-Al₂O₃ (0.100 g) at 275 °C for 24 h under $P(\text{initial H}_2)$ from (c) 0, (d) 1 bar, (e) 2 bar, (f) 3 bar, (g) 4 bar, (h) 5 bar, (i) 6 bar, and (j) 8 bar, respectively.

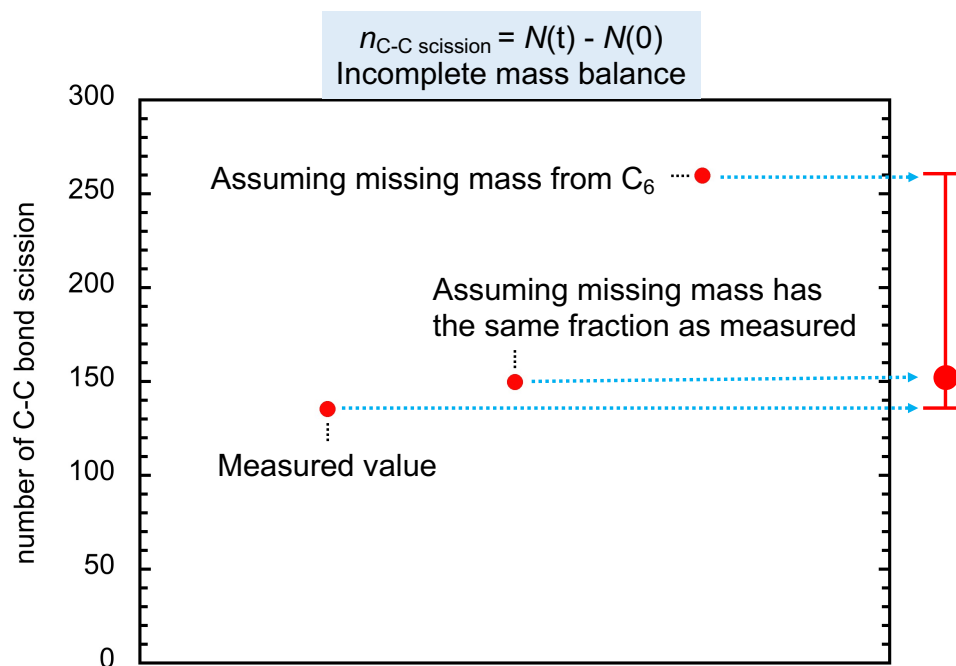


Figure A4.14. Measured C-C bond scission and mass-corrected C-C bond scission by assuming missing mass from different mass fraction in the reaction of PE (0.200, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) catalyzed by Pt/SiO₂-Al₂O₃ (0.100 g), at 275 °C under $P(\text{initial H}_2) = 0$ bar.

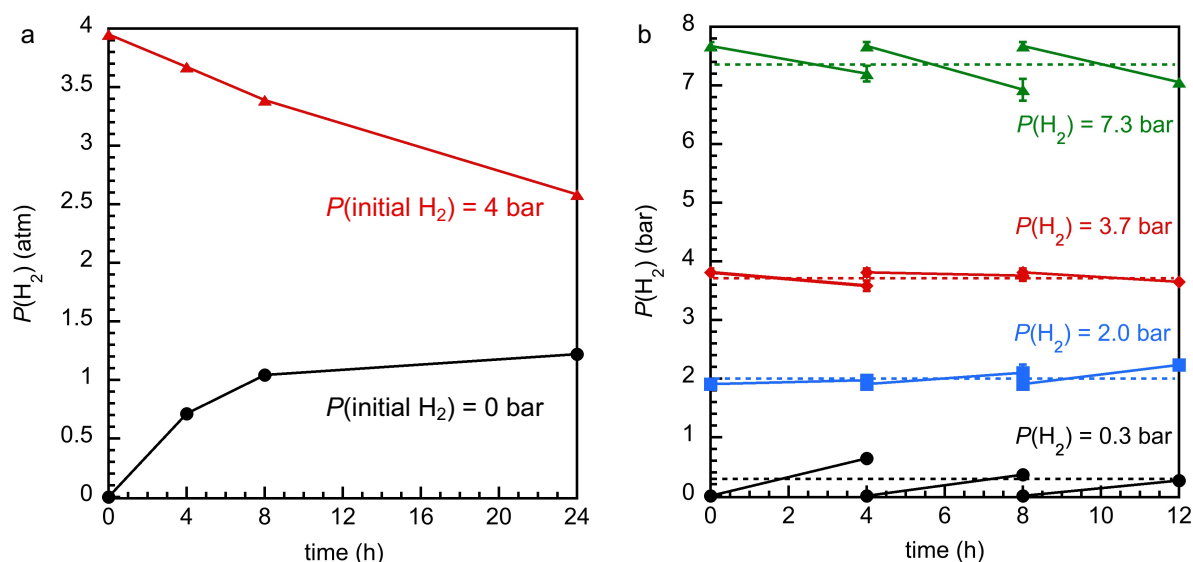


Figure A4.15. (a) $P(\text{H}_2)$ at various reaction times, measured at room temperature, with $P(\text{initial H}_2)$ of 0 (black) and 4 bar (red), respectively, in the reaction of PE (0.200, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) catalyzed by Pt/SiO₂-Al₂O₃ (0.100 g), at 275 °C. (b) $P(\text{H}_2)$ before and after each 4-h reaction (connected by a solid line) under $P(\text{initial H}_2)$ from 0 (black), 2 bar (blue), 4 bar (red), and 8 bar (green), respectively, in the reaction of PE (0.200, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) catalyzed by Pt/SiO₂-Al₂O₃ (0.100 g), at 275 °C. Between each short reactions, the target gas is refilled before the next stage of the reaction, maintaining a relatively constant $P(\text{H}_2)$, more details please see **Section 4.7.2.3.2. Pseudo-Constant $P(\text{H}_2)$ Depolymerization**. Dashed lines represent the average $P(\text{H}_2)$ in one set of reactions, calculated as the average $P(\text{H}_2)$ of 6 measured points.

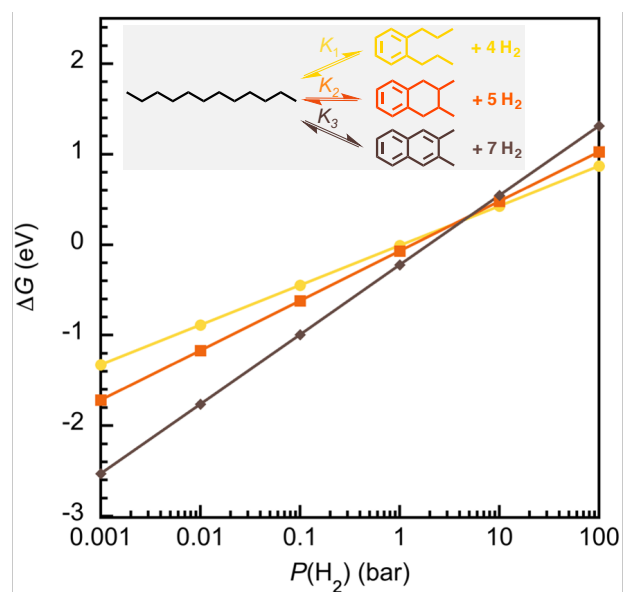


Figure A4.16. DFT calculated Gibbs free energy for the conversion of *n*-dodecane to 1,2-dipropylbenzene (reaction 1, yellow), 2,3-dimethyl-1,2,3,4-tetrahydronaphthalene (reaction 2, orange), 2,3-dimethylnaphthalene (reaction 3, brown), respectively, at 280 °C under different $P(\text{H}_2)$.

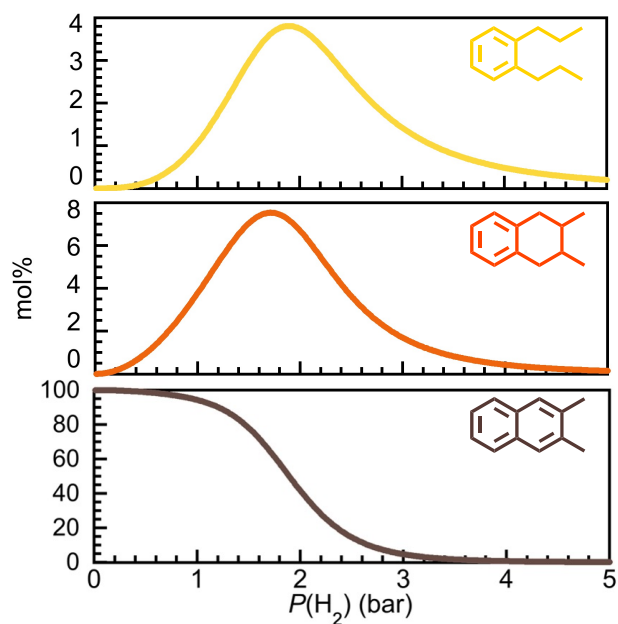


Figure A4.17. Equilibrium yield of 1,2-dipropylbenzene (yellow), 2,3-dimethyl-1,2,3,4-tetrahydronaphthalene (orange), and 2,3-dimethylnaphthalene (brown) from the conversion of *n*-dodecane at 280 °C under various $P(\text{H}_2)$, based on **eq A4.45**. K_1 , K_2 , and K_3 were computed using DFT.

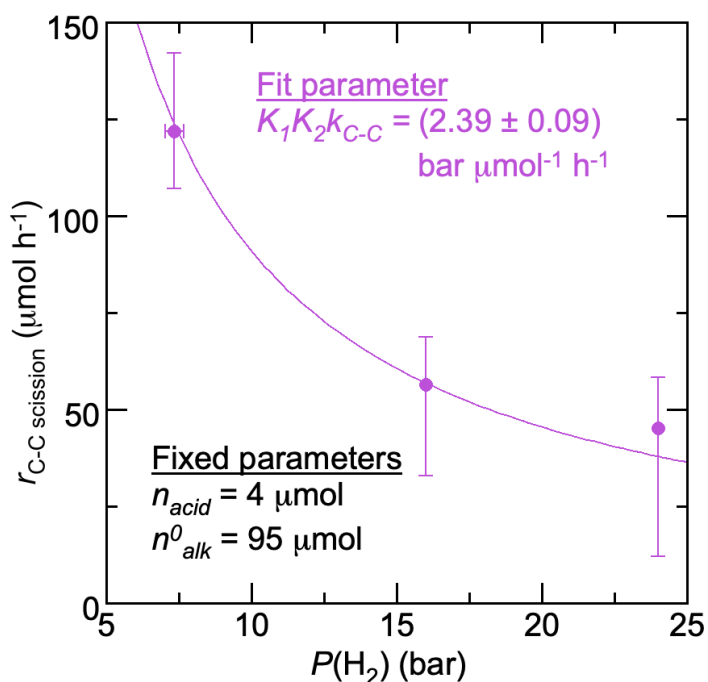


Figure A4.18. Effect of $P(\text{H}_2)$ on the rate of C-C bond scission for high pressure range of $P(\text{H}_2)$, showing curvefit of **eq 4.4**; ordinate error bars arise from the linear fits to the lower and upper bounds for $n_{\text{C-C scission}}$ as a function of time. Batch reaction conditions: 0.200 g PE ($M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$), Pt/SiO₂-Al₂O₃ (0.100 g), 275 °C. The reactor was evacuated and refilled with the appropriate amount of H₂ after each measurement.

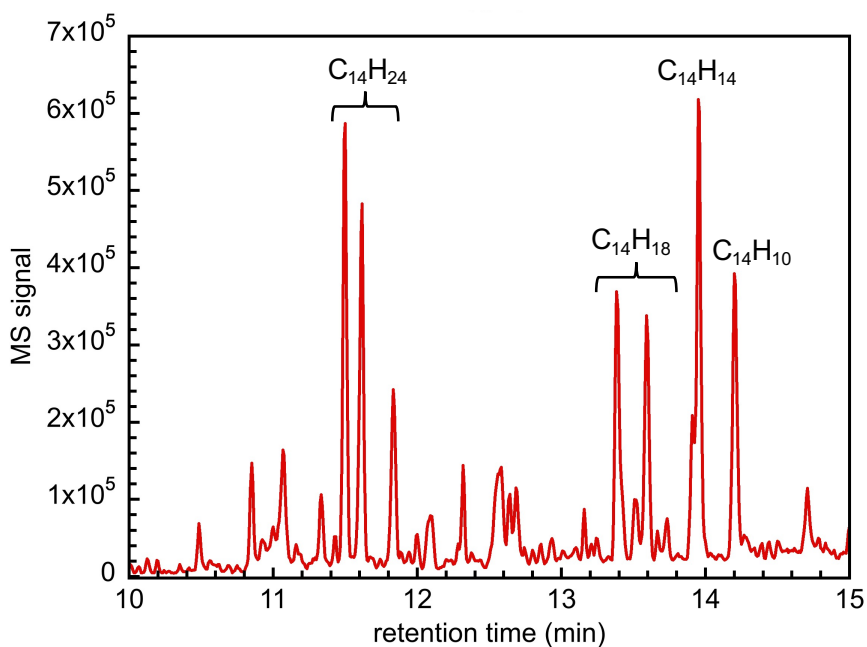


Figure A4.19. GC-MS of liquid products obtained from the reaction of a mixture of PE (0.200, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) and naphthalene (0.02 g) catalyzed by Pt/SiO₂-Al₂O₃ (0.100 g), at 275 °C under $P(\text{H}_2)$ of 4 bar after 12 h (three consecutive 4-h reactions). The major peaks are phenanthrene ($C_{14}H_{10}$) and its hydrogenated forms ($C_{14}H_{14}$, $C_{14}H_{18}$, and $C_{14}H_{24}$), as indicated. They were assigned using the NIST MS library. The most probable chemical structures are indicated in **Figure A4.20**.

