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Catalyst control of alkylbenzene molecular architecture in tandem catalytic hydrogenolysis-aromatization of polyethylene

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Abstract

Upcycling of polyethylene (PE) can transform waste material into chemically valuable building blocks such as linear alkylbenzenes, with potential use in anionic surfactants. Alkylbenzenes can be formed by tandem hydrogenolysis-aromatization of PE, catalyzed by Pt nanoparticles supported on an acidic oxide. In the complex mixture of hydrocarbon products, the difficulty in identifying precise structures makes it hard to predict how the choice of catalyst and variations in PE feedstock will influence molecular architectures. Here, we report a detailed characterization of the alkylbenzenes, with insight into the catalytic mechanism that controls their formation. Acid-catalyzed skeletal isomerization is the key factor that determines branching, initiates cyclization, and dictates aromatic substitution patterns. Highly acidic Pt/F-Al₂O₃ catalyst yields predominantly 3,4-dialkyl-substituted toluenes, in which the lightly branched alkyl substituents have a very small number of (mostly methyl) branches, located predominantly in non-benzylic positions. In contrast, less acidic Pt/ γ -Al₂O₃ catalyzes the formation of virtually unbranched 2,3-dialkyltoluenes. The unexpected difference in aromatic substitution reflects the dependence of the alkane cyclization mechanism on catalyst acidity. However, the structures of the alkylbenzenes are almost independent of the initial PE microstructure (e.g., LDPE vs. HDPE). Furthermore, the type of PE feedstock has little effect on the average alkyl chain length and negligible influence on the branch frequency and distribution in the alkyl side-chains of the alkylbenzene products, resulting in a consistent, low prevalence of benzylic branching compared to conventional alkylbenzenes. These features make the process well-suited to the conversion of mixed post-consumer PE, while the insights into alkylbenzene regioselectivity inform catalyst design to obtain desired linear alkylbenzene structures, and facilitate investigation of structure-property relationships in surfactants sourced from waste PE.

Keywords

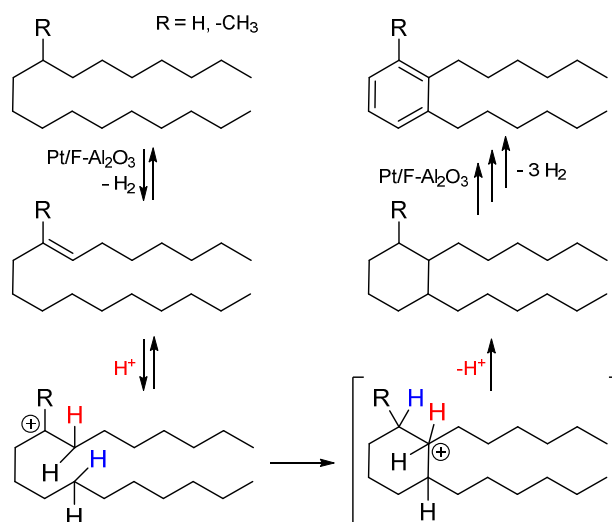
Polyethylene upcycling, linear alkylbenzene, plastic waste, bifunctional catalysis, aromatization, dehydroaromatization, structural characterization, skeletal isomerization, alkane cyclization mechanism

Introduction

Polyethylene (PE) is the world's most abundant synthetic polymer. It is manufactured for a multitude of uses, both short-term (e.g., packaging) and long-term (e.g., construction materials). The many commercial grades of PE differ widely in their materials properties. This feature makes the materials highly versatile, but imposes severe limits on mechanical recycling of mixtures.¹ Chemical recycling is impeded by the uniform chemical structure of PE, which consists solely of very similar, strong, non-polar C-C and C-H bonds.^{2,3} Consequently, the vast majority of PE is neither reused nor recycled, but is instead discarded in landfills or incinerated at the end of its (often quite short) service-life.⁴

Scalable methods to convert post-consumer PE to chemical intermediates could recover a large fraction of the chemical value and energy content from these high-volume materials. Plastic waste can be converted by pyrolysis,⁵⁻⁸ hydrogenolysis,⁹⁻¹¹ or gasification^{7,8,12,13} to liquid hydrocarbons suitable as fuels and naphtha replacements. Although these approaches are often promoted as enabling carbon circularity and plastic waste valorization, practical implementation remains economically challenging.⁵ In targeting higher value hydrocarbons, chemical upcycling seeks instead to convert PE directly to commercially useful building blocks. One class of such building blocks is alkylaromatics, which find use as lubricants, coolant liquids, dielectric fluids, and intermediates in chemical manufacturing.¹⁴ Obtaining them from PE could even be more efficient than making them from virgin fossil carbon, since the latter involves multistep processes with large greenhouse gas footprints.^{1,15}

Linear alkylbenzenes (LAB) are an important class of alkylaromatics. They are the immediate precursors of linear alkylbenzene sulfonates (LABS) that are widely used as active ingredients in household and industrial detergents.¹⁶ Conventional LAB manufacturing starts with the synthesis of linear olefins, which are then used to alkylate crude oil-derived benzene (Scheme 1).¹⁶ Recently, we demonstrated a direct synthesis of surfactant-range (C₁₆₋₂₂) alkylaromatics from waste PE by tandem-catalytic hydrogenolysis-aromatization, using a bifunctional (metal/acid) catalyst (e.g., Pt/ γ -Al₂O₃ or Pt/F-Al₂O₃).¹⁷⁻¹⁹ The process generates a complex mixture of saturated and unsaturated hydrocarbons with a significant aromatic fraction (up to 30 wt%). The aromatic products include (in order of decreasing abundance): alkylbenzenes, alkylnaphthalenes, and alkylphenanthrenes.^{17,18} Reactive separation of the crude by sulfonation mixture yielded alkylbenzene sulfonates, which exhibit several properties (e.g., solubility, critical micelle concentration, and surface activity) comparable to those of dodecylbenzene sulfonate.²⁰



Scheme 2. Possible mechanism for dialkylbenzene/toluene formation during PE depolymerization, based on a cascade of Pt-catalyzed dehydrogenation and Brønsted acid-catalyzed isomerization/cyclization steps.

The molecular structures of LAB/LABS are key to their surfactant properties.²¹ For example, the placement and frequency of branches on the alkyl chains,^{21,22} the location of the phenyl ring along the alkyl chains,^{21,23,24} and the alkyl chain lengths,²¹ can alter the relative sizes and shapes of the hydrophobic/hydrophilic domains. These domains control self-assembly and interfacial packing, thereby affecting behavior in detergent applications.²¹ For example, increased alkyl chain lengths result in a lower critical micelle concentration and more efficient reduction of surface tension, while shorter alkyl chains generally confer better solubility, improved detergency at low temperatures, and improved hard water tolerance.^{21,23–26} Crucially, biodegradability depends on aspects of alkylbenzene structure, particularly on the extent and location of side-chain branching.²⁷ When the widespread use of highly branched alkylbenzene sulfonates (BABS) in detergents was banned due to their poor biodegradability, they were replaced by more readily degradable LABS.²⁷ In the case of PE-derived LAB, the limited information about their molecular structures and how the catalyst influences them is an impediment to investigating their potential as surfactant precursors.

We now report how catalyst acidity influences the average alkylbenzene structure by promoting depolymerization and aromatization. While much of the investigation focuses on the most effective Pt/F-Al₂O₃ catalyst, we compare the outcome for less acidic Pt/γ-Al₂O₃. We also investigate the influence of initial microstructure in the PE feedstock (i.e., branch type and frequency). The resulting insights provide a deeper understanding of individual steps in the depolymerization mechanism, in particular, how acid-catalyzed isomerization determines the alkylbenzene branching and substitution pattern.

Results and Discussion

Scale-up and separation of alkane and linear alkylbenzene depolymerization products. Our initial reports of PE depolymerization by tandem hydrogenolysis-aromatization were mostly based on smaller-scale experiments.^{17,18} The products were analyzed to provide insight into the reaction and catalyst performance,¹⁸ but our ability to characterize the complex hydrocarbon mixtures was limited to identifying major hydrocarbon product classes (alkanes, alkylaromatics), average carbon number, etc. More in-depth characterization of the depolymerization products required sufficient crude material in the desired carbon-number range to facilitate separation. Reaction scale-up is not trivial for catalytic PE depolymerization, due to heat and mass transfer limitations in the viscous, poorly heat-conducting polymer melt. Our previous attempt using a larger batch of PE as starting material yielded a significant amount of products with carbon numbers above the desired surfactant range.¹⁷ Efficient mixing, especially at high polymer loadings, is necessary to ensure good contact between the catalyst with the polymer melt and to avoid hotspots. In previous experiments that relied on the use of a magnetic stir bar,^{18,20} mixing was limited especially in the early stages of depolymerization. In this work, experiments were conducted instead in a reactor equipped with a magnetically coupled, crossed-blade impeller (Figure S2).

A low molecular weight low density polyethylene (M_n 1,300 g mol⁻¹) with a relatively low dispersity (M_w/M_n = 2.5, Figure S9a), likely synthesized by radical polymerization using an aldehyde as chain-transfer agent (due to the observation of carbonyls by ¹H NMR, Figure S3), was used as a model PE to optimized depolymerization catalyzed by Pt/F-Al₂O₃ (1.5 wt% Pt, 0.6 wt% F) as the catalyst. The amount of this PE starting material was increased gradually, while keeping the PE-to-catalyst ratio constant (Table S2, entries 1 – 4). The overall aromatic selectivity declined as the PE amount increased. Extending the reaction time restored the selectivity but gave more of the undesired polyaromatic products, which form in a cascade of multiple cyclization-dehydrogenation events.¹⁷ Shorter reaction times limit these side-reactions: reducing the depolymerization time from 8 to 4 h suppressed the yield of polyaromatics (relative to total liquid hydrocarbons) from 30 to 17 wt% (Table S2, entries 4 and 5).

When the amount of PE was increased to >1.5 g, the liquid hydrocarbon yield remained unchanged (60 – 70 wt%), but the alkylbenzene selectivity declined to <10 % (Table S2, entry 6), likely due to the onset of mass transport limitations in the small batch reactor with inadequate mixing efficiency at higher PE loadings. Therefore, a scale of ca. 1 g PE was selected for the appropriate balance between selectivity and efficiency under the reaction conditions (Table S2, entry 4).

Consistent with our previous reports,^{17,18} the liquid hydrocarbons obtained by catalytic hydrogenolysis-aromatization of PE consist of an alkane fraction (ca. 60 wt%) and an alkylaromatic fraction (ca. 40 wt%), based on ¹H NMR analysis of the crude mixture (Figures 1a and S9 – S12). The alkylaromatics are comprised of alkylbenzenes (ca. 25 wt%) as well as polyaromatic hydrocarbons such as alkylnaphthalenes and alkylphenanthrenes (ca. 15 wt%).