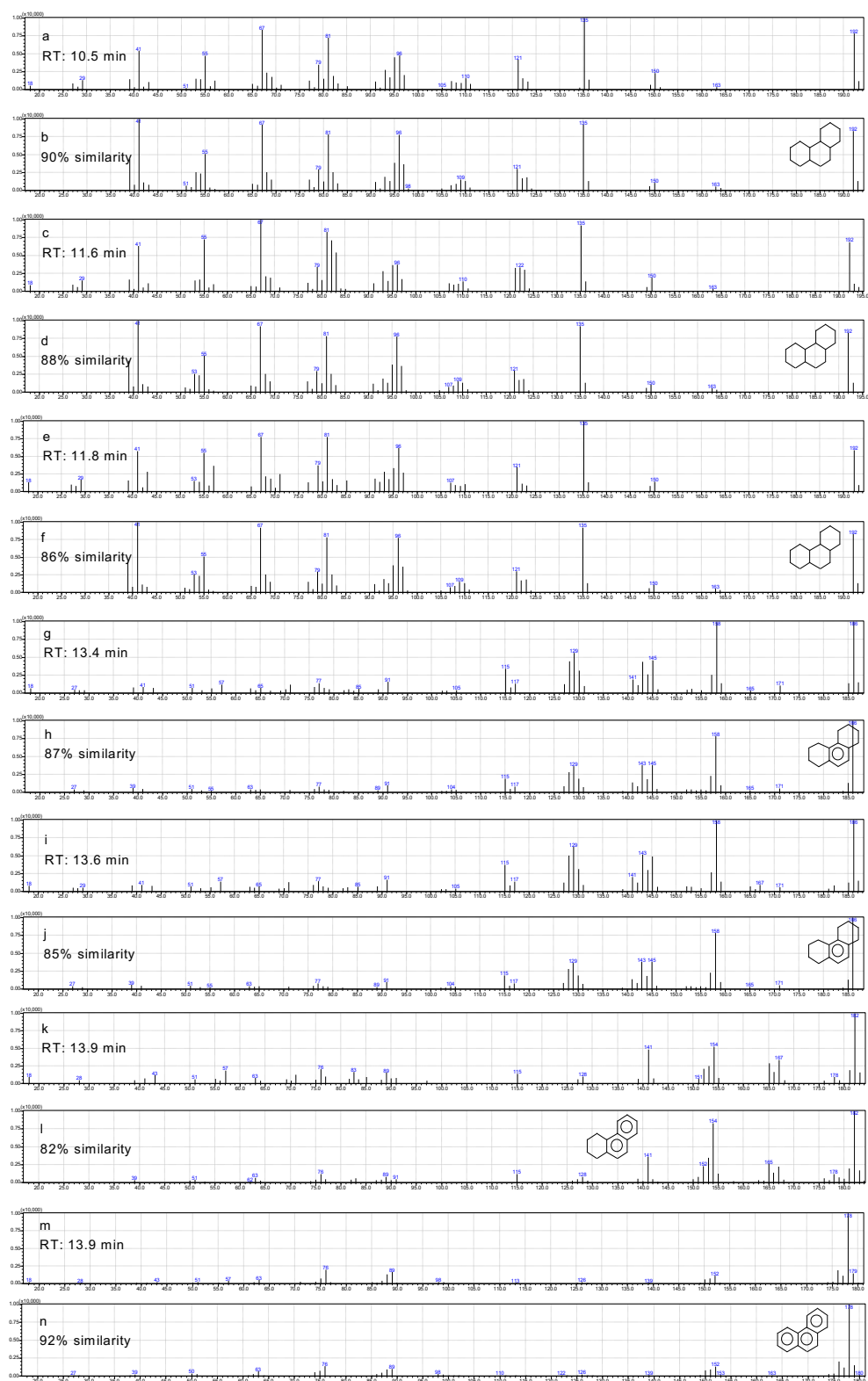


Figure A4.20. Comparison of mass spectra for products (a, c, e, g, i, k, m) with those from the NIST MS library (b, d, f, h, j, l, n). The reaction of PE (0.200, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) and phenanthrene (0.020 g) catalyzed by Pt/SiO₂-Al₂O₃ (0.100 g), at 275 °C under $P(\text{H}_2)$ of 4 bar after 12 h (three consecutive 4-h reactions).

4.7.4. Supplemental Tables

Table A4.1. Example of the reproducibility of distribution of hydrocarbon products generated in PE depolymerization reaction ^a

Masses of				Mass	$\bar{l}_{liq+wax}^c$	$n_{c-c \text{ scission}}^d$	n_{benz}^e	n_{naph}^e	n_{phen}^e	n_{benz}
hydrocarbon product recovery						(mmol)	(μmol)	(μmol)	(μmol)	$/n_{arom}$
types				^b						^f
(wt%)				(wt%)						(%)
GasLiquid Wax Solid										
g	h	i	j							
2	7	73	12	94	77	0.15	5	8	41	9
(12)	(162)	(6)								
3	6	66	21	96	80	0.14	5	5	34	11
(14)	(142)	(17)								

^a Reaction conditions: PE (0.200 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$), Pt/SiO₂-Al₂O₃ (0.100 g, 1.7 wt% Pt), stirred 10 mL Parr reactor, 275 °C, 24 h, under 2 bar of Ar (measured at room temperature at the start of the experiment). ^b Sum of masses for recovered gas, liquid, wax and solid hydrocarbons. ^c Average carbon number in combined liquid and wax fractions, estimated as $M_n/14$. ^d Number of C-C

bond scission events in 24 h, calculated as $N(24)-N(0)$, where $N(24)$ and $N(t)$ represent the total numbers of hydrocarbon chains present initially and after 24 h, respectively. Any missing mass was assumed to have the same molecular weight distribution as the recovered mass (**Section 4.7.2.5: Analysis of Carbon-Carbon Bond Scission**). ^e Yields of alkanes (n_{alk}), alkylbenzenes (n_{benz}), alkylnaphthalenes (n_{naph}), and alkylphenanthrenes (n_{phen}), estimated by combining the integrated ^1H NMR intensity and the GC-FID product distribution (**Section 4.7.2.4.2: Analysis on Selectivity and Yield of Aromatics**). ^f Molar selectivity of alkylbenzene relative to total aromatics. ^g $\text{C}_1\text{-C}_6$, as measured by GC-FID. ^h $\text{C}_7\text{-C}_{30}$, as measured by GC-FID. The value in parentheses is the number-averaged carbon number. ⁱ $\text{C}_{>30}$, measured by GPC-RI and calibrated using PS standards. The value in parentheses is the number-averaged carbon number, estimated as $M_n/14$. ^j Measured by TGA. The value in parentheses is the amount of unreacted PE, judged by being fully oxidized in air below 350 °C.

Table A4.2. ^1H NMR analysis of aromatic protons ^a

$P(\text{initial H}_2)$ ^b	Alkylbenzene ^c	Polyaromatic ^d		$H_{\text{aro}}/H_{\text{total}}$ (%)
(bar)	$H_{6.5-7.5}/H_{\text{arom}}$	$H_{7.5-8.3}/H_{\text{arom}}$	$H_{8.3-9.0}/H_{\text{arom}}$	
	(%)	(%)	(%)	
0	31	45	24	1.5
1	35	42	24	1.1
2	37	42	21	1.0
3	47	42	12	0.8
4	55	37	8	0.7
5	70	25	5	0.4
6	80	15	5	0.3
8	100	0	0	<0.1

^a Reaction condition: PE (0.200, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $\bar{D} = 1.9$) catalyzed by Pt/SiO₂-Al₂O₃ (0.100 g), at 275 °C for 24 h under $P(\text{initial H}_2)$ from 0 to 8 bar. ^b Pressure measured at room temperature before the reaction. Fraction of ^c alkylbenzene (6.5-7.5 ppm) and ^d polyaromatic protons (7.5-9.0 ppm, separately reported as 7.5-8.3 ppm and 8.3-9 ppm), respectively.

Table A4.3. ¹H NMR analysis of alkyl substituents on the aromatics ^a

<i>P</i> (initial H ₂) ^b (bar)	CH ₃ , <i>H</i> _{2-2.5} ^c	CH ₂ , <i>H</i> _{2.5-3.1} ^c	CH, <i>H</i> _{3.1-3.5} ^c	<i>q</i> average <i>H</i> _α per chain	<i>H</i> _α / <i>H</i> _{aro}	Average number of substituents
0	20	70	10	1.9	1.2	3
1	22	67	11	1.9	1.2	3
2	22	68	10	1.9	1.3	3
3	37	58	6	2.1	1.4	3
4	43	41	5	2.2	1.7	3
5	40	38	12	2.1	2.0	3
6	46	37	12	2.2	2.5	3
8	86	8	3	2.7	2.4	3

^a Reaction condition: PE (0.200, $M_w = 3.5 \times 10^3$ g mol⁻¹, $\bar{D} = 1.9$) catalyzed by Pt/SiO₂-Al₂O₃ (0.100 g) at 275 °C for 24 h under *P*(initial H₂) from 0 to 8 bar. ^b Pressure measured at room temperature before the reaction. ^c Fraction of different types of α-protons.

Table A4.4. Effect of assumptions on products distribution in the calculation of aromatic yield and selectivity in PE depolymerization products ^a

<i>P</i> (initial H ₂) ^b (bar)	Assumption one ^c			Assumption two ^d		
	<i>n</i> _{benz} (μmol)	<i>n</i> _{benz} / <i>n</i> _{arom} (%)	<i>n</i> _{arom} / <i>n</i> _{total} (%)	<i>n</i> _{benz} (μmol)	<i>n</i> _{benz} / <i>n</i> _{arom} (%)	<i>n</i> _{arom} / <i>n</i> _{total} (%)
0	5	9	65	5	9	67
1	8	19	27	9	19	28
2	10	26	17	10	26	17
3	18	45	12	18	45	12
4	22	57	9	22	57	9
5	20	75	5	20	75	4
6	14	85	2	14	85	2
8	<1	100	<1	<1	100	<1

^a Reaction conditions: PE (0.200 g, $M_w = 3.5 \times 10^3$ g mol⁻¹, $\bar{D} = 1.9$), Pt/SA (0.100 g, 1.7 wt% Pt), 275

°C, 24 h, 10 mL, in a stirred Parr reactor. ^b Pressure measured at room temperature before the reaction.

^c The average carbon number ($\bar{i}$) of alkylbenzenes, alkylnapthalenes, alkylphenanthrenes, and alkanes is assumed to be similar in the liquid range, see **Section 4.7.2.4.2: Analysis on Selectivity and Yield of Aromatics**.

^d The average carbon number of alkylbenzenes, alkylnapthalenes, and alkylphenanthrenes is assumed to be equal to the average carbon number of alkanes within the range of C₆₋₃₀, C₁₀₋₃₀, and C₁₄₋₃₀, respectively, see **Section 4.7.2.4.2: Analysis on Selectivity and Yield of Aromatics**.

Table A4.5. H₂ balance (mmol) in catalytic conversion of PE ^a

$P_{\text{initial H}_2}$ ^b (bar)	$n_{\text{H}_2(\text{I})}$ ^c	$n_{\text{H}_2(\text{G})}$ ^d	$n_{\text{H}_2(\text{C})}$ ^e	$n_{\text{H}_2(\text{F})}$ ^f	$n_{\text{H}_2(\text{I})} + n_{\text{H}_2(\text{G})} -$ $n_{\text{H}_2(\text{C})}$ ^g
0	0	0.49	0.12(0.26)	0.49 ^h	0.37(0.23)
1.0	0.40	0.38	0.27(0.48)	0.56	0.51(0.30)
2.0	0.81	0.32	0.40(0.67)	0.71	0.73(0.46)
3.0	1.2	0.26	0.52(0.82)	0.92	0.64(0.94)
4.0	1.6	0.23	0.77(1.0)	1.0	0.83(1.1)
5.0	2.0	0.13	1.0(1.3)	1.2	0.8(1.1)
6.0	2.4	0.07	1.3(1.5)	1.3	1.0(1.2)
8.0	3.2	0.04	1.6(2.1)	1.4	1.1(1.6)
0	0	0.42	0.16(0.36)	0.51 ^h	0.06(0.26)
4.0	1.6	0.22	0.69(1.1)	1.2	0.72(1.1)

^a Reaction conditions: PE (0.200 g, $M_w = 3.5 \times 10^3$ g mol⁻¹, $D = 1.9$), Pt/SiO₂-Al₂O₃ (0.100 g, 1.7 wt% Pt), stirred 10 mL Parr reactor, 275 °C, 24 h, except as noted below. ^b Measured at room temperature at the start of the experiment. ^c Initial amount of H₂, calculated using ideal gas law, $n_{\text{H}_2(\text{I})} = P_{\text{initial H}_2} \cdot V / RT$. ^d Amount of H₂, generated by aromatization, calculated as $n_{\text{H}_2(\text{G})} = 4n_{\text{benz}} + 7n_{\text{naph}} + 10n_{\text{phen}}$. ^e Equals to the number of measured C-C bond scission, calculated by **eq A4.15**. The number in the parenthesis show the upper limit of number of C-C bond scission, due to incomplete collection of mass, calculated by **eq A4.16**. ^f Amount of free H₂ in the reactor headspace after reaction, calculated using **eq A4.18-4.19**,

except where noted. ^g Amount of predicted free H₂ based on measured aromatics yield and number of C-C bond scission. The number in the parenthesis show the low limit of predicted amount of H₂, due to the impact of incomplete collection of mass on the number of C-C bond scission. ^h Measured by GC-TCD, using **eq A4.17**.

Table A4.6. Effect of $P(\text{H}_2)$ on hydrocarbon product distribution, and C-C bond scission events in PE depolymerization ^a

$P_{\text{H}_2}^{\text{b}}$	Reaction	Gas ^c	Liquid ^c		Wax ^d		$m_{\text{solid}}^{\text{e}}$	$\frac{I_{\text{liq}}}{wax}^{\text{f}}$	$n_{\text{c-c}}$	$n_{\text{arom}}^{\text{h}}$	$n_{\text{arom}}^{\text{i}}$	$n_{\text{arom}}^{\text{j}}$
(bar)	time	m_{gas}	m	$\bar{t}$	m	$\bar{t}$	(wt%)		scission,	(μmol)	rings ⁱ	rings/ n_{total}
	(h)	(wt%)	(wt%)		(wt%)				$C_{\text{total}}^{\text{g}}$	(μmol)	(μmol)	j
									(μmol)			(%)
0.2	1	1	3	11	23	136	69	58	65	28	44	64
	2	1	4	11	31	127	61	58	76	31	50	64
	4	1	8	16	54	169	31	75	85	38	94	52
	8	2	8	16	46	125	38	60	150	41	93	53
(4+4)												
2.0	1	1	5	13	70	167	23	64	62	10	19	18
	2	2	13	14	73	125	10	55	183	16	30	12
	4	3	22	16	66	139	3	52	248	20	43	11
	8	4	29	16	51	112	1	28	416	17	41	7
(4+4+4)												

(4+4)												
12	7	32	16	42	90	0	16	590	23	45	8	
(4+4+4)												
3.7	1	2	8	10	72	180	15	64	137	3	4	2
	2	3	17	15	64	168	7	55	233	5	8	3
	4	6	17	16	63	139	1	52	341	9	15	6
	8	7	40	16	41	92	0	28	595	11	14	3
(4+4)												
12	9	62	14	10	59	0	16	1005	10	13	2	
(4+4+4)												
7.3	1	1	6	9	33	147	58	45	107	<1	<1	<1
	2	1	18	12	36	155	34	31	252	<1	<1	<1
	4	6	23	15	66	134	0	44	394	<1	<1	<1
	8	14	46	14	31	90	0	21	942	<1	<1	<1
(4+4)												
12	28	42	13	12	52	0	16	1498	<1	<1	<1	

(4+4+4)												
16	12	5	43	14	30	109	4	22	678	-	-	-
(4+4+4)												
24	12	4	29	14	40	77	3	27	542	-	-	-
(4+4+4)												
3.7 ^k	12	6	48	15	10	80	13	18	759	15	21	3
(4+4+4)												
3.7 ^l	12	1	5	14	58	185	37	98	0	64	117	100
(4+4+4)												

^a Reaction conditions: PE (0.200 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) catalyzed by Pt/SA (0.100 g, 1.7 wt% Pt) at 275 °C for 1-12 h. ^b Average pressure during the reaction, see **Figure A4.15b**. ^c C₇-C₃₀. Measured by GC-FID. ^d C_{>30}. Measured by GPC-RI, calibrated with PS standards. ^e Measured by weighing mass. ^f Average carbon number in combined liquid and wax products, estimated as $M_w/14$. ^g C-C bond scission events ($n_{C-C \text{ scission}}$), calculated as $N(t)-N(0)$, where $N(0)$ and $N(t)$ represent the total numbers of chains present at time 0 and time t , respectively. To calculate $n_{C-C \text{ scission}}$, any missing mass was assumed to have the same molecular weight distribution as the fraction collected (**Section 4.7.2.5: Analysis of Carbon-Carbon Bond Scission**). ^h Total yield of alkylaromatics, calculated as $n_{arom} = n_{benz} + n_{naph} + n_{phen}$. ⁱ Yield of six-member aromatic rings, calculated as $n_{arom \text{ rings}} = n_{benz} + 2n_{naph} + 3n_{phen}$. Here, each naphthalene and phenanthrene contains 2 and 3 aromatic rings, respectively. ^j Molar selectivity of alkylaromatics relative to total hydrocarbons (n_{total}), where $n_{total} = n_{alk} + n_{benz} + n_{naph} + n_{phen}$. Along with PE, ^k 2.0 mg and ^l 20.0 mg of phenanthrene (C₁₄H₁₀) were loaded as reactants, respectively.