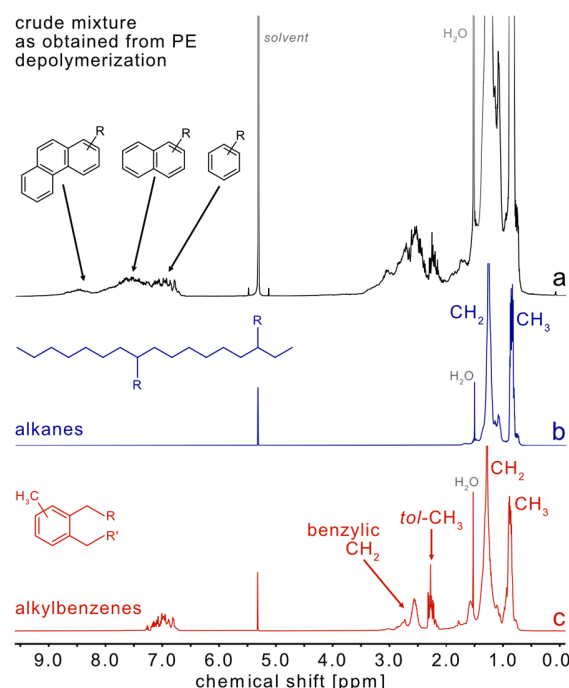


Figure 1. ^1H NMR spectra (500 MHz, CD_2Cl_2 , 300 K) of liquid hydrocarbons obtained by catalytic depolymerization of a model PE (M_n 1,300 g mol^{-1}), catalyzed by $\text{Pt/F-Al}_2\text{O}_3$: (a) the crude product mixture, consisting of alkanes and a variety of alkylated mono- and polyaromatics, (b) the isolated alkane fraction (avg. C_{20}), and (c) the isolated alkylbenzene fraction (avg. C_{19}).

Scale-up allowed us to generate enough material for separation of the crude hydrocarbon product mixture and more detailed structural characterization. The valuable linear alkylbenzenes were separated from the lower-value alkanes and undesired polyaromatics by silica gel column chromatography, using hexanes as the eluent. The first-eluting fraction consisted largely of alkanes ($R_f \geq 0.91$, 52 wt%), containing a negligible amount ($< 1\%$) of aromatics (Figure 1b). Alkylbenzenes eluted next (Figure 1c, $0.81 \leq R_f \leq 0.90$, 10 wt%) while the alkylated polyaromatics showed even longer retention times and mostly remained on the stationary phase.

Structural characterization of alkane products. The alkane fraction consists mostly of acyclic alkanes, with average carbon number C_{20} according to GC-FID analysis (see the Supporting Information for details). A small amount of alkylcyclohexanes is also present, as evidenced by the ^{13}C peak at 47.3 ppm (Figure S15). It was assigned based on 2D HSQC/HMBC and 135-DEPT- ^{13}C NMR (Figures S16, S23, S24). This minor product class is significant because such species are key intermediates in the aromatization mechanism, Scheme 2.

Alkyl branches are observed by ^{13}C NMR (Figures S14 – S22), confirming that *iso*-alkanes are present. Based on the CH_2/CH_3 integral ratio in the ^1H NMR spectrum (Figure 1b), each alkane has, on average, 2.3 branches (eq. S5). Thus, the major saturated products are *iso*-alkanes with similar isomer distributions, and therefore similar branching frequencies, for each carbon number (as observed by GC-FID, Figures S25 – 28). A detailed analysis of the branching structure was performed (see Figure S15 and Tables S5 – S6) using 2D NMR, literature assignments^{28–37} and

quantitative ^{13}C NMR, which identified the prevailing branch type as Me (70 % of total branches). Longer alkyl branches such as Et (12 %), *n*-Pr (10 %), and *n*-Bu (8 %) are also present, in smaller amounts. Most Me branches are in-chain (71 %), with the remainder located near a chain end (i.e., in the α - or β -positions), as *i*-Pr (15 %) or *s*-Bu (14 %) motifs. Weaker ^{13}C NMR signatures characteristic of Me branches in γ - and δ -positions relative to the chain end are also present, as well as pairs of Me branches located in 1,3-, 1,4- and 1,6- positions along the chain (Figure S15).

The branching frequency in the alkane products is significantly higher, at 118 branches/1000C, than in the model PE (23 branches/1000C, see Supporting Information for details of PE characterization). Most branches in the products therefore originate from skeletal isomerization during depolymerization, catalyzed by the strongly acidic Pt/F- Al_2O_3 .^{38–41} Furthermore, microstructure analysis of the model PE by ^{13}C NMR revealed only branches longer than C_4 (Figure S4). Thus, all shorter (C_{1-3}) branches and more complex branching structures in the alkane products arise by acid-catalyzed isomerization.

The structural composition of the PE derived *iso*-alkanes resembles paraffins used in the formulation and refining of diesel and aviation fuels.^{9,11} Incorporating these alkanes into sustainable aviation fuel refining could make the overall process of PE derived alkylbenzene synthesis more economically viable by also extracting additional value from the alkane fraction.

Structural characterization of alkylbenzene products. According to GC-FID, the average carbon number in the alkylbenzene fraction is C_{19} , consistent with previous reports that molecular weight profiles are similar for different hydrocarbon classes formed by random chain scission,^{17,18} and suggesting that chain cleavage occurs independently of aromatization. Based on the ratio of aromatic protons to CH_α protons (Figure 1c and eqs. S7 – 9), the average structure is a trialkyl-substituted benzene (avg. 3.1 ± 0.1 alkyl substituents per aromatic ring). The alkyl substituents are comprised of one-third Me groups (^1H NMR multiplet centered at 2.27 ppm) and two-thirds longer alkyl chains. Thus, the alkylbenzene products are best described as dialkyltoluenes containing two. The Me-substituted core structure highlights the mechanistic importance of these branches in the formation of aromatic rings.

The non-Me alkyl substituents have an average carbon number of approximately C_8 , calculated from ^1H NMR integration (eq. S10), with shorter Et and *n*-Pr chains being minor contributors. A broad distribution of alkyl chain lengths is expected when the location of cyclization is random. According to the CH_2/CH_3 ratio obtained by ^1H NMR (Figures 1c and S29), the alkyl substituents are mildly branched with, on average, one branch per alkylbenzene molecule. ^{13}C NMR shows that the motifs in the alkylbenzene fraction closely resemble those in the alkane fraction (Figure 2), with Me being the most abundant branch type (76 %), accompanied by smaller amounts of Et (13 %), *n*-Pr (10 %) and *n*-Bu (5 %) branches. The locations of the Me branches resemble those observed in the alkane products, with in-chain Me groups (57 %) dominating. Me branches close to an alkyl chain end are present mostly in *i*-Pr (19 %) and *s*-Bu (24 %) motifs, with smaller amounts of γ - and δ - CH_3 branches. Spectroscopic signatures for 1,3-, 1,4- and 1,6-dimethyl

branch pairs are also observed. A similar branch structure for both alkane and alkylbenzene products is expected, since the latter form by cyclization of the former. This expectation is further supported by the calculated average alkylbenzene branching frequency of 96 br/1000C (eq. S12), which resembles that of the alkane fraction (118 br/1000C). This result suggests that aromatization proceeds without significant further isomerization of the alkyl substituents.

Notably, few branches (ca. 10 %) are present in benzylic positions relative to the aromatic ring (Figure S30), and no dibranched benzylic carbons were observed. The low prevalence of benzylic branches compared to conventional alkylbenzenes is a direct consequence of the difference in mechanisms for their formation. Conventional alkylbenzenes synthesized by acid-catalyzed benzene alkylation with α -olefins tend to undergo electrophilic addition at the β -carbon, where the carbenium ion is more stable (Scheme 1). In contrast, catalytic dehydroaromatization involves acid-catalyzed cyclization of long-chain alkanes followed by dehydrogenation of the resulting cycloalkanes (Scheme 2). Since the original polymer chains are mostly linear, there is little chance of forming a benzyl branch except when the alkane segment contains a 1,6-dimethyl-branched motif (ca. 8 % of alkane products, Figure S15). The ability to achieve a low frequency of benzylic branching is key for LAB applications, since LABS with more highly substituted benzylic carbons tend to be less readily biodegraded than LABS with less substitution in this position.²⁷ In commercial applications, no more than 35 % of monobranched isomers and no more than 1 % dibranched isomers are allowed, to ensure adequate surfactant biodegradability.⁴² Formation of PE-derived alkylbenzenes by dehydroaromatization therefore represents a potential route to more biodegradable LABS surfactants, compared to established methods based on aromatic alkylation.

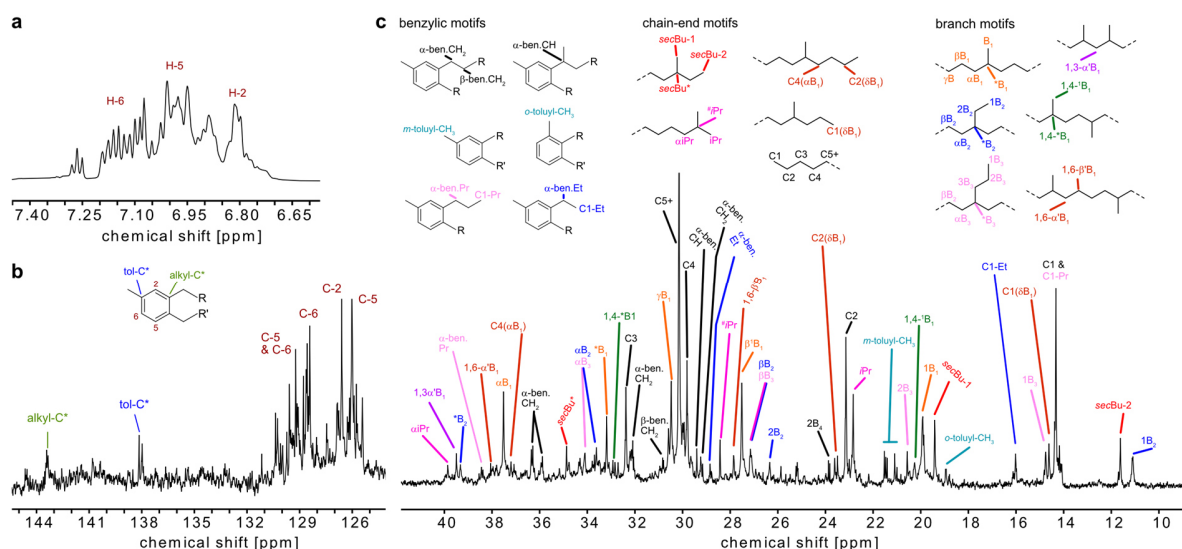


Figure 2. NMR characterization of alkylbenzenes obtained from tandem depolymerization of a low molecular weight PE (M_n 1,300 g mol⁻¹), catalyzed by Pt/F-Al₂O₃ (Table 1, entry 1), showing assignments for: (a) the aromatic region in the ¹H NMR (500 MHz, CD₂Cl₂, 300 K), (b) the aromatic region in the ¹³C NMR (126 MHz, CD₂Cl₂, 300 K), and (c) the alkyl region in the ¹³C NMR (126 MHz, CD₂Cl₂, 300 K).

Dialkyl-substituted toluenes may have several possible aromatic substitution patterns, including ‘all-*ortho*’ (i.e., 2,3-dialkyltoluene) and ‘all-*meta*’ (i.e., 3,5-dialkyltoluene), Figure 3. In dialkyltoluenes made by Pt/F-Al₂O₃-catalyzed PE depolymerization, the location of the toluene-CH₃ is predominantly *meta* to the nearest alkyl substituent (Figure 3D), based on the absence of strong multi-bond correlations between the toluene-CH₃ group and the aromatic ring carbons bearing the alkyl substituents in the 2D ¹H-¹³C HMBC (Figure S47). This conclusion was further confirmed by comparing the toluene-CH₃ ¹³C NMR chemical shift in the dialkyltoluene mixture to the corresponding spectra of two model compounds (3,5-diethyltoluene and 1-methyl-2-octylbenzene), as well as a comparison of their HMBC multi-bond correlations (Figures S46 – S47). Quantitative analysis of ¹³C NMR toluene-CH₃ signals revealed *meta*- and *ortho*-toluene-CH₃ groups in a ca. 3:1 ratio (Figures 4 and S47, and Table S9). This finding contrasts with our earlier speculation that the toluene-CH₃ should be located *ortho* to an alkyl substituent, due to its role in stabilizing the cationic intermediate and facilitating cyclohexane ring closure.¹⁸ The prevalence of the *meta*-toluene-CH₃ orientation suggests either that such stabilization is not necessary for cyclization, or that cyclization proceeds *via* a different mechanism (*vide infra*).