Table A4.6. Fitting result of aromatization kinetics ^a

$P(\text{H}_2)$	k_c ^b (h^{-1})	$K_2 n_{\text{alk}}^0 / (P_{\text{H}_2}^3 + K_2)$ ^c (μmol)
0.2	0.6(0.1)	95(4)
2.0	0.6(0.1)	44(2)
3.7	0.4(0.2)	15(2)
7.3	3.7(9.6)	0.2(0.1)

^a Reaction condition: catalytic conversion of PE (0.200 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $\mathcal{D} = 1.9$) using Pt/SiO₂-Al₂O₃ (0.100 g) at 275 °C under $P(\text{H}_2)$ from 0.2 to 7.3 bar. ^b Rate constant of alkane dehydrocyclization. ^c Number of aromatic rings ($n_{\text{arom rings}}$) used in the fitting are reported in **Table A4.4**. Numbers in parenthesis indicate standard deviation.

Table A4.7. Fitting result of H₂ dependence on the maximum yield of aromatic rings ^a

n_{alk}^0 ^b (μmol)	K_a ^c
95(2)	7(1)

^a Reaction condition: catalytic conversion of PE (0.200 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $\mathcal{D} = 1.9$) using Pt/SiO₂-Al₂O₃ (0.100 g) at 275 °C under $P(\text{H}_2)$ from 0.2 to 7.3 bar. ^b Number of starting alkanes. ^c Equilibrium constant of dehydrogenation of cycloalkane to aromatic. Numbers in parenthesis indicate standard deviation.

Table A4.8. Linear fitting result of C-C bond scission kinetics ^a

$P(\text{H}_2)$	$r_{\text{C-C, measured}}$ ^b ($\mu\text{mol/h}$)	$r_{\text{C-C, Ctotal}}$ ^c ($\mu\text{mol/h}$)	$r_{\text{C-C, C6}}$ ^d ($\mu\text{mol/h}$)
0.2	16.8	18.5	31.2

2.0	43.2	54.0	83.0
3.7	68.3	84.0	108.6
7.3	101.6	121.8	136.6
16	44.3	56.5	80.0
24	32.1	45.2	78.2

^a Reaction condition: catalytic conversion of PE (0.200 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) using Pt/SiO₂-Al₂O₃ (0.100 g) at 275 °C under $P(\text{H}_2)$ from 0.2 to 24 bar. ^b Number of C-C bond scission ($n_{\text{C-C}}$ scission) used in the fitting are reported in **Table A4.4**. ^c Mass-corrected number of C-C bond scissions. Any missing mass was assumed to have the same molecular weight distribution as the fraction collected, see **Section 4.7.2.5 Analysis of Carbon-Carbon Bond Scission**, the numbers are reported in **Table A4.3**. ^d Mass-corrected number of C-C bond scissions. Any missing mass was assumed to come from C₆, see **Section 4.7.2.5 Analysis of Carbon-Carbon Bond Scission**.

4.7.5. Additional References

1. Marinho, R.S., Silva, C.N. da, Afonso, J.C., and Cunha, J.W.S.D. da (2011). Recovery of platinum, tin and indium from spent catalysts in chloride medium using strong basic anion exchange resins. *J. Hazard. Mater.* 192, 1155–1160. 10.1016/j.jhazmat.2011.06.021.
2. Sun, J., Lee, Y.-H., Yappert, R.D., LaPointe, A.M., Coates, G.W., Peters, B., Abu-Omar, M.M., and Scott, S.L. (2023). Bifunctional tandem catalytic upcycling of polyethylene to surfactant-range alkylaromatics. *Chem.* 9, 2318–2336. 10.1016/j.chempr.2023.05.017.
3. Lee, Y.-H., Sun, J., Scott, S.L., and Abu-Omar, M.M. (2023). Quantitative analyses of products and rates in polyethylene depolymerization and upcycling. *STAR Protoc.* 4, 102575. 10.1016/j.xpro.2023.102575.

4. Itakura, M., Sato, K., Lusenкова, M.A., Matsuyama, S., Shimada, K., Saito, T., and Kinugasa, S. (2004). Molecular weight dependency of refractive index increment of polystyrene determined by uniform oligomers. *J. Appl. Polym. Sci.* *94*, 1101–1106. 10.1002/app.21006.
5. Zhang, F., Zeng, M., Yappert, R.D., Sun, J., Lee, Y.-H., LaPointe, A.M., Peters, B., Abu-Omar, M.M., and Scott, S.L. (2020). Polyethylene upcycling to long-chain alkylaromatics by tandem hydrogenolysis/aromatization. *Science* *370*, 437–441. 10.1126/science.abc5441.
6. Madhushaw, R.J., Lo, C.-Y., Hwang, C.-W., Su, M.-D., Shen, H.-C., Pal, S., Shaikh, I.R., and Liu, R.-S. (2004). Ruthenium-catalyzed cycloisomerization of o-(ethynyl)phenylalkenes to diene derivatives via skeletal rearrangement. *J. Am. Chem. Soc.* *126*, 15560–15565. 10.1021/ja045516n.
7. Cao, C.-T., Chen, M., Fang, Z., Au, C., and Cao, C. (2020). Relationship Investigation between $C(sp^2)-X$ and $C(sp^3)-X$ Bond Energies Based on Substituted Benzene and Methane. *ACS Omega* *5*, 19304–19311. 10.1021/acsomega.0c02964.
8. Ahlrichs, R., Bär, M., Häser, M., Horn, H., and Kölmel, C. (1989). Electronic structure calculations on workstation computers: The program system turbomole. *Chem. Phys. Lett.* *162*, 165–169. 10.1016/0009-2614(89)85118-8.
9. Treutler, O., and Ahlrichs, R. (1995). Efficient molecular numerical integration schemes. *J. Chem. Phys.* *102*, 346–354. 10.1063/1.469408.

10. Von Arnim, M., and Ahlrichs, R. (1998). Performance of parallel TURBOMOLE for density functional calculations. *J. Comput. Chem.* *19*, 1746–1757. 10.1002/(SICI)1096-987X(19981130)19:15<1746::AID-JCC7>3.0.CO;2-N.
11. Mardirossian, N., and Head-Gordon, M. (2016). ω B97M-V: A combinatorially optimized, range-separated hybrid, meta-GGA density functional with VV10 nonlocal correlation. *J. Chem. Phys.* *144*, 214110. 10.1063/1.4952647.
12. Perdew, J.P., Burke, K., and Ernzerhof, M. (1996). Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* *77*, 3865–3868. 10.1103/PhysRevLett.77.3865.
13. Grimme, S., Antony, J., Ehrlich, S., and Krieg, H. (2010). A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* *132*, 154104. 10.1063/1.3382344.

Chapter 5. Quantitative Analyses of Products and Rates in Polyethylene Depolymerization and Upcycling

Note: This chapter was adapted from the following publication.

Publication: Lee, Y.-H.,[#] **Sun, J.**,[#] Scott, S. L., Abu-Omar, M. M., “Quantitative Analyses of Products and Rates in Polyethylene Depolymerization and Upcycling,” *STAR Protocol*, **2023**, 4, 102575. ([#] co-first authors).

5.1. Abstract

Depolymerization and upcycling are promising approaches to managing plastic waste. However, quantitative measurements of reaction rates and analyses of complex hydrocarbon product mixtures arising from the depolymerization of polyolefins constitute significant challenges in this emerging field. Here, we detail methods for recovery and analysis of all products arising from batch depolymerization of polyethylene. We also describe quantitative analyses of reaction rates and selectivity for alkanes and aromatic products. This protocol can be extended to depolymerization of other plastics such as polypropylene, and to characterization of other product mixtures (including long-chain olefins). For complete details on the use and execution of this protocol, please refer to Sun et al. (2023).¹

5.2. Introduction

Two polyolefins, polyethylene (PE) and polypropylene (PP), comprise half of the annual global plastic production.² Due to their extensive use in single-use products, they also account for half of the resulting plastic waste.² Depolymerization of polyolefins is challenging because of the thermodynamic strength and low reactivity of the non-polar C-C bonds, as well as the

absence of chemical functionality in the polymers. Pyrolysis, practiced at elevated temperatures (typically ≥ 400 °C), results in a complex pyrolytic oil, as well as a large amount of non-volatiles and insoluble char.³ Molecular recycling/upcycling of polyolefins at milder temperatures can yield more useful and more targeted distributions of hydrocarbon products. Catalytic hydrogenolysis and/or hydrocracking of polyolefins in the presence of excess H₂ produces liquid hydrocarbons that may be suitable for use as fuels and lubricants.^{4,5} Tandem hydrogenolysis/aromatization at ≤ 300 °C without added H₂ can generate valuable long-chain alkylaromatics,⁶ which may be used to manufacture anionic surfactants.⁷ Although the process generated a narrow molecular weight distribution (carbon number average $C_{\sim 30}$, $D = 1.1$) relative to the starting polyethylene (carbon number average $C_{\sim 132}$, $D = 1.9$),⁶ the products were a complex mixture of hydrocarbons which may include *n*-alkanes, *iso*-alkanes, naphthenes, alkyltetralins, alkylbenzenes, alkyl naphthalenes, alkylphenanthrenes, and other polycyclic aromatics.

The challenges involved in analyzing such mixtures are both qualitative and quantitative. To characterize hydrocarbons ranging from C₁ to C₄₀, gas chromatography (GC) is typically used to separate components based primarily on their boiling points, followed by mass spectrometry (MS) or flame ionization detection (FID).^{8,9} Due to the diversity in hydrocarbon product structures associated with similar physical properties, 1D separation may not be sufficient. When available, 2D GC x GC with polarity separation as an additional dimension can be used to improve the separation.^{10,11} Since hydrocarbons are susceptible to extensive fragmentation under electron ionization (EI), information about the mass of the parent ion is often lost with conventional GC-EIMS. Alternatives include soft ionization techniques

including matrix-assisted laser desorption ionization (MALDI),¹² field desorption (FD),⁶ and nitric oxide ionization spectrometry evaluation (NOISE)¹³ where the masses of the molecular ions are desired. For mixtures that include heavier hydrocarbons ($C_{>40}$), gel permeation chromatography (GPC) can be used to assess the molecular weight distribution.¹⁴ However, the limited solubility of the hydrocarbons in GPC solvents may necessitate special equipment in the form of high temperature GPC. Alternatively, insoluble hydrocarbons can be characterized using MALDI-MS or FD-MS. In many cases, analysis is barely attempted, and catalytic depolymerization activity is simply reported as the mass yields of gas, liquid and solid hydrocarbons. Since these categories are poorly defined, they can be misleading when used to compare and rank catalysts and reaction conditions.

Here, we describe a comprehensive approach to obtaining quantitative rates for partial polyethylene depolymerization. It involves inferring the number of C-C bond scission events from the molecular weight distribution, in combination with product yields. Methods for estimating yields and selectivities are presented. Specifically, we quantify the alkylaromatics in complex mixtures of hydrocarbons (alkanes and alkylaromatics) derived from polyethylene. While the reaction kinetics are complex and apparent rate constants do not represent elementary reaction steps, measuring average C-C bond scission rates can facilitate direct comparison of catalysts and the effect of reaction conditions, accelerating catalyst design and discovery.

5.3. Step-by-Step Method Details

In this section, we describe in detail how to accomplish polyethylene depolymerization and the steps for recovery and quantification of hydrocarbon reaction products.

5.3.1. Polyethylene Depolymerization

Timing: Variable – 24 h for our study

Depolymerization was carried out in a batch reactor at a set temperature under an inert atmosphere.

1. Prior to each reaction, place a stainless-steel autoclave (90 mL), its lid and a Pyrex-encapsulated stir bar into the antechamber of an Ar-filled glovebox and evacuate for 12 h, then bring the autoclave into the glovebox.
2. Inside the glovebox, load the stir bar, the desired masses of polyethylene (typically, 0.120 g), and a freshly reduced Pt catalyst (0.200 g, Pt/F-Al₂O₃ as an example) into the autoclave.
 - a. Mix the solids with a spatula.
 - b. Seal and remove the reactor from the glovebox.

Note: The solid catalyst can be pre-activated under H₂ (please refer to Sun et al.)¹ and stored in the glovebox prior to use.

Note: To accelerate the initial mass transport of PE and promote heat transfer to the polymer, grind and sieve the polymer into a fine powder (250-425 µm) before loading it into the reactor.

Cryogenic grinding: Under air, place the polymer beads (5-10 g) into a clean Dewar flask (500 mL). Next, add enough liquid N₂ to cover the beads. Allow the majority of the liquid N₂ to boil off, then promptly pour the beads into a coffee grinder and grind for a few seconds to obtain polymer powder.

3. Place the sealed reactor inside an external vessel heater, insert a thermocouple through a feedthrough into the reactor.

- a. Set the desired temperature, stirring rate, and reaction time (typically, 250 °C, 675 rpm, 8 h, **Figure 5.1A**).

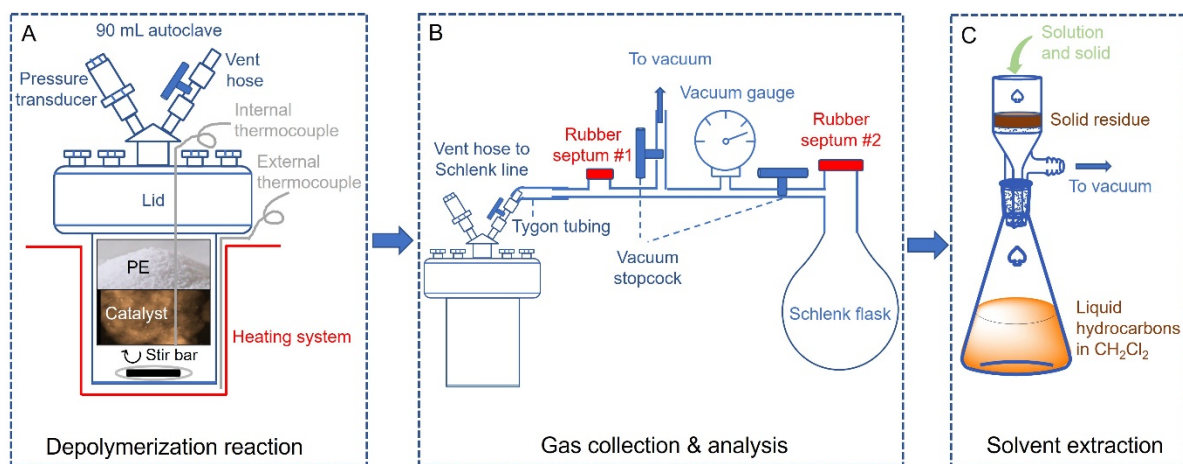


Figure 5.1. Schematic representation of (A) depolymerization batch reaction, (B) post-reaction gas collection, and (C) post-reaction solvent extraction of soluble hydrocarbons and solid recovery.

- b. Start the reaction timer when the reactor reaches the set temperature (~ 25 min).

Note: If the internal thermocouple does not touch the polymer/catalyst mixture, it may measure the internal gas temperature rather than the temperature of the solid/liquid phase. We also used a thermocouple to measure the external temperature of the autoclave wall and found that, typically, the temperature of the reactor wall is 280 ± 5 °C, i.e., 30 °C higher than that of the gas inside the reactor).

Note: The temperature at which the depolymerization reaction occurs relies on the measurement of the external temperature of the reactor. For autoclaves that do not contain an

internal thermocouple, the desired temperature can be set through the external heating system and the temperature can be measured externally.

4. After the desired reaction time, remove the reactor from the vessel heater and quench the reaction by immersing the reactor vessel in a water bath at 20-25 °C for ca. 30 min.

5.3.2. Recovery and Quantification of Hydrocarbon Products

Timing: ~12 h for workup and analyses (steps 5-21 below)

These steps describe the recovery and quantification of each class of hydrocarbon products (gas, liquid, and solid) generated by polyethylene depolymerization.

5. Connect the autoclave and a Schlenk flask (typically, 100 mL) capped with rubber septum #2 to a Schlenk line equipped with a vacuum gauge and rubber septum #1, as shown in **Figure 5.1B**.