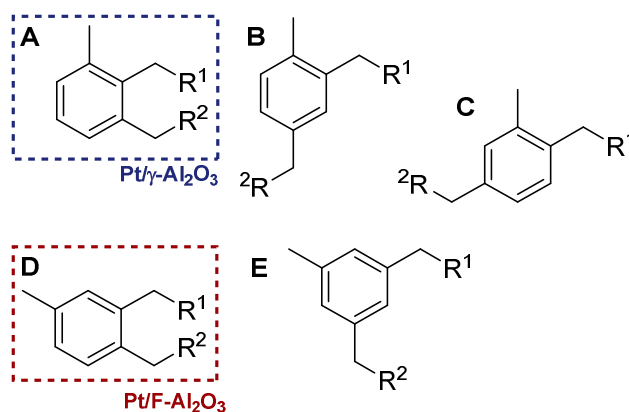


Figure 3. Possible aromatic substitution patterns in PE-derived dialkyltoluenes, highlighting the difference between the dominant structures arising from the use of less acidic Pt/γ-Al₂O₃ (A) or more acidic Pt/F-Al₂O₃ (D) as the depolymerization catalyst. Other possible aromatic structures (B, C and E) were not detected.

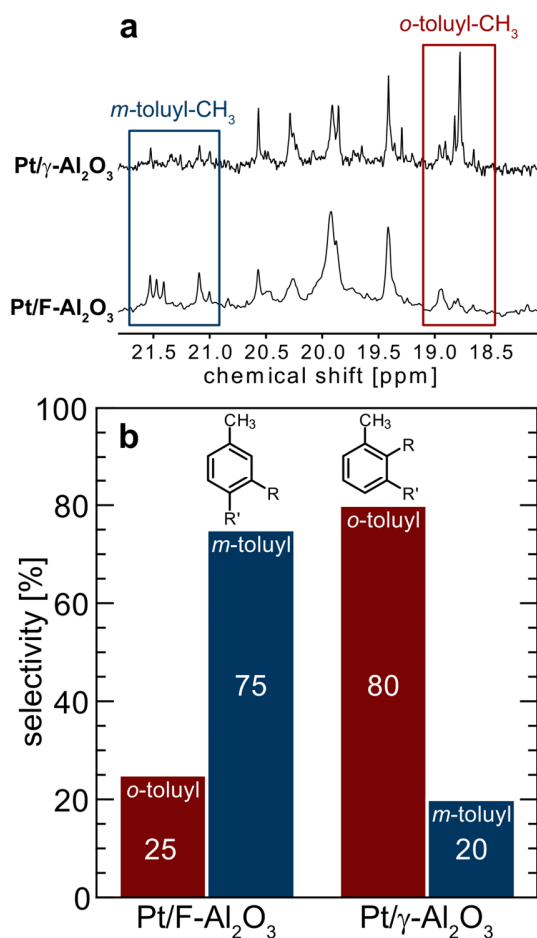


Figure 4. Inversion of toluene-CH₃ position selectivities in dialkyltoluenes, in: (a) the Me region of the ^{13}C NMR spectra (126 MHz, CD_2Cl_2 , 300 K), highlighting signals corresponding to *ortho*- and *meta*-toluene-CH₃, and (b) quantitative distribution of *ortho*- and *meta*-toluene-CH₃ groups, for alkylbenzenes obtained with $\text{Pt}/\text{F-Al}_2\text{O}_3$ and $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$.

The dialkyl substituents can be present as mutually *ortho*- or *meta*-isomers. *Ortho*-orientation was proposed previously, also based on the expected outcome of random cationic 1,6-cyclization.¹⁸ Analysis and assignment using 2D ^1H - ^{13}C HMBC and HSQC NMR (Figure S51) combined with comparison to spectra of two model compounds (1,2-diethylbenzene and 3,5-diethyltoluene, Figures S49 – S50) suggest that this is indeed the prevailing substitution pattern.

In summary, alkylbenzenes formed by PE depolymerization catalyzed by $\text{Pt}/\text{F-Al}_2\text{O}_3$ are best described as 3,4-dialkyl-substituted toluenes (Figure 3D). Each alkyl substituent has an average length of C_8 , and one alkyl branch located on one of the two alkyl substituents.

Effect of catalyst acidity on molecular architectures

After resolving the molecular structures of these alkanes and alkylbenzenes, the effect of catalyst acidity on skeletal isomerization and cyclization was investigated by replacing the $\text{Pt}/\text{F-Al}_2\text{O}_3$ catalyst with the less acidic $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$. Fluorination of $\gamma\text{-Al}_2\text{O}_3$ dramatically increases support

acidity by polarizing residual AlO-H bonds, resulting in an increase in strong Brønsted acid sites (ca. 4x BAS/g in F-Al₂O₃ compared to γ -Al₂O₃) and elimination of weak BAS. The number of strong Lewis acid sites also increases due to the inductive effect of F, but to a smaller extent (ca. 1.5x LAS/g for in F-Al₂O₃ compared to γ -Al₂O₃).¹⁸ Consequently, fluorination leads to a large difference in the BAS/LAS ratio between the two oxides, which has catalytic consequences for the rates and selectivities in catalytic depolymerization.” Depolymerization of the low-molecular weight PE (23 br/1000C) using the less acidic Pt/ γ -Al₂O₃ as catalyst under the reaction conditions optimized for liquid production with Pt/F-Al₂O₃ gave a crude hydrocarbon mixture comparable to that obtained with Pt/F-Al₂O₃ with respect to overall liquid yield, average carbon number, aromatic yield, and mono- vs. polyaromatic selectivity (Table S3, entries 1 and 2). However, the isolated alkanes made with Pt/ γ -Al₂O₃ are solid at room temperature, while alkanes made with Pt/F-Al₂O₃ are liquid. The change in physical appearance is consistent with a difference in intermolecular interactions caused by branching, which disrupts hydrocarbon chain packing. According to ¹H and ¹³C NMR, alkanes made with Pt/ γ -Al₂O₃ have 33 br/1000C (0.6 br/chain), which is only slightly higher than the PE branch frequency (23 br/1000C, Figures S21 – S22), while alkanes made with Pt/F-Al₂O₃ have 118 br/1000C (Figure 5a). Thus, Pt/ γ -Al₂O₃ is much less active than Pt/F-Al₂O₃ for skeletal isomerization.

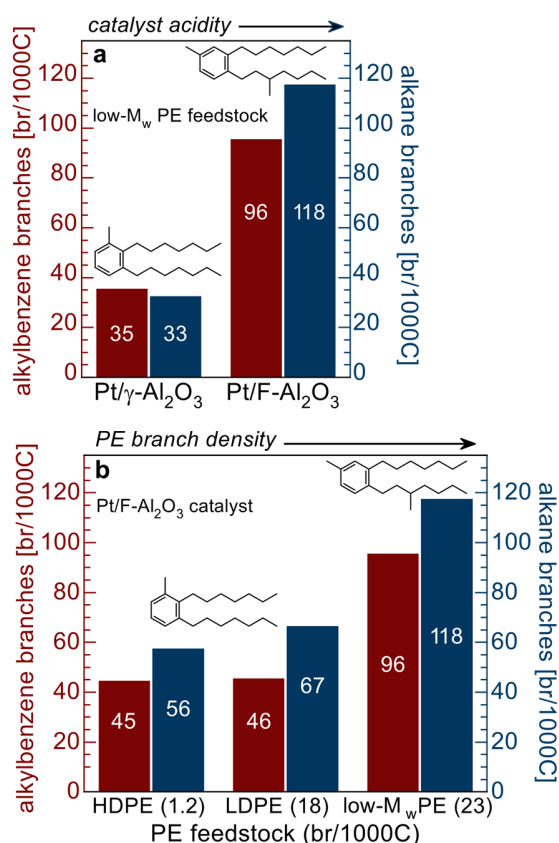


Figure 5. Branching frequencies in alkylbenzenes (blue) and alkanes (red), arising from catalytic PE depolymerization: (a) effect of catalyst acidity, and (b) effect of initial PE microstructure. Frequencies, obtained by integration of the ^1H NMR spectra, are reported in branches/1000C.

Alkylbenzenes made using the $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ catalyst are also less branched (Table 1, entry 2 and Figure 5a). Indeed, the alkyl substituents are mostly linear (< 0.1 br/molecule). The average alkyl chain length is similar to alkylbenzenes made with $\text{Pt}/\text{F-Al}_2\text{O}_3$ (C_8). The prevailing branch type is still Me (ca. 40 % for both alkanes and alkylbenzenes) arising from skeletal isomerization, however, longer-chain branches (i.e., Et, *n*-Pr and *n*-Bu) make relatively higher contributions (see Figure 6, Tables S6 and S8). In particular, the elevated abundance of *n*-Bu branches (28 % in the alkane fraction; 13% in the alkylbenzene fraction) resembles that in the PE, indicating that a higher proportion of the branches in the depolymerization products is derived from the original polymer microstructure.

Table 1. Branch densities in alkylbenzenes obtained by catalytic depolymerization of various polyethylenes

#	PE	PE branches /1000C ^a	Catalyst	C _n		Aromatic substituents C _{≥2} /CH ₃ ^d	Alkylbenzene branches		α-branches ^g [mol%]
				Overall ^b	Alkyl chain ^c		per 1000C ^e	per molecule ^f	
1	Low-MW	23	Pt/F-Al ₂ O ₃	19	7.6	2.1 / 0.9	96	1	11
2	Low-MW	23	Pt/γ-Al ₂ O ₃	23	7.5	2.5 / 0.5	35	< 0.1	20
3	LDPE	18	Pt/F-Al ₂ O ₃	21	6.2	2.4 / 0.6	46	0.3	14
4	HDPE	1.2	Pt/F-Al ₂ O ₃	20	5.5	2.4 / 0.6	45	0.3	14

^a Determined by ^1H NMR (see Supporting information). ^b Determined by GC-FID according to previously reported procedures, and assuming that alkylbenzene isomers elute in the same order as alkane isomers with the same carbon number.¹⁸ This assumption can lead to minor differences in C_n values determined *via* GC-FID and NMR. ^c Determined by ^1H NMR using the integral ratios of aliphatic to α-protons (eq. S10). ^d Determined by ^1H NMR, comparing the integral ratios of aromatic protons (6.60 – 7.30 ppm, eqs. S8 – 9), α-protons (α-CH₂ 2.40 – 2.90 ppm, α-CH 3.00 ppm) and toluene-CH₃ protons (2.27 ppm). ^e Theoretical value, predicted using the CH₂/CH₃ ratio from ^1H NMR integration and the average carbon number obtained by GC-FID (eq. S12). The value includes both alkyl branches and toluene-CH₃ substituents. ^f Determined by ^1H NMR, by calculating the number of CH₃ groups on aliphatic chains (0.89 ppm) in excess of the number of CH₃ end-groups (one per alkyl chain, eq. S11). ^g Determined by ^1H NMR, comparing the area of the α-CH signal (3.00 ppm) with that of the α-CH₂ signals (2.40 – 2.90 ppm, eq. S13).