6. Evacuate the Schlenk flask and line ($\leq 10^{-2}$ Torr), then isolate both from the vacuum pump.

7. Expand the gases from the autoclave headspace into the line and Schlenk flask. Isolate the Schlenk flask.

Note: Wait an additional minute or so after the pressure reading stabilizes in the Schlenk line before closing the Schlenk flask, to ensure all gas components are well-mixed.

CRITICAL: Ensure the pressure of the line and the Schlenk flask will be lower than 1 atm after gas expansion, to avoid ejecting the rubber septum. The pressure in the reactor, post-reaction, can be measured using a pressure transducer, and this value can be used with the ideal gas law to estimate the pressure that will be generated in the line and the Schlenk flask

after gas expansion. Adjust the size of the Schlenk flask so that the pressure after expansion does not exceed 1 atm.

8. Remove an aliquot of gas (400 μL) via rubber septum #1 (**Figure 5.1B**) using a Luerlock gas-tight syringe,

- a. Inject the aliquot into the GC-FID to record the initial chromatogram.
- b. Perform this step twice to ensure consistency of the result.

9. Inject propene (400 μL , 200-400 mbar) as internal standard into the Schlenk flask via rubber septum #2 (**Figure 5.1B**).

Note: Pull and push the syringe plunger several times to ensure good mixing between the internal standard and the gases in the Schlenk flask.

10. Remove an aliquot (200 μL) of gas from the Schlenk flask using a Luerlock gas-tight syringe.

- a. Inject into the GC-FID for light hydrocarbon analysis ($\text{C}_1\text{-C}_8$).

Note: The difference in areas for the propene peaks in both chromatograms can be used to calculate the amount of propene present as a reaction product, relative to the amount added as an internal standard.

- b. Perform this step twice to ensure well-mixing of the gaseous products and the internal standard.

11. Disconnect the reactor vent hose from the Schlenk line. Prior to opening the reactor, add 5 mL of methylene chloride (in 5x 1 mL aliquots) via the vent hose (**Figure 5.1B**).

Note: This step ensures that any liquid hydrocarbons that have condensed in the upper part of the reactor including the reactor's lid will dissolve and combine with the liquids present at the bottom of the reactor vessel.

12. Open the reactor, allow the CH_2Cl_2 to enter, and transfer the solution and solid using a glass Pasteur pipette onto a Buchner filter funnel equipped with a fine glass frit (4.0-5.5 μm).

13. Add another 5 mL CH_2Cl_2 to wash the solid remaining on the frit to increase the recovery of liquid hydrocarbons adsorbed on the solid residue in the filtrate.

14. Transfer the filtrate to a volumetric flask and dilute to 10.00 mL volume using CH_2Cl_2 .

- a. Filter ~1 mL of the solution through a 0.2 μm PTFE filter attached to a 1 mL plastic syringe for analysis by GC-FID.

15. Evaporate the majority of the CH_2Cl_2 solvent using rotary evaporation (30 $^{\circ}\text{C}$, 350 Torr, 15 min), then remove residual solvent under reduced pressure on a vacuum line (0.1 Torr, 1 h) at 20-25 $^{\circ}\text{C}$.

Note: These steps also remove volatile liquid hydrocarbons (mostly $\text{C}_7\text{-C}_{11}$).

16. Weigh the mass of the remaining liquid products ($\text{C}_{>11}$).

17. Re-dissolve the liquid products in CH_2Cl_2 in a volumetric flask and dilute with CH_2Cl_2 to 10.00 mL.

- a. Filter ~1 mL of this solution through a 0.2 μm PTFE syringe filter for analysis by GC-FID.

Note: Comparison of the results from this step with those from step 13 identify and quantify hydrocarbons lost during solvent evaporation/removal.

18. Prepare sample analysis for ^1H NMR, quantitative ^{13}C NMR, GPC, and UV-vis (optional).
- Dissolve 2 mg of the liquid product in 1,1,2,2-tetrachloroethane- d_2 for ^1H NMR analysis.
 - Dissolve 60 mg of the liquid product and 22.4 mg $\text{Cr}(\text{acac})_3$ (80 mM) in CDCl_3 for quantitative ^{13}C NMR analysis.
 - Dissolve 6 mg of the liquid product in 1.5 mL CHCl_3 containing 0.25 vol% triethylamine for GPC analysis.
 - Dissolve 0.5 mg of the liquid product in HPLC-grade hexanes and dilute with hexanes to 3.00 mL in a volumetric flask. Transfer this solution into a 1-cm pathlength quartz cuvette for UV-vis measurement.
19. Add ~10 mL CH_2Cl_2 to the solid mixture on the frit to create a suspension and transfer this suspension by a glass Pasteur pipette to a vial.
- Evaporate the majority of the CH_2Cl_2 solvent using rotary evaporation (30 °C, 350 Torr, 15 min),
 - Remove residual solvent under reduced pressure on a vacuum line (0.1 Torr, 1 h) at 20-25 °C .
20. Weigh the mass of the recovered solid.
21. Perform TGA of the solid residue (~3 mg) in air.

5.4. Expected Outcomes

In this section, we describe in detail the characterization of the hydrocarbon products formed in the catalytic conversion of PE (0.120 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $\bar{D} = 1.9$) over Pt/F-

Al₂O₃ (0.200 g, 1.6 wt % Pt, 0.8 wt % F) at 280 °C under Ar, as a representative example.

Results for other catalysts were presented in Sun et al.¹

After 8 h, the yields of hydrocarbon gases (C₁-C₈), volatile liquids (C₇-C₁₁), and heavy liquids (C_{>11}) are 7 (1) , 7 (1), and 64 (1) wt %, respectively. The solid residue (12 (1) wt %) is mostly coke, based on the temperature of its oxidation according to TGA.¹ The uncertainties are presented in parenthesis based on duplicates. Further characterization of the gas and liquid products is detailed below.

5.4.1. Gas Chromatographic Analysis of Gaseous Hydrocarbons

GC-FID chromatograms of the gas products can be recorded before and after addition of an internal standard, shown in **Figure 5.2**. The initial chromatogram (**Figure 5.2A**) shows the presence of alkanes (C₁-C₈) but no propene (absence of a signal at 3.2 min), suggesting that propene is a good choice for internal standard.

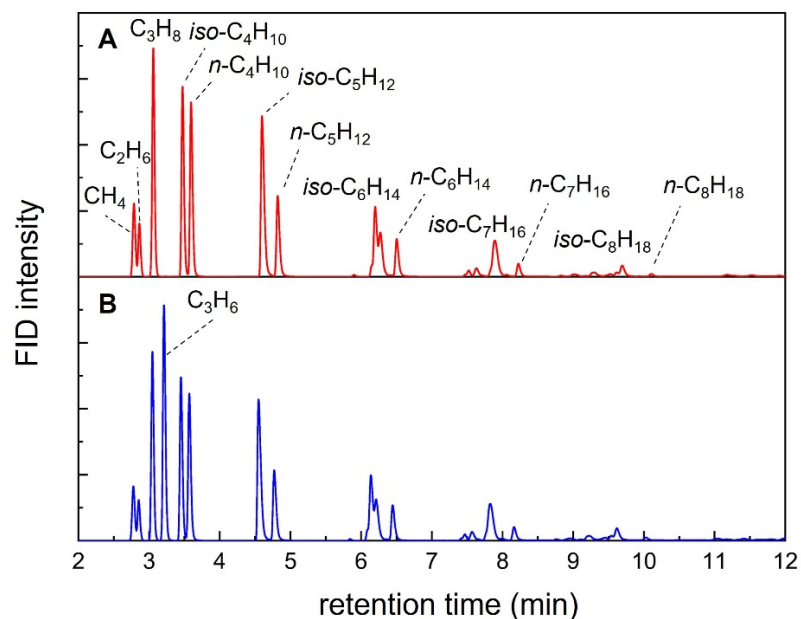


Figure 5.2. GC-FID chromatograms of gas products (A) before, and (B) after adding propene as an internal standard. n-alkanes and iso-alkanes were assigned based on their retention times.

5.4.2. Gas Chromatographic Analysis of Volatile Liquid Hydrocarbons

GC-FID analysis of the liquid products dissolved in CH_2Cl_2 can be conducted with and without solvent removal. The broad, intense solvent peak obscures other signals that may be present with retention times between 2 to 4 min (**Figure 5.3A**). Comparison to the chromatogram after solvent evaporation (**Figure 5.3B**) shows that most of the hydrocarbons lost during solvent removal are in the range $\text{C}_7\text{-C}_{11}$, which we refer to as volatile liquid hydrocarbons.

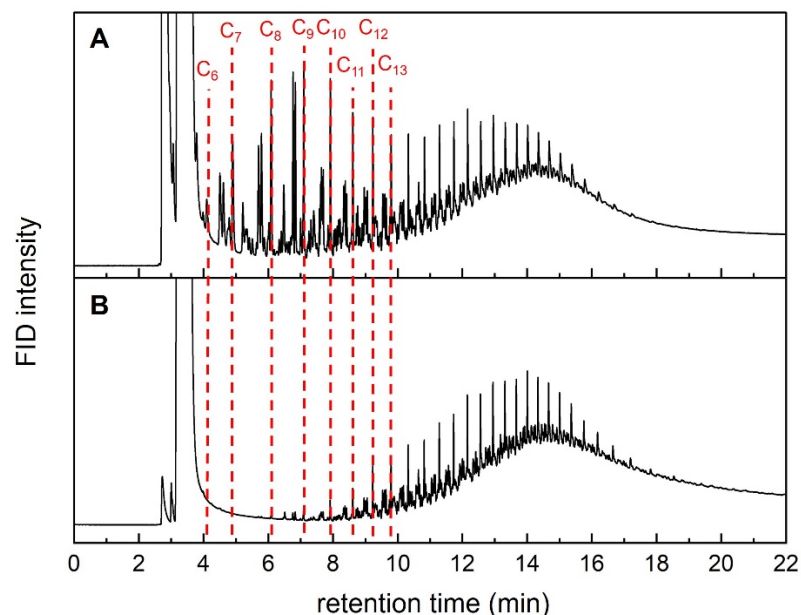


Figure 5.3. GC-FID of liquid products (A) before, and (B) after removal of CH_2Cl_2 solvent by evaporation. The dashed lines indicate the signals for norm-alkanes.

5.4.3. Quantitative NMR Analysis of Heavy Liquid Hydrocarbons

Solution-state ^1H and ^{13}C NMR spectra of the liquid products can be recorded at 20-25 $^\circ\text{C}$ (we used a Varian Unity Inova AS600 spectrometer and a Bruker Avance NEO 500 spectrometer for ^1H and ^{13}C NMR, respectively). A typical ^1H NMR experiment was performed at an acquisition time of 2.5 s with 64 accumulated scans. The ^1H NMR spectrum reveals signals for aromatic protons at 6.5-9.0 ppm and for benzylic protons (H_α , including the benzylic positions of alkyl substituents on fused aromatics such as naphthalenes and phenanthrenes) at 2.0-3.5 ppm, indicating the presence of alkylaromatics (**Figure 5.4A**).^{15,16} To ensure that the ^{13}C NMR information is quantitative, $\text{Cr}(\text{acac})_3$ is added as a relaxation agent to reduce long ^{13}C spin-lattice relaxation times (T_1). The spectrum of a model

compound, dodecylbenzene (60 mg), is measured with an inversion recovery pulse sequence¹⁷ to choose a suitable relaxation delay (t) (**Figure 5.5**). An inversion recovery measurement conducted at 25 °C with 80 mM Cr(acac)₃ (22.4 mg) in CDCl₃ (800 μL) gave approximate values for T_1 and t according to **Equations 5.1 and 5.2**, respectively, where τ is the variable recovery delay between the 180 and 90 ° pulses.¹⁷

$$T_1 = \tau / \ln 2 \quad (\text{Equation 5.1})$$

$$t \geq 5 \times T_1 \quad (\text{Equation 5.2})$$

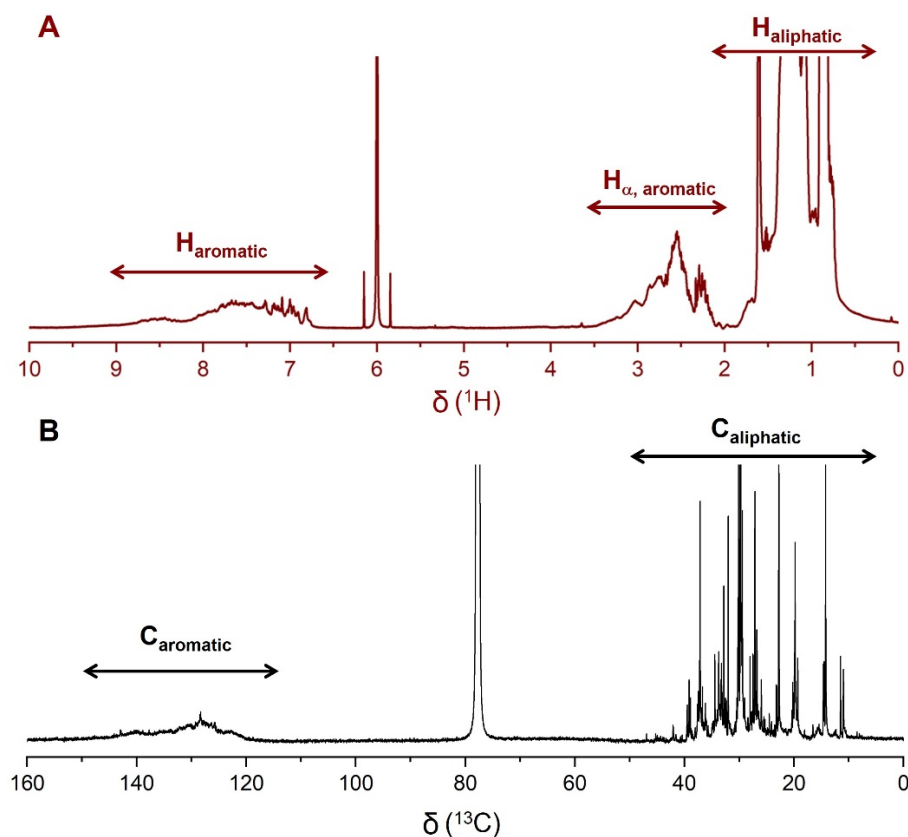


Figure 5.4. Quantitative solution-state NMR spectra of the heavy hydrocarbon liquid products ($C_{>11}$): (A) 1H NMR, and (B) ^{13}C NMR.

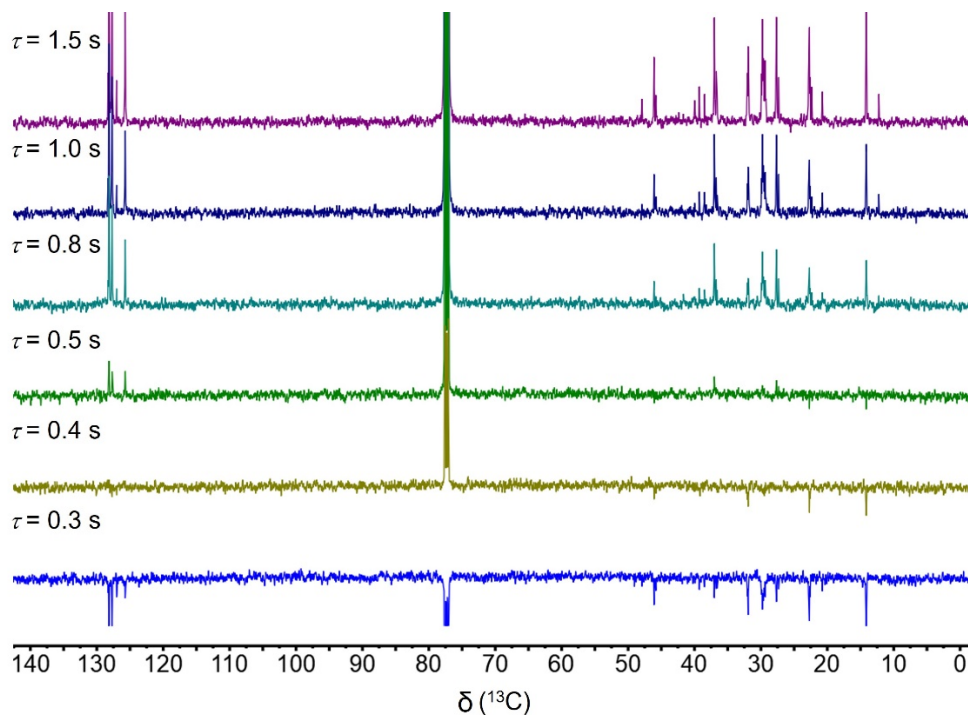


Figure 5.5. ^{13}C NMR spectra of dodecylbenzene, acquired using an inversion recovery pulse sequence¹⁷ with variable delays (τ) between the 180 and 90 ° pulses, to assess the acquisition parameters needed for quantitative measurements.