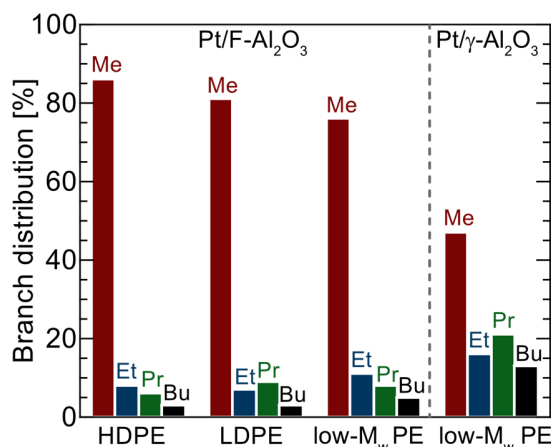


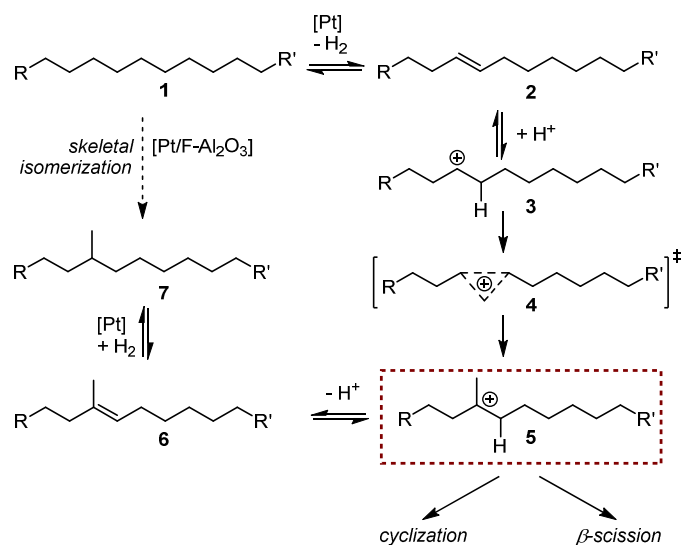
Figure 6. Effect of PE type and catalyst acidity ($\text{F-Al}_2\text{O}_3 > \gamma\text{-Al}_2\text{O}_3$) on the branch length distribution for alkylbenzenes obtained by PE depolymerization, as determined by quantitative ^{13}C NMR spectroscopy.

While alkylbenzenes made with the $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ catalyst are still trialkyl-substituted, the average number of toluene- CH_3 groups (0.5) is slightly lower relative to longer ($\text{C}_{\geq 2}$) alkyl substituents (2.5), compared to the trialkylbenzenes made with the $\text{Pt}/\text{F-Al}_2\text{O}_3$ catalyst (Table 1, entries 1 vs. 2). The lower toluene selectivity is likely due to lower absolute and relative amounts of Me branches in the alkane depolymerization products, resulting in more cyclization events induced by longer alkyl branches. Furthermore, the aromatic substitution pattern is different: in alkylbenzenes made with $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$, the toluene- CH_3 is located predominantly *ortho* to a neighboring alkyl chain (80 %), with only a minor amount of *meta*-toluene- CH_3 (20 %) (Figure 4 and Table S9). Nevertheless, the majority of longer alkyl substituents remain *ortho* relative to each other (see Figure S49 – S51).

The origin of the change in isomer selectivity was considered. In principle, an alkyl substituent could migrate after an alkylbenzene forms, *via* acid-catalyzed aromatic (de-)alkylation followed by realkylation of the aromatic ring.⁴³ Such isomerization would result in the observed difference in aromatic substitution patterns, especially since 3,4-dialkyltoluenes are expected to have fewer steric interactions and therefore be more stable than the corresponding 2,3-dialkyltoluenes. However, none of the model compounds 1,2-diethylbenzene, dodecylbenzene and 2-octyltoluene isomerized when each was exposed to $\text{F-Al}_2\text{O}_3$ under depolymerization conditions (280 °C, 4 h, Figure S56). The difference in toluene-substitution patterns must therefore originate during initial alkylbenzene formation, suggesting that a catalyst-dependent cyclization mechanism determines the aromatic structure. Once the cyclohexane intermediate forms, the substituent locations do not change because aromatization is effectively irreversible.⁴⁴

Mechanism of tandem-catalytic dehydroaromatization

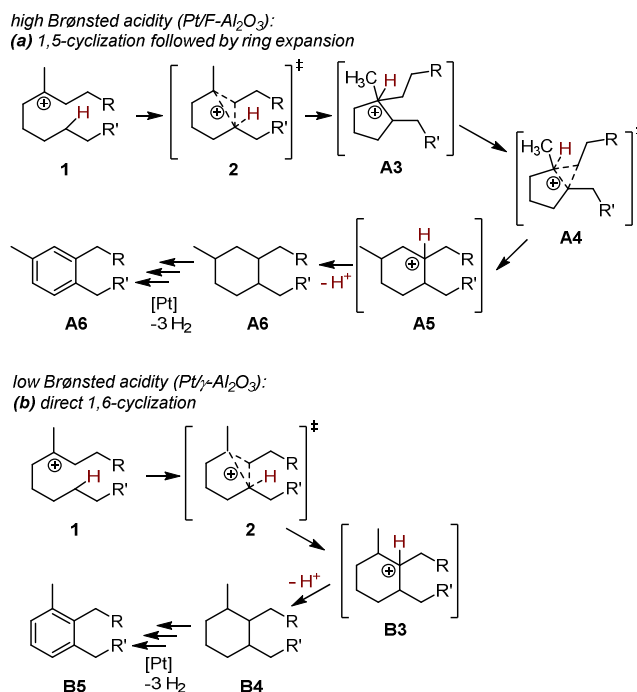
The findings above demonstrate that acid-catalyzed isomerization of PE/alkane chains during depolymerization plays an important role not only in chain cleavage by β -scission (as previously reported),⁴⁵ but also in the mechanism and outcome of alkylaromatic formation. The consistent observation of a trialkyl-substitution pattern for alkylbenzenes regardless of catalyst acidity affirms the importance of branch formation in the stabilization of the carbenium intermediate that undergoes cyclization. A proposed mechanism that accounts for this stabilization is shown in Scheme 3. The first step is Pt-catalyzed alkane dehydrogenation to olefins (**2**), whose activation by protonation forms carbenium ions (**3**). (Alternatively, direct alkane protonation proceeds via carbonium ions, which can be converted to carbenium ions by elimination of H_2 .) Secondary carbenium ions rearrange through cationic cyclopropyl transition states (**4**) to more stable tertiary carbenium ions, thereby forming a Me branch (**5**).^{39–41} Longer C_{2-4} branches can also form by this type of isomerization, since alkyl chains can undergo multiple, consecutive skeletal rearrangements at the same position.^{38,41}



Scheme 3. Mechanism of acid-catalyzed skeletal isomerization to form new Me branches by carbocation rearrangement, as a key step prior to cyclization.

Deprotonation of the tertiary carbenium ions followed by hydrogenation leads to the observed *iso*-alkane products. Alternatively, carbocations can undergo either chain cleavage via β-scission, or cyclization/dehydroaromatization resulting in alkylbenzene products. The consistent appearance of trialkylbenzenes independent of catalyst acidity suggests that cyclization is highly preferred adjacent to a tertiary carbenium (**5**) rather than a secondary carbenium (**3**). Initial branch formation by acid-catalyzed skeletal isomerization prior to cyclization is likely key to alkylbenzene formation, since cyclization is rate-determining in bifunctional alkane dehydroaromatization.⁴⁴

The precise cyclization pathway is influenced by catalyst acidity, leading to different positions of the carbenium ion-stabilizing branch (usually Me) on the cyclohexane ring, relative to the longer alkyl substituents. Since alkylbenzene isomerization can be ruled out (see above, and Figure S56), cyclization of **5** determines the structure of the substituted cyclohexyl cation prior to aromatization.⁴⁴ Cyclohexyl intermediates can form either directly *via* 1,6-ring closure, or indirectly by 1,5-ring closure followed by ring expansion.^{44,46–49} The two cyclization pathways result in distinct substitution patterns (Scheme 4). Both mechanisms initiate from a tertiary carbenium ion stabilized by a Me (most likely) or longer alkyl (occasionally) branch (**5**). When the catalyst is highly acidic Pt/F-Al₂O₃, the most likely fate of the carbenium ion is 1,5-cyclization to form a di-substituted cyclopentylcarbonium (**A2**). The latter undergoes ring expansion to cyclohexylcarbonium (**A4**), prior to irreversible dehydrogenation to give the alkylbenzene (**A5**). When the catalyst is less Brønsted acidic Pt/γ-Al₂O₃, direct 1,6-cyclization to a cyclohexylcarbonium ion (**B2**) is favored instead.



Scheme 4. Proposed Brønsted acidity-dependent cyclization pathways when the catalyst is (a) highly acidic $\text{Pt}/\text{F-Al}_2\text{O}_3$, or (b) less acidic $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$.

Support acidity has been reported to affect the relative rates of cyclization pathways in catalytic alkane dehydrocyclization,^{44,48,49} with computational studies involving H-ITQ-13 and H-ZSM-5 zeolite catalysts predicting comparable barriers for both pathways.^{47,48} The influence of acidity on dehydroaromatization of small-molecule alkanes was previously investigated by comparing Pt supported on acidic $\text{Cl-Al}_2\text{O}_3$ and non-acidic $\text{K-Al}_2\text{O}_3$. In the latter, Brønsted acid sites were eliminated by treating $\eta\text{-Al}_2\text{O}_3$ with KOH, with the effect of exclusively obtaining products of direct 1,6-cyclization in reactions of various alkanes. For example, $\text{Pt}/\text{K-Al}_2\text{O}_3$ predominantly yielded *o*-xylene whereas $\text{Pt}/\text{Cl-Al}_2\text{O}_3$ was selective for the *meta*-isomer.⁴⁴ Similar to our observations (Figure S56) a secondary restructuring of once formed aromatics by the acidic catalyst was ruled out in isomerization experiments.⁴⁴ These reports support the proposed competition between catalytic PE dehydroaromatization pathways.

The origin of the catalyst-dependent mechanistic preference for either 1,5- or 1,6-cyclization may be differences in carbocation-support interactions, as suggested by DFT calculations involving H-ITQ-13.⁴⁷ Another computational study predicted a preference for 1,6-cyclization of the highly localized carbocation formed by protonation of 1,5-hexadiene, while Lewis acid activation of a double-bond led to a steric preference for 1,5-cyclization, although the energy differences were subtle and subject to substituent effects.⁵⁰ A similar switch in the mechanism of olefin activation may cause the support-dependence of selectivity in solid acid-catalyzed PE dehydroaromatization. Free carbocations formed by the strong Brønsted sites of $\text{Pt-F-Al}_2\text{O}_3$ might lead to a potential kinetic preference for the five-membered ring (**A3**), which rearranges to the six-

membered ring (**A5**) needed for aromatization. In contrast, Lewis acid-base activation by Pt/ γ -Al₂O₃ possibly favors formation of the less sterically hindered six-membered ring (**B3**). Mild fluorination of γ -Al₂O₃ or ZSM-5 predominantly increases the Brønsted acidity, particularly the number of strong BAS. Although the number of strong Lewis acid sites also increases slightly, the effect is surpassed by the change in strong BAS and thus the BAS/LAS ratio increases.^{18,51} This finding is consistent with the proposed switch from a Lewis acid-dominant cyclization mechanism (for Pt/ γ -Al₂O₃) to a Brønsted acid-dominant mechanism (for Pt/F-Al₂O₃).

Although the observed differences in molecular structure associated with the difference in catalyst acidity allowed us to propose a modified PE dehydroaromatization mechanism, including competing, acidity-dependent cyclization pathways, the underlying causes of the mechanistic variations warrant further investigation, inspired by computational studies of alkane dehydroaromatization.^{46,47}

Effect of PE microstructure. PE grades vary considerably, not only in average chain length and molecular weight distribution