Since all peaks in **Figure 5.5** are positive for $\tau \geq 0.8$ s, the estimated value of T_1 is 1.2 s. Quantitative ^{13}C NMR spectra therefore require a relaxation delay $t \geq 5.8$ s. The NMR sample of heavy liquid hydrocarbons resulting from PE depolymerization was prepared at the same $Cr(acac)_3$ concentration and the T_1 and t values determined in the inversion recovery experiment with dodecylbenzene are then used to record quantitative ^{13}C NMR spectrum at

an acquisition time of 1.5 s with 4096 accumulated scans. **Figure 5.4B** shows signals for aromatic carbons in the region from 118 to 150 ppm.¹⁸ Their integration will be used to estimate aromatic yields and selectivities (see below).

5.4.4. GC-MS Analysis of Heavy Liquid Hydrocarbons

GC-MS can be used to determine the average carbon number for different classes of hydrocarbons present in complex mixtures. Characteristic ion chromatograms for each type of hydrocarbon (alkylbenzenes, alkyl-naphthalenes, alkylphenanthrenes, and alkanes) are extracted from the total ion chromatogram, as shown in **Figure 5.6**.

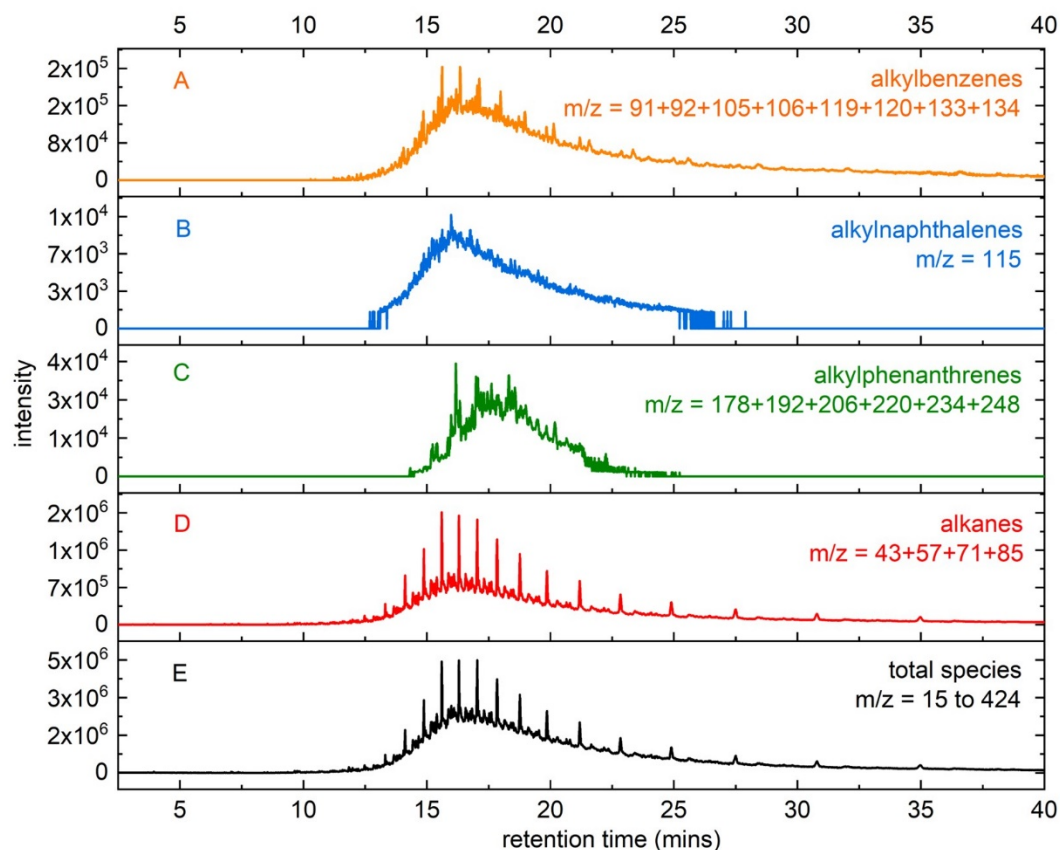


Figure 5.6. Characteristic ion chromatograms, obtained by GC-MS, for (A) alkylbenzenes, (B) alkylnaphthalenes, (C) alkylphenanthrenes, and (D) alkanes (including naphthenes), extracted from the total chromatogram (E) of a mixture of heavy liquid hydrocarbons (adapted from reference 1).

5.4.5. Size Exclusion Chromatographic Analysis of Heavy Liquid Hydrocarbons

While PE analysis generally requires access to high temperature gel permeation chromatography (GPC), it is possible to analyze low molecular weight PE and depolymerization products using more widely available room temperature GPC, performed in a solvent such as chloroform or tetrahydrofuran. The instrument is typically equipped with RI (refractive index) and/or UV detectors. The system is usually calibrated with either PE or PS standards (the use of more readily available PS standards requires a conversion process to obtain PE molecular weights).¹⁹ Typical results for the heavy liquid products resulting from the conversion of PE (0.120 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$) catalyzed by Pt/F-Al₂O₃ (0.200 g, 1.6 wt % Pt, 0.8 wt % F) after 8 h at 280 °C under Ar are shown in **Figure 5.7A** for a low molecular weight PE and its depolymerization products, revealing a decrease in M_w and dispersity ($D = M_w / M_n$). A comparison of results using RI and UV detectors shows how the UV-active chromophores are distributed relative to the total hydrocarbons (**Figure 5.7B**). In this case, both detection methods give similar distributions, suggesting that aromatic products are evenly distributed over the entire molecular weight range of liquid hydrocarbon products.

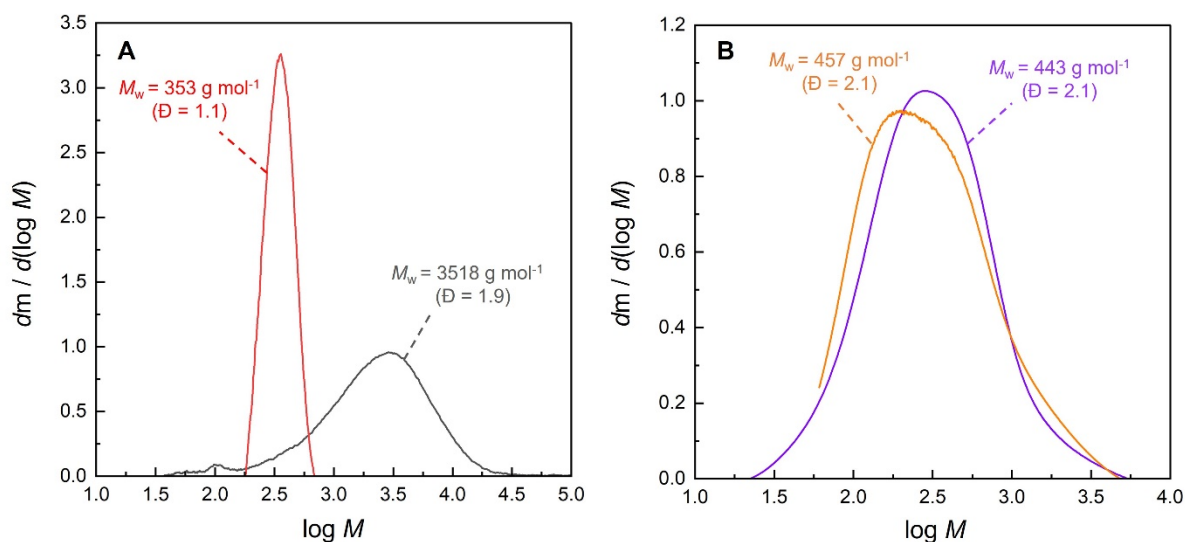


Figure 4.7. GPC analysis of (A) a low molecular weight PE (gray) and its heavy liquid depolymerization products (red), obtained with RI detection and PE standards, and (B) heavy liquid depolymerization product analyzed using both RI (purple) and UV (orange) detectors, calibrated using PS standards (7B adapted from reference 1).

5.4.6. Thermogravimetric Analysis of Solid Hydrocarbons

To characterize solid hydrocarbons, TGA is performed in air while ramping the temperature at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from 50 to $700\text{ }^{\circ}\text{C}$. Intact PE is oxidized at ca. $300\text{ }^{\circ}\text{C}$, while oxidation of coke requires higher temperatures.²⁰ The peak positions are readily identified in the derivative data. TGA and DTGA of the insoluble solid recovered from the conversion of PE (0.120 g , $M_w = 3.5 \times 10^3\text{ g mol}^{-1}$, $\bar{D} = 1.9$) catalyzed by Pt/Cl- Al_2O_3 (0.200 g , $1.5\text{ wt \% Pt}$, $1.4\text{ wt \% Cl}$) after 8 h at $280\text{ }^{\circ}\text{C}$ under Ar shows the two distinct mass loss events (**Figure 5.8**).

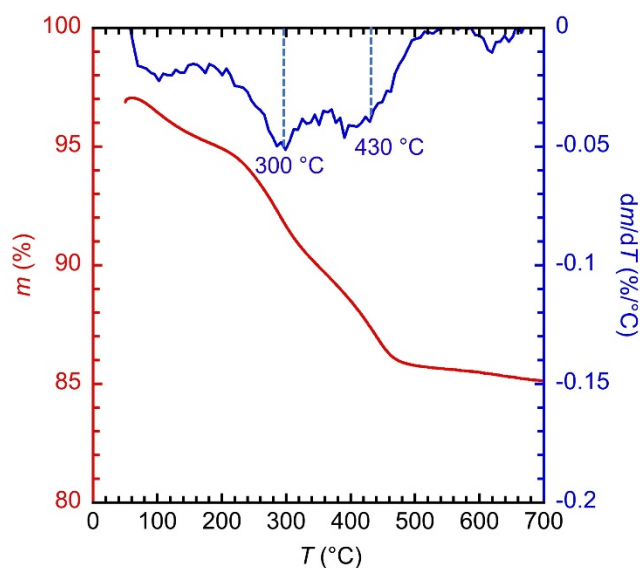


Figure 5.8. TGA (red) and corresponding DTGA (blue) for the solid residue recovered from PE depolymerization catalyzed by Pt/Cl-Al₂O₃.

5.5. Quantification and Statistical Analysis

In this section, we describe methods to quantify the overall mass balance as well as specific types of hydrocarbon products in the gas, liquid, and solid phases. It includes the method for calculating the selectivities of various types of hydrocarbons (aromatics vs. alkanes, etc.) in the heavy liquid products. We also describe how to assess the depolymerization rate, by determining the rate of C-C bond scission.

5.5.1. Hydrocarbon Distribution

5.5.1.1. Quantification of Gas products (C₁-C₈)

1. Calculate the individual and total amounts of gas products based on the GC-FID analysis.

- a. Assign the peaks for each carbon number (i) according to their retention times (assigned by comparison to individual norm-alkane standards from C_1 to *norm*- C_8).
- i. Assign all peaks that elute between *norm*- $C_{i-1}H_{2i}$ and *norm*- C_iH_{2i+2} to have carbon number C_i .

Note: The *norm*-alkane has the highest boiling point of all alkane isomers.

- b. Calculate the amount of propene added using ideal gas law (**Equation 5.3**), where n_{propene} is the moles of propene added as internal standard, P is the propene partial pressure, V is the injected volume, R is the ideal gas constant and T is the absolute temperature.

$$n_{\text{propene}} = (PV) / (RT) \quad (\text{Equation 5.3})$$

Note: Propene was selected as our calibration standard because we typically did not detect it among our gas phase products. If propene is a reaction product, it can still be used for calibration, but its yield will need to be quantified using the method of standard additions.

- c. Calculate the number of moles (n_i) and mass (m_i) contributed by each species to the gas phase products, using its peak area (A_i) relative to that of propene (A_{propene}) using **Equations 5.4 and 5.5**. The volume expansion factor, V_2/V_1 , is the total volume (V_2) including the reactor, Schlenk line, and flask, relative to the volume of the Schlenk flask (V_1).

$$n_i = ((A_i / i) n_{\text{propene}} / (A_{\text{propene}} / 3)) \times (V_2/V_1) \quad (\text{Equation 5.4})$$

$$m_i = n_i (14i + 2) \quad (\text{Equation 5.5})$$

Note: It is reasonable to assume the same relative carbon response factor for all hydrocarbons in GC-FID analysis.²¹

- d. Calculate the total moles and the total mass of gas products by summing the contributions of each gas phase species.

5.5.1.2. Quantification of volatile liquids (C₇-C₁₁) and heavy liquids (C_{>11})

2. Calculate the individual and total amounts of volatile liquid product based on the GC-FID analysis.

- a. Assign carbon numbers to each peak according to its retention time, by comparison to the retention times for a standard mixture of norm-alkanes (C₇-C₄₀).
 - i. Assign all peaks eluting between norm-C_{i-1}C_{2i} and *norm*-C_iC_{2i+2} to have carbon number *i*.
- b. For each carbon number in the region corresponding to C₇-C₁₁ (**Figure 5.3**), calculate the difference in peak areas (*A*) before and after solvent removal by evaporation. Calculate the moles of each species with a given carbon number species (*n_i*) using the external standard method according to **Equation 5.6**, where *V*₀ is the solution volume and *f* is the relative carbon response factor.

$$n_i = A_i V_0 / (f i) \quad (\text{Equation 5.6})$$

Note: *norm*-octane in CH₂Cl₂ can be used as an external standard. A calibration curve is constructed using the peak areas for *norm*-octane at different concentrations.

Note: It is reasonable to assume the same relative carbon response factor (*f*) for all hydrocarbons in GC-FID analysis.²¹

- c. Estimate the mass of each species with a given carbon number (m_i), assuming its molecular weight to be that of the alkane (**Equation 5.7**).

$$m_i = n_i(14i + 2) \quad (\text{Equation 5.7})$$

- d. Calculate the mass yield of volatile liquids by summing the difference in masses for each carbon number in the C₇-C₁₁ region before and after solvent removal by evaporation.

3. Calculate the individual and total amounts of heavy liquid products.

- a. Obtain the mass of the heavy liquid by weighing the liquid remaining after solvent evaporation.
- b. Calculate the number of moles of heavy liquid using **Equation 5.8**, where $n_{\text{heavy liq}}$ and $m_{\text{heavy liq}}$ refer to the moles and mass of heavy liquid products, respectively.

$$n_{\text{heavy liq}} = m_{\text{heavy liq}} / M_{n, \text{heavy liq}} \quad (\text{Equation 5.8})$$

Here, $M_{n, \text{heavy liq}}$ is the number-averaged molecular weight of the heavy liquid products, measured using GPC with PE calibration standards and RI detection.

4. Calculate the total liquid mass yield (wt %) using **Equation 5.9**, where $m_{\text{volatile liq}}$ and $m_{\text{initial PE}}$ refer to the mass of volatile liquids obtained in step 2d and the initial mass of PE, respectively.

$$\text{Liquid yield (wt \%)} = (m_{\text{volatile liq}} + m_{\text{heavy liq}}) / m_{\text{initial PE}} \times 100\% \quad (\text{Equation 5.9})$$

5.5.1.3. Quantification of Solid Carbon Residue

5. Obtain the yield of solid carbon residue by weighing the recovered solid and subtracting the catalyst mass, **Equation 5.10**, where $m_{\text{solid residue}}$ and m_{catalyst} refer to the masses of solid carbon residue and catalyst, respectively.

$$\text{insoluble hydrocarbons (wt \%)} = (m_{\text{solid residue}} - m_{\text{catalyst}}) / m_{\text{initial PE}} \times 100\% \quad (\text{Equation 5.10})$$

Here, we assume no mass loss of catalyst compared to the initial charge.

6. Calculate the individual masses of unreacted PE and coke in the recovered solid, using the TGA results (**Figure 5.8**).

- a. Calculate the contribution of unreacted PE ($m_{\text{unreacted PE}}\%$) to the recovered solid, using the % mass loss between 200 °C ($m_{200}\%$) and 350 °C ($m_{350}\%$) in the TGA, as shown in **Equation 5.11**.

$$m_{\text{unreacted PE}}\% = m_{200}\% - m_{350}\% \quad (\text{Equation 5.11})$$

- b. Calculate the contribution of coke ($m_{\text{coke}}\%$) to the recovered solid, using the % mass loss between 350 °C ($m_{350}\%$) and 600 °C ($m_{600}\%$) in the TGA, as shown in **Equation 5.12**.

$$m_{\text{coke}}\% = m_{350}\% - m_{600}\% \quad (\text{Equation 5.12})$$

- c. Calculate the contribution of the solid carbon residue relative to catalyst, using **Equation 5.13**.

$$m_{\text{carbon residue, relative to catalyst}}\% = (m_{\text{unreacted PE}}\% + m_{\text{coke}}\%)/m_{600}\% \times 100\% \quad (\text{Equation 5.13})$$

Note: Since no mass loss was observed by TGA between 600 and 700 °C (**Figure 5.8**), coke was assumed to be fully oxidized below 600 °C and the remaining mass ($m_{600}\%$) was considered to correspond to the catalyst. Depending on its structure, complete oxidation of coke may require temperatures higher than 600 °C.

- d. Use the results from step 6c to obtain the % mass of solid carbon residue (unreacted PE and coke) relative to initial PE, **Equation 5.14**.

$$m_{\text{carbon residue}}\% = m_{\text{carbon residue, relative to catalyst}}\% \times (m_{\text{catalyst}}/m_{\text{initial PE}}) \quad (\text{Equation 5.14})$$

- e. Check that the mass of carbon residue derived from the TGA measurement is consistent with the total solid hydrocarbon mass obtained directly by weighing in step 5 (**Equation 5.10**).

5.5.2. Average Rate of C-C Bond Scission

7. Calculate the number of C-C bond scission events using **Equation 5.15**, where $N(0)$ is the number of moles of PE chains initially, and $N(t)$ is the number of moles of hydrocarbons (polymer chains and small molecules) present at time t . ΔN therefore represents number of moles of new chains, which is equal to the moles of C-C bond scission events.

$$\Delta N = N(t) - N(0) \quad (\text{Equation 5.15})$$

- a. Calculate $N(t)$ by summing the number of moles of hydrocarbons present in the gas and liquid phases (**Table 5.1**) and adding the contributions from the solid phase using **Equation 5.16**, where n_{solid} is the number of moles of chains present in the solid residue.

$$N(t) = \sum_1^{11} n_i + n_{\text{heavy liq}} + n_{\text{solid}} \quad (\text{Equation 5.16})$$

Here, n_{solid} is estimated as $m_{\text{solid}}/M_{n,\text{PE}}$, where m_{solid} refers to the mass of solid residue and $M_{n,\text{PE}}$ is the initial number-averaged molecular weight of PE.

Note: Using $M_{n,\text{PE}}$ to calculate the number of chains in the solid residue is inaccurate if the residue contains partially depolymerized, but still insoluble, polymer chains. However, these chains contribute little to the number of chain cleavage events, relative to the gas and liquid products, therefore the error is small relative to other uncertainties inherent in the method.

Note: If the mass balance is incomplete (i.e., less than 100 wt %), the missing mass must be assigned to one or more hydrocarbon components prior to using **Equation 5.16**. We assumed

the missing mass to be unreacted PE. If a different assumption is made, the masses of the other presumed contributions to the total product mass should be scaled as appropriate.

Note: Typically, the overall mass balance is 90 wt % or better using the mass recovery method described above. A poor mass balance will lead to a large error in the calculation of number of moles of C-C bond scission events.

Table 5.1. Sample hydrocarbon distribution from conversion of PE catalyzed by Pt/F-Al₂O₃^a

Carbon number (<i>i</i>)	Gases (μmol)	Volatile liquids (μmol)	Heavy liquids (μmol)	Solid residue (μmol)	Total (μmol)
1	34.4	-	-	-	34.4
2	11.7	-	-	-	11.7
3	32.3	-	-	-	32.3
4	41.5	-	-	-	41.5
5	27.7	-	-	-	27.7
6	16.0	1.3	-	-	17.3
7	7.7	4.3	-	-	12.0
8	2.6	19.1	-	-	21.7
9	-	12.7	-	-	13.7
10	-	8.4	-	-	8.4
11	-	4.6	-	-	4.6
$\bar{i} = 24$	-	-	231.3	-	231.3

$\bar{i} = 132$	-	-	-	7.8	7.8
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^a Reaction conditions: PE (0.120 g, $M_w = 3.5 \times 10^3 \text{ g mol}^{-1}$, $D = 1.9$), Pt/F-Al₂O₃ (0.200 g, 1.6 wt % Pt, 0.8 wt % F), Ar, (280 ± 5)°C, 8 h.

- b. Calculate $N(0)$ using **Equation 5.17**, where $m_{\text{initial PE}}$ is the initial mass of PE and M_n , PE is its initial number-averaged molecular weight.

$$N(0) = m_{\text{initial PE}} / M_{n,\text{PE}} \quad (\text{Equation 5.17})$$

8. Calculate the average rate of C-C bond scission ($r_{\text{C-C}}$) using **Equation 5.18**.

$$r_{\text{C-C}} = \Delta N / t \quad (\text{Equation 5.18})$$

Note: This approach assumes the rate law is pseudo-zeroth-order in the number of C-C bonds, which is appropriate for our reaction. If the reaction order is not zero, **Equation 5.18** will still give the average rate. However, the numerical value will depend on the time interval chosen for the measurement.

5.5.3. Assessment of Hydrocarbon Types and Selectivities

9. Identify the specific types of hydrocarbons present in the liquid products using ¹H NMR.
- Identify aliphatic protons (H_{ali}) via their signals in the range δ 0.5-2.0 ppm.
 - Identify aromatic protons (H_{arom}) by their signals in the range δ 6.5-9.0 ppm.

- c. Identify the aliphatic protons (H_α) of the alkyl substituents of any aromatic ring (benzene, naphthalene, etc.) at the carbon directly bonded to the ring by their distinctive signals in the region δ 2.0-3.5 ppm.

Note: ^1H NMR analysis does not readily differentiate naphthenes from alkanes, or alkyltetralins from alkylbenzenes. For simplicity, the possible naphthenes and alkyltetralins contributions are simply combined with the contributions of alkanes and alkylbenzenes, respectively, in calculating alkane and aromatic selectivities.

Note: Further identification of individual molecular components can be discerned from the mass (FD-MS)⁶ and mass fragmentation (GC-EIMS) patterns for alkanes, cycloalkanes, alkylbenzenes, alkylnaphthalenes.

10. Estimate the aromatic yields and selectivities using ^1H NMR.

- a. Identify each type of aromatic protons.
 - i. Assign signals in the range δ 6.5-7.5 ppm (H_1) to the aromatic protons of alkylbenzenes, alkylnaphthalenes, and polycyclic alkylaromatics.
 - ii. Assign signals in the range δ 7.5-8.3 ppm (H_2) to the aromatic protons of alkylnaphthalenes and polycyclic aromatics.
 - iii. Assign signals in the range δ 8.3-9.0 ppm (H_3) to the aromatic protons of polycyclic aromatics.

Note: More information about the types of aromatic ring structures present in the liquids can be obtained by mass spectrometry and UV-vis spectroscopy. For example, three-ring structures were assessed as likely alkylphenanthrenes rather than alkylanthracenes and the

presence of larger fused aromatics (e.g., chrysenes) was deemed unlikely on the basis of the UV-vis spectra.¹

- b. Quantify the relative amounts of alkyl substituent types present on the aromatic rings.
 - i. Integrate the signals for methyl substituents (H_{α,CH_3}), which appear in the range δ 2.0-2.5 ppm.
 - ii. Integrate the signals for methylene-linked substituents (H_{α,CH_2R}), which appear in the range δ 2.5-3.1 ppm.
 - iii. Integrate the signals for methine-linked substituents (H_{α,CHR_2}), which appear in the range δ 3.1-3.5 ppm.
 - iv. Calculate the average number of H_{α} per alkyl substituent (C_{α}), q , using **Equation 5.19**.

$$q = H_{\alpha}/C_{\alpha} = (H_{\alpha,CH_3} + H_{\alpha,CH_2R} + H_{\alpha,CHR_2}) / (H_{\alpha,CH_3}/3 + H_{\alpha,CH_2R}/2 + H_{\alpha,CHR_2})$$

(Equation 5.19)

- c. Estimate the average number of alkyl substituents per aromatic molecule.
 - i. Calculate the ratio of H_{α} signals (in the region δ 2.0-3.5 ppm) to H_{arom} signals (in the region δ 6.5-9.0 ppm), H_{α}/H_{arom} , by integrating the corresponding regions.
 - ii. Calculate the ratio of C_{arom-H} signals (proton-bearing aromatic carbons, in the region δ 118-130 ppm) to C_{arom-C} signals (in the region δ 130-150 ppm), C_{arom-H} / C_{arom-C} , by integrating the corresponding regions.¹⁸

iii. Determine the average number of alkyl substituents (n) by comparing the experimental ratio $H_{\alpha}/H_{\text{arom}}$ and $C_{\text{arom-H}} / C_{\text{arom-C}}$ to the predicted value for the major type of aromatic product (or products, as appropriate), according to the value of q found in step 10b. The example of $q = 2$ (i.e., on average, $C_{\alpha}H_2R$ substituents) is shown in **Figures 5.9** and **5.10**. For simplicity, we assume that each type of aromatic product (e.g., alkylbenzenes, alkylnaphthalenes) in the liquid product mixture has the same number of alkyl substituents (see Limitation below). Thus, the lower and upper bounds of $H_{\alpha}/H_{\text{arom}}$ for a mixture of alkylaromatics are enclosed in the red, dashed box (**Figure 5.9**). For $H_{\alpha}/H_{\text{arom}} = 1.5$, the number of substituents could be 3 or 4 (dashed line in **Figure 5.9**), depending on the relative concentrations of alkylbenzenes, alkylnaphthalenes, and alkylphenanthrenes. Combining this information with the experimental ratio $C_{\text{arom-H}} / C_{\text{arom-C}}$ (where $C_{\text{arom-H}} / C_{\text{arom-R}} = 1.0$ in our study), we estimate that each aromatic molecule has, on average, 3 alkyl substituents.

Note: This method works best when $n \leq 4$, or the major types of aromatic products are ≤ 3 rings. Alkylaromatics with more than 4 substituents or higher polycyclic aromatics are not considered here.

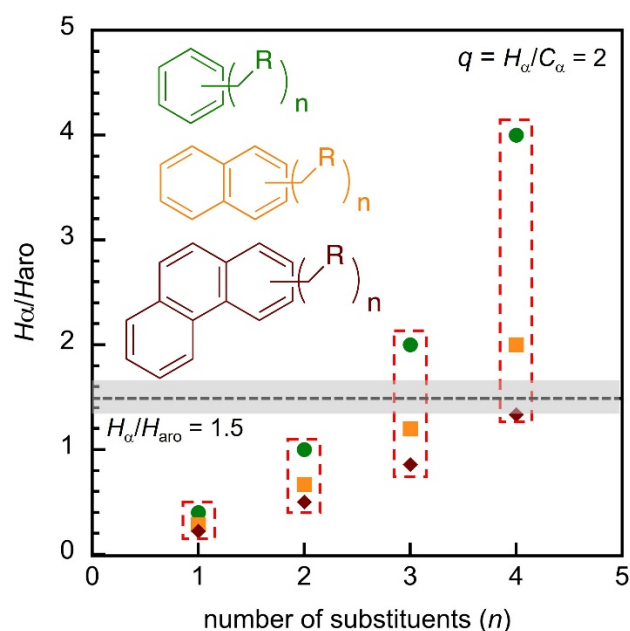


Figure 5.9. H_α/H_{aro} ratios characteristic of alkylbenzenes (green), alkylnaphthalenes (orange), and alkylphenanthrenes (brown) with various numbers (n) of alkyl substituents (with average H_α content $-C_\alpha H_2 R$, corresponding to $q = 2$). The red boxes indicate the lower and upper bounds of H_α/H_{aro} for a mixture of alkylaromatics. The black dashed line indicates the experimental ratio $H_\alpha/H_{aro} = 1.5$ obtained in our study, and the gray shaded area represents the error boundary from NMR integration ($\pm 10\%$).

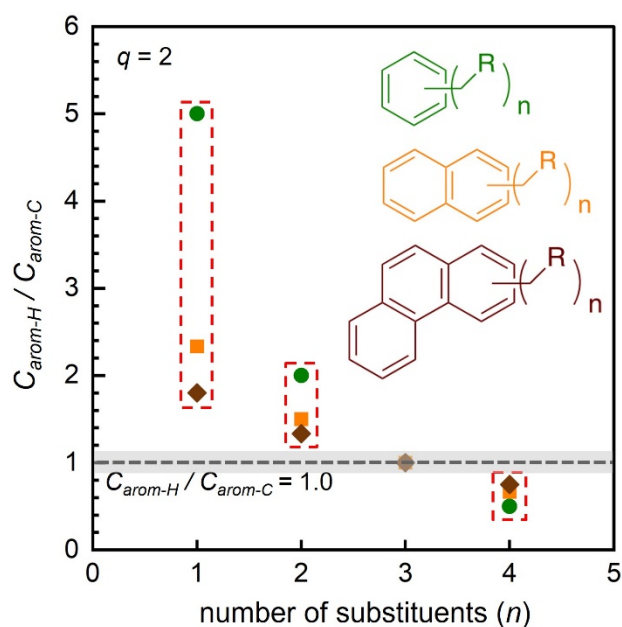
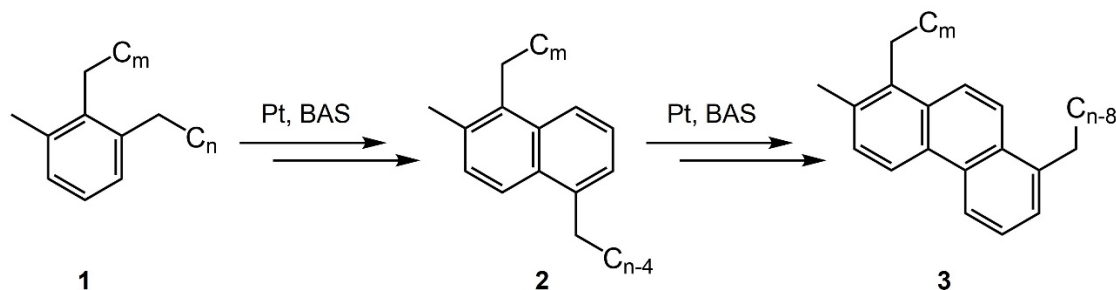


Figure 5.10. $C_{\text{arom-H}}/C_{\text{arom-C}}$ ratios characteristic of alkylbenzenes (green), alkylnaphthalenes (orange), and alkylphenanthrenes (brown) with various numbers (n) of alkyl substituents (with average H_α content $-C_\alpha H_2 R$, corresponding to $q = 2$). The red box indicates the lower and upper bounds of H_α/H_{arom} for a mixture of alkylaromatics. The black dashed line indicates the experimental ratio $C_{\text{arom-H}}/C_{\text{arom-C}} = 1.0$ obtained in our study, and the gray shaded area represents the error boundary from NMR integration ($\pm 10\%$).

- d. If desired, predict the likely locations of the alkyl substituents based on the most plausible mechanism of aromatic ring formation.¹

Note: It is challenging to precisely identify the locations of substituents on aromatic rings present in a complex mixture of hydrocarbon products. Thermodynamics can provide guidance about the most stable substituent positions. For our methyldialkylaromatic products, we proposed the following plausible structures, based on the likely formation mechanism:1

1,2-dialkyl-3-methylbenzenes (**1**), 1,5-dialkyl-2-methylnaphthalenes (**2**), and 1,8-dialkyl-2-methylphenanthrenes (**3**), **Scheme 5.1**.



Scheme 5.1. Plausible structures for methyldialkylaromatic products, proposed based on their likely formation mechanism.

- e. Estimate the average carbon number for each type of hydrocarbon product, using MS
 - i. Calculate the number-averaged carbon numbers for different types of hydrocarbons (e.g., alkanes, alkylbenzenes) using mass spectrometry with either hard ionization (GC-EIMS, with ion chromatograms isolated for individual classes of hydrocarbons)²³⁻²⁶ or soft ionization (FD-MS, with the corresponding molecular ion chromatograms). An example of data obtained using GC-EIMS is shown in **Figure 5.6**, where the individual ion chromatograms for alkylbenzene, alkylnaphthalene, alkylphenanthrene, and alkane products (**Figure 5.6A-5.6D**) were generated by summing the individual ion intensities (I) for each ion characteristic of a particular product group. The results allow us to calculate a separate number-averaged carbon number for each hydrocarbon type.

Note: The characteristic ions for each species represented in **Figure 5.6** are not fully exclusive. For example, alkylaromatics may also contribute ions to the alkane series ($m/z = 43+57+71+85$) due to the fragmentation of their alkyl chains. Additionally, alkyltetralins could contribute to the alkylbenzene ion series ($m/z = 91 + 92 + 105 + 106 + 119 + 120 + 133 + 134$). Consequently, this method is approximate.

Note: Alkylbenzenes do not elute in precisely the same range as alkanes with the same carbon numbers. While branched alkanes typically elute just before the norm-alkane with the same mass, alkylbenzenes may elute either before or after the corresponding norm-alkane. Most alkylbenzenes have slightly longer retention times than the norm-alkanes, with retention times mostly between those of the *norm*-alkanes with carbon numbers i and $i+1$.²² Thus, when alkylbenzenes are a major component of the products, the average carbon number may be underestimated by ca. 1. This error is generally less than the accuracy of the analysis. Alkyl-naphthalenes and alkyl-phenanthrenes generally elute later than alkylbenzenes with the same carbon number, although they usually represent a small fraction of the alkylaromatic products and therefore do not have a large impact on the calculation of the average carbon number.

- ii. The calculations use one of two equations for each type of hydrocarbon, depending on the assumption made about the MS response factors (in the absence of individual response factors for each species). The example shown here applies to alkylbenzenes. **Equation 5.20** assumes that the MS response factor is a function only of the type of hydrocarbon (e.g., alkane vs. alkylbenzene), not on its molecular weight (M). Alternatively, **Equation 5.21** assumes that the MS response

factor for each type of hydrocarbon also depends on its molecular weight. Typically, the estimated average carbon number calculated for each type of hydrocarbon is similar using either method (see Sun et al. for another sample calculation).¹

$$\overline{i_{ben}} = \sum(i \cdot I_{ben,i}) / \sum I_{ben,i} \quad (\text{Equation 5.20})$$

$$\overline{i_{ben}} = \sum(i \cdot \frac{I_{ben,i}}{M_{ben,i}}) / \sum \frac{I_{ben,i}}{M_{ben,i}} \quad (\text{Equation 5.21})$$

Note: Assign the carbon number of each species using norm-alkane standard compounds, according to the GC-FID method described above (see **Hydrocarbon distribution**).

As an alternative to step 10e.i, the average carbon number for heavier hydrocarbons can be identified by GPC using **Equation 5.22**, where $\bar{i}$ represents the number-averaged carbon number.

$$\bar{i} = M_{n, \text{heavy liquid}} / 14 \quad (\text{Equation 5.22})$$

Note: GPC analysis can be performed using both RI and UV detectors to reveal the distribution of aromatics (which absorb light) relative to the total hydrocarbon distribution (which includes alkanes that do not absorb UV light). The comparison may confirm that aromatics are evenly distributed across the molecular weight range of the liquid products, or reveal that aromatics are concentrated in a particular molecular weight range.

Note: For simplicity, we assume the molecular formula to be C_nH_{2n} , based on the most intense signal at 1.2-1.7 ppm (CH_2) in the 1H NMR spectrum.

- f. Estimate the contributions of each type of alkylaromatic to the 1H NMR signals.
- i. Integrate the relevant aromatic regions in the 1H NMR spectrum to obtain the ratios $H_1 : H_2 : H_3$ (defined in step 10a above). These values are used in **Equations 5.23-5.26** to represent the molar amounts of each aromatic structure type. The relative molar selectivities (S_{ben} , S_{nap} , S_{phe}) are obtained by solving **Equations 5.23-5.25** simultaneously, as shown in **Equation 5.26**.

$$H_1 = a n_{ben} + b n_{nap} + c n_{phe} \quad \text{(Equation 5.23)}$$

$$H_2 = d n_{nap} + e n_{phe} \quad \text{(Equation 5.24)}$$

$$H_3 = f n_{phe} \quad \text{(Equation 5.25)}$$

$$S_{ben} : S_{nap} : S_{phe} = (d \times f H_1 - b \times f H_2 + b \times e H_3 - c \times d H_3) / (a d f) : (f H_2 - e H_3) / (d \times f) : H_3 / f \quad \text{(Equation 5.26)}$$

Note: The integrated intensities of the aromatic 1H NMR signals depend on the number and locations of the alkyl substituents on each aromatic ring (see Sun *et al.* for a sample calculation for methyldialkylaromatics).¹

- g. Estimate the fraction of all aromatic protons, H_{arom}/H_{total} , by integrating the relevant regions of the 1H NMR spectrum, where H_{total} is the sum of H_{ali} and H_{arom} . **Equation 5.27** shows how the ratio is related to the chemical formulas and selectivities for each aromatic structure type.

$$\frac{H_{arom}}{H_{total}} = \frac{3S_{ben} + 5S_{nap} + 7S_{phe}}{(2\overline{i_{ben}} - 6)S_{ben} + (2\overline{i_{nap}} - 12)S_{nap} + (2\overline{i_{phe}} - 18)S_{phe} + (2\overline{i_{alk}} + 2)S_{alk}} \quad (\text{Equation 5.27})$$

Note: The numerical coefficients will change depending on the average number of alkyl substituents. **Equation 5.27** is written for the specific case of trialkyl-substituted aromatics.

Note: Calculating aromatic selectivity using the number-averaged carbon number is mathematically equivalent to a calculation using the full carbon number distribution instead. This equivalence is demonstrated below. The fraction of aromatic protons, H_{arom}/H_{total} , is obtained from the carbon number distribution in **Equation 5.28**:

$$\frac{H_{arom}}{H_{total}} = \frac{3\sum_i n_{ben,i} + 5\sum_i n_{nap,i} + 7\sum_i n_{phe,i}}{\sum_i [(2i - 6)n_{ben,i}] + \sum_i [(2i - 12)n_{nap,i}] + \sum_i [(2i - 18)n_{phe,i}] + \sum_i [(2i + 2)n_{alk,i}]} \quad (\text{Equation 5.28})$$

Since the number-averaged carbon number for each product type can be expressed in terms of the carbon number distribution (e.g., $\overline{i_{ben}} = \sum(i \cdot n_{ben,i}) / \sum n_{ben,i}$), each denominator term is rearranged as follows:

$$\sum_i [(2i - 6)n_{ben,i}] = 2\overline{i_{ben}} \sum_i n_{ben,i} - 6 \sum_i n_{ben,i} = (2\overline{i_{ben}} - 6) \sum_i n_{ben,i} \quad (\text{Equation 5.29})$$

Thus, **Equation 5.28** can be rewritten as **Equation 5.30**:

$$\frac{H_{arom}}{H_{total}} = \frac{3\sum_i n_{ben,i} + 5\sum_i n_{nap,i} + 7\sum_i n_{phe,i}}{(2\overline{i_{ben}} - 6) \sum_i n_{ben,i} + (2\overline{i_{nap}} - 12) \sum_i n_{nap,i} + (2\overline{i_{phe}} - 18) \sum_i n_{phe,i} + (2\overline{i_{alk}} + 2) \sum_i n_{alk,i}}$$

(Equation 5.30)

The molar selectivity to alkylbenzenes (S_{ben}) is defined in **Equation 5.31** (molar selectivity for other components are defined similarly):

$$S_{ben} = \frac{\sum_i n_{ben,i}}{\sum_i n_{ben,i} + \sum_i n_{nap,i} + \sum_i n_{phe,i} + \sum_i n_{alk,i}} \quad (\text{Equation 5.31})$$

Finally, dividing each term in **Equation 5.30** affords **Equation 5.27**.

- h. Assess the selectivity ($S = n/n_{total}$) for alkane (S_{alk}) and each type of alkylaromatics (S_{ben} , S_{nap} , and S_{phe}) by solving **Equations 5.26**, **5.27**, and **5.32** simultaneously.

$$S_{ben} + S_{nap} + S_{phe} + S_{alk} = 1 \quad (\text{Equation 5.32})$$

Note: The fractional selectivities sum to 1 (**Equation 5.32**) only if the liquid products consist only of various alkylaromatics and alkanes, as we have assumed.

- i. Calculate the molar yields of alkylbenzenes (n_{ben}), alkylnaphthalenes (n_{nap}), and alkylphenanthrenes (n_{phe}) using **Equation 5.33**, and the total aromatics yield (n_{arom}) using **Equation 5.34**.

$$n_{ben}, n_{nap} \text{ or } n_{phe} = (S_{ben}, S_{nap} \text{ or } S_{phe}) (m_{heavy\ liq} / M_{n,liq}) \quad (\text{Equation 5.33})$$

$$n_{arom} = n_{ben} + n_{nap} + n_{phe} \quad (\text{Equation 5.34})$$

11. As an alternative to the method described in step 10, estimate aromatic yields and selectivities using quantitative ^{13}C NMR.

- a. Identify signals for aromatic and aliphatic carbons.
 - i. Assign and integrate signals for aliphatic carbons (C_{ali}) in the range δ 5-50 ppm.
 - ii. Assign and integrate signals for aromatic carbons (C_{arom}) in the range δ 118-150 ppm.
- b. Establish the potential contributions of alkylaromatic carbons to the ^{13}C NMR signals using **Equation 5.35**.

$$C_{\text{arom}} = 6 n_{\text{ben},C} + 10 n_{\text{nap},C} + 14 n_{\text{phe},C} \quad (\text{Equation 5.35})$$

Note: The use of C in the subscripts of **Equations 5.35-5.37** distinguishes the amounts and selectivities of different hydrocarbons obtained by ^{13}C NMR analysis from those obtained by ^1H NMR analysis, which are identified with a subscript H in **Equation 5.37** below.

- c. Establish the relative contributions of the carbons present in each type of aromatic compound to the ^{13}C NMR signals of all carbons using **Equation 5.36**, where C_{total} is the sum of C_{ali} and C_{arom} .

$$C_{\text{total}} = n_{\text{ben},C} \cdot \overline{i_{\text{ben}}} + n_{\text{nap},C} \cdot \overline{i_{\text{nap}}} + n_{\text{phe},C} \cdot \overline{i_{\text{phe}}} + n_{\text{alk},C} \cdot \overline{i_{\text{alk}}} \quad (\text{Equation 5.36})$$

- d. Calculate the fraction of aromatic carbons, $C_{\text{arom}}/C_{\text{total}}$, based on the integration of the quantitative ^{13}C NMR spectrum. The integrated ratio can be set equal to that

established from the chemical formulas and molar yields for each aromatic structure type, in accordance with **Equation 5.37**.

$$\frac{C_{arom}}{C_{total}} = \frac{6 n_{ben,C} + 10 n_{nap,C} + 14 n_{phe,C}}{n_{ben,C} \cdot i_{ben} + n_{nap,C} \cdot i_{nap} + n_{phe,C} \cdot i_{phe} + n_{alk,C} \cdot i_{alk}} \quad (\text{Equation 5.37})$$

Note: Since quantitative ^{13}C NMR does not readily differentiate between types of aromatic rings, the molar ratios of the individual aromatic types must be assumed to be the same as those obtained from ^1H NMR analysis.

- e. Calculate the selectivity for alkanes and for each aromatic structure type by solving **Equations 5.32** and **5.37-5.38** simultaneously.
- f. Compare the total aromatic selectivity obtained using quantitative ^{13}C NMR (or **Equations 5.32** and **5.37**) to that obtained from the ^1H NMR analysis described above (Steps 10f-h and **Equations 5.26-5.27** and **5.32**).

5.6. Limitations

This protocol considers polyolefin depolymerization product mixtures that contain alkylaromatics (alkylbenzenes, alkylnaphthalenes and alkylphenanthrenes) and alkanes as the major components. Other types of hydrocarbons including naphthenes, alkyltetralins, and compounds with multiple, unfused aromatic rings are potential contributors to ^1H NMR signals. For the purpose of this study, any naphthenes were combined with alkanes and all compounds containing aromatic rings were combined with alkylbenzenes in the calculations

of selectivities towards alkanes and aromatics. However, if their contributions are significant, it could affect the corresponding calculations.

The locations of alkyl substituents on aromatic rings can be proposed based on plausible mechanisms for their formation (**Scheme 5.1**).¹ The number of alkyl substituents is assumed to be similar for each aromatic structure type, based on the depolymerization mechanism. This assumption may not accurately represent the precise contributions of aromatic protons from each structure type. Characterization of the number of substituents and their positions for each aromatic structure type would improve the accuracy of the calculations. This characterization might be accomplished using GCxGC or other advanced separation methods, if available.

The number-averaged carbon number $\bar{i}$ for each type of hydrocarbon determined by mass spectrometry based on fragmentation patterns is semi-quantitative, because hydrocarbons with different structure types and chain lengths may have different ionization efficiencies in the mass spectrometer.

5.7. Troubleshooting

Problem 1: Unclosed mass balance due to incomplete recovery of gas products in Step 7 of the section titled “Recovery and quantification of reaction products” under “Step-by-step method details.” This problem leads to an error in the calculation of number of C-C bond scission events.

Potential Solution 1: Check for leaks before expanding the gas from the reactor to the Schlenk flask. Very small leaks in the reactor, glass joints, rubber septa or the syringe connecting the

reactor to the Schlenk collection flask via the Schlenk line can cause significant gas losses. Therefore, the reactor itself and each part of the set-up should be carefully leak-checked.

Problem 2: Unclosed mass balance due to loss of volatile liquid products to the filtration in Step 13 of the section titled “Recovery and quantification of reaction products” under “Step-by-step method details.” This problem also introduces error in the calculation of number of C-C bond scission events.

Potential Solution 2: Either direct distillation or cold filtration of the liquid products after reaction may be performed as an alternative to vacuum filtration to recover the volatile liquid products.

Problem 3: Inability to quantify C₅-C₇ hydrocarbon products in step 2 of the section titled “hydrocarbon distribution” under “quantification and statistical analysis,” due to overlap of their signals in the GC-FID with the solvent signal. This issue reduces the apparent recovery and underestimates the number of C-C bond scission events.

Potential Solution 3: DCM can be substituted by norm-decane for extraction in an otherwise duplicate experiment. The mass of light hydrocarbons and the number of C-C bond scission events can then be evaluated by combining results for the different hydrocarbon ranges accessible using each extracting solvent.

Problem 4: Incomplete mass balance as a result of a leak in the reactor for Step 1 of the section titled “Polyethylene depolymerization” under “Step-by-step method details.”. A leaky reactor may result in a poor mass balance and potential exposure of the catalyst to air, which would affect reactivity.

Potential Solution 4: Since the depolymerization reaction is conducted under 1 atmosphere of inert gas, it might be difficult to detect a leak in the reactor during reaction. Therefore, the reactor can be checked for leaks prior to use by pressurizing the reactor (> 1 atm) with inert gas and monitoring for pressure drop. The pressure should stabilize for an extended period. A leak typically happens at the connection between the upper part of the reactor and the reactor's vessel. Replacing the O-rings should remedy a leaky reactor.

Problem 5: Usage of DCM (a hazardous chemical) as the extracting solvent in Steps 11-15, 17 and 19 of the section titled “Recovery and quantification of reaction products” under “Step-by-step method details.”

Potential Solution 5: Hexane and ethyl acetate can be used as alternatives for extraction of the liquid product from the depolymerization reaction.

5.8. References

1. Sun, J., Lee, Y.-H., Yappert, R.D., LaPointe, A.M., Coates, G.W., Peters, B., Abu-Omar, M.M., and Scott, S.L. (2023). Bifunctional tandem catalytic upcycling of polyethylene to surfactant-range alkylaromatics. *Chem.* 9, 2318–2336. 10.1016/j.chempr.2023.05.017.
2. Geyer, R., Jambeck, J.R., and Law, K.L. (2017). Production, use, and fate of all plastics ever made. *Sci. Adv.* 3, e1700782. 10.1126/sciadv.1700782.
3. Anuar Sharuddin, S.D., Abnisa, F., Wan Daud, W.M.A., and Aroua, M.K. (2016). A review on pyrolysis of plastic wastes. *Energy Convers. Manag.* 115, 308–326. 10.1016/j.enconman.2016.02.037.
4. Jia, C., Xie, S., Zhang, W., Intan, N.N., Sampath, J., Pfaendtner, J., and Lin, H. (2021). Deconstruction of high-density polyethylene into liquid hydrocarbon fuels and lubricants

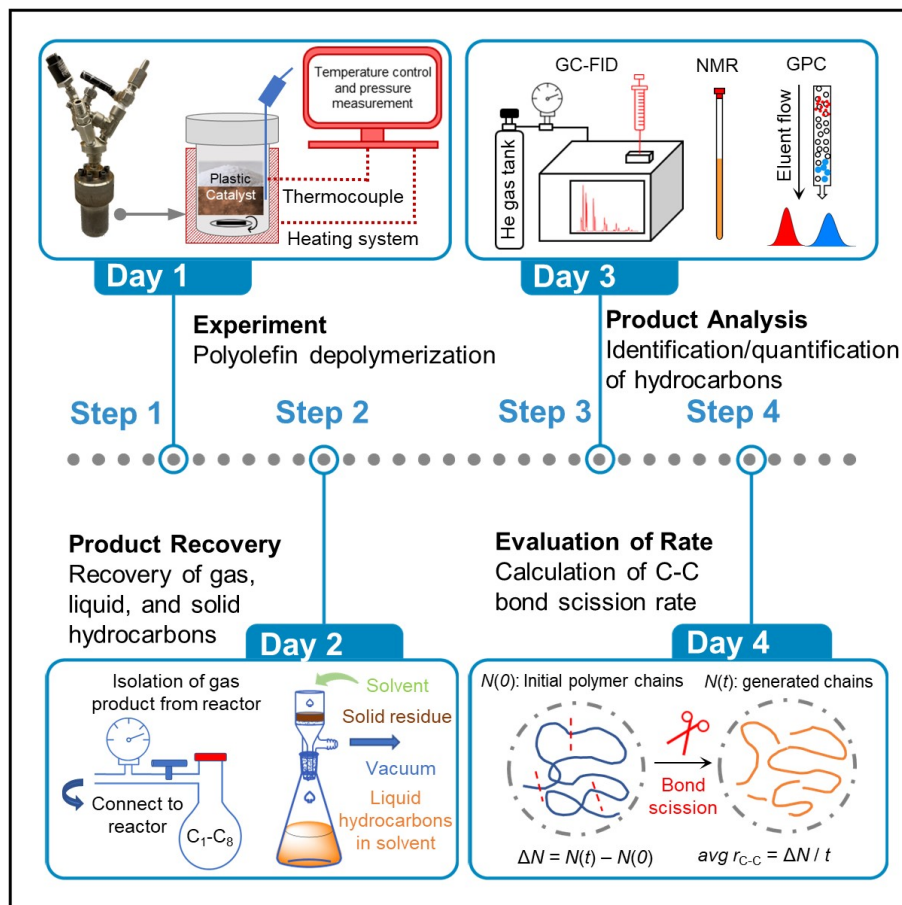
- by hydrogenolysis over Ru catalyst. *Chem Catal.* *1*, 437–455. 10.1016/j.checat.2021.04.002.
5. Liu, S., Kots, P.A., Vance, B.C., Danielson, A., and Vlachos, D.G. (2021). Plastic waste to fuels by hydrocracking at mild conditions. *Sci. Adv.* *7*, eabf8283. 10.1126/sciadv.abf8283.
 6. Zhang, F., Zeng, M., Yappert, R.D., Sun, J., Lee, Y.-H., LaPointe, A.M., Peters, B., Abu-Omar, M.M., and Scott, S.L. (2020). Polyethylene upcycling to long-chain alkylaromatics by tandem hydrogenolysis/aromatization. *Science* *370*, 437–441. 10.1126/science.abc5441.
 7. Rudnick, L.R. *Synthetics, Mineral Oils, and Bio-Based Lubricants; Chemistry and Technology*, Third Edition (CRC Press), 161-180.
 8. Celik, G., Kennedy, R.M., Hackler, R.A., Ferrandon, M., Tennakoon, A., Patnaik, S., LaPointe, A.M., Ammal, S.C., Heyden, A., Perras, F.A., et al. (2019). Upcycling single-use polyethylene into high-quality liquid products. *ACS Cent. Sci.* *5*, 1795–1803. 10.1021/acscentsci.9b00722.
 9. Soják, L., Kubinec, R., Jurdáková, H., Hájeková, E., and Bajus, M. (2007). High resolution gas chromatographic–mass spectrometric analysis of polyethylene and polypropylene thermal cracking products. *J. Anal. Appl. Pyrolysis* *78*, 387–399. 10.1016/j.jaap.2006.09.012.
 10. Toraman, H.E., Dijkmans, T., Djokic, M.R., Van Geem, K.M., and Marin, G.B. (2014). Detailed compositional characterization of plastic waste pyrolysis oil by comprehensive two-dimensional gas-chromatography coupled to multiple detectors. *J. Chromatogr. A* *1359*, 237–246. 10.1016/j.chroma.2014.07.017.

11. Dutriez, T., Courtiade, M., Thiébaud, D., Dulot, H., Bertoncini, F., and Hennion, M.-C. (2010). Extended characterization of a vacuum gas oil by offline LC-high-temperature comprehensive two-dimensional gas chromatography. *J. Sep. Sci.* 33, 1787–1796. <https://doi.org/10.1002/jssc.201000102>.
12. Zhang, W., Andersson, J.T., Räder, H.J., and Müllen, K. (2015). Molecular characterization of large polycyclic aromatic hydrocarbons in solid petroleum pitch and coal tar pitch by high resolution MALDI ToF MS and insights from ion mobility separation. *Carbon* 95, 672–680. [10.1016/j.carbon.2015.08.057](https://doi.org/10.1016/j.carbon.2015.08.057).
13. Villalanti, D.C., and Wadsworth, P.A. (1993). Application of NOISE (Nitric Oxide Ionization Spectrometry Evaluation) GC/MS analysis to reformulated gasolines and their blending components. *J. Chromatogr. Sci.* 31, 100–104. [10.1093/chromsci/31.3.100](https://doi.org/10.1093/chromsci/31.3.100).
14. Vance, B.C., Kots, P.A., Wang, C., Hinton, Z.R., Quinn, C.M., Epps, T.H., Korley, L.T.J., and Vlachos, D.G. (2021). Single pot catalyst strategy to branched products via adhesive isomerization and hydrocracking of polyethylene over platinum tungstated zirconia. *Appl. Catal. B Environ.* 299, 120483. [10.1016/j.apcatb.2021.120483](https://doi.org/10.1016/j.apcatb.2021.120483).
15. Ernst, L., and Schulz, P. (1992). ^{13}C and ^1H NMR chemical shift assignments of 1- and 2-alkylnaphthalenes ($\text{R} = \text{Me}, \text{Et}, \text{i-Pr}, \text{t-Bu}$) and determination of substituent effects on ^{13}C and ^1H chemical shifts. *Magn. Reson. Chem.* 30, 73–76. [10.1002/mrc.1260300114](https://doi.org/10.1002/mrc.1260300114).
16. Bartle, K.D., and Smith, J.A.S. (1967). High-resolution nuclear magnetic resonance spectra of phenanthrenes—I Phenanthrene and some alkyl derivatives. *Spectrochim. Acta Part Mol. Spectrosc.* 23, 1689–1714. [10.1016/0584-8539\(67\)80053-9](https://doi.org/10.1016/0584-8539(67)80053-9).

17. Zhou, Z., He, Y., Qiu, X., Redwine, D., Potter, J., Cong, R., and Miller, M. (2013). Optimum $\text{Cr}(\text{acac})_3$ concentration for NMR quantitative analysis of polyolefins. *Macromol. Symp.* 330, 115–122. 10.1002/masy.201300034.
18. Rakhmatullin, I.Z., Efimov, S.V., Klochkov, A.V., Gnezdilov, O.I., Varfolomeev, M.A., and Klochkov, V.V. (2022). NMR chemical shifts of carbon atoms and characteristic shift ranges in the oil sample. *Pet. Res.* 7, 269–274. 10.1016/j.ptlrs.2021.10.001.
19. Hiemenz, P.C., and Lodge, T. (2007). *Polymer chemistry* 2nd ed. (CRC Press), 360–372.
20. Chen, Z., Xu, L., and Zhang, X. (2022). Upgrading of polyethylene to hydrocarbon fuels over the Fe-modified $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts at a mild condition without external H_2 . *Chem. Eng. J.* 446, 136213. 10.1016/j.cej.2022.136213.
21. Dietz, W.A. (1967). Response factors for gas chromatographic analyses. *J. Chromatogr. Sci.* 5, 68–71. 10.1093/chromsci/5.2.68.
22. Hoekman, S.K. (1993). Improved gas chromatography procedure for speciated hydrocarbon measurements of vehicle emissions. *J. Chromatogr. A* 639, 239–253. 10.1016/0021-9673(93)80260-F.
23. Johnson, J.V., Pedder, R.E., and Yost, R.A. (1991). MS-MS parent scans on a quadrupole ion trap mass spectrometer by simultaneous resonant excitation of multiple ions. *Int. J. Mass Spectrom. Ion Process.* 106, 197–212. 10.1016/0168-1176(91)85019-I.
24. McCLENNEN, W.H., Arnold, N.S., Roberts, K.A., Meuzelaar, H.L.C., Lighty, J.S., and Lindgren, E.R. (1990). Fast, repetitive GC/MS analysis of thermally desorbed polycyclic aromatic hydrocarbons (PAHs) from contaminated soils. *Combust. Sci. Technol.* 74, 297–309. 10.1080/00102209008951694.

25. Chen, J., Zhang, H., Huang, H., Li, X., Shi, S., Liu, F., and Chen, L. (2013). Impact of anaerobic biodegradation on alkylphenanthrenes in crude oil. *Org. Geochem.* *61*, 6–14. 10.1016/j.orggeochem.2013.05.003.
26. Krauß, S., and Vetter, W. (2018). Phytol and phytol fatty acid esters: occurrence, concentrations, and relevance. *Eur. J. Lipid Sci. Technol.* *120*, 1700387. 10.1002/ejlt.201700387.

5.9. Table of Content Graph



Chapter 6. Conclusion and Perspective

Note: This chapter was partially adapted from sections of the following publication.

Publication: **Sun, J.**, Dong, J., Gao, L., Zhao, Y.-Q., Moon, H., Scott, S. L., “Catalytic Upcycling of Polyolefins,” *Chem. Rev.* (invited), in review.

6.1. Conclusion

Polyolefin conversion to aromatics has attracted significant attention due to the higher value of the products. Traditionally, the primary focus has been polyolefin conversion to light aromatics (BTX). We reported the first direct conversion of high-value long-chain alkylbenzenes from polyolefins by coupling C-C bond scission and aromatization catalyzed by Pt/ γ -Al₂O₃, as an alternative to their bottom-up synthesis from BTX.

More acidic Pt/Cl-Al₂O₃ and Pt/F-Al₂O₃ catalysts are more effective in the PE conversion to alkylaromatics than Pt/ γ -Al₂O₃. The metal and acid sites showed complementary roles in the tandem conversion of PE to long-chain alkylaromatics. Pt sites are principally responsible for alkane hydrogenation/dehydrogenation, while strong BASs protonate alkenes to give carbenium ions that undergo C-C bond cleavage and isomerization, as well as cyclization. When metal catalyzed hydrogenation/dehydrogenation reach equilibrium, Brønsted acidity controls the rates of C-C bond cleavage, skeletal isomerization, and alkylaromatic formation. Although increased acidity results in faster PE conversion and a higher fraction of alkylaromatics, strongly acidic catalysts also produce polyaromatics, and coke during PE upcycling.

The hydrogen pressure is a critical parameter in the bifunctional catalytic depolymerization of polyethylene to alkylaromatics. The amount of hydrogen significantly affects the selectivity to alkylbenzenes and polyaromatics. The highest yield of alkylbenzenes is obtained at a moderate hydrogen pressure level, in alignment with the thermodynamic prediction. Increasing the amount of hydrogen also promotes C-C bond scission and results in a reduction in the molecular weight of hydrocarbons through hydrocracking. The study also provides insight into the kinetics of aromatization and C-C bond scission, which could guide the optimization of catalyst design and reaction conditions for the selective conversion of polyethylene to valuable alkylaromatics.

6.2. Perspective

The one-pot synthesis of alkylbenzene from polyolefins may be beneficial compared with traditional bottom-up synthesis in terms of efficiency; however, the complexity of the reaction network and the large number of possible products make characterization and separation, as well as prediction of the thermodynamics, very challenging.

While acid sites promote the formation of aromatics, the extensive skeletal isomerization induced by these sites leads to methyl branches directly on the aromatic rings and/or in the alkyl substituents, potentially altering product properties. For example, branching could affect the ease of sulfonation, surfactant performance, and biodegradability.

Zeolite pore sizes affect the yield and type of aromatics, due to the effect on diffusion of intermediate alkenes as well as confinement effects. Some monofunctional metal catalysts known to convert *n*-C₆H₁₄ selectively to benzene are less effective in polyolefin conversion, especially at lower temperatures (ca. 300 °C). Yet, these catalysts could be of interest for

further study, potentially with higher energy input but with better selectivity and catalyst stability. Overall, converting polyolefins to aromatics offers significant potential for advancing the circular economy but requires more research and development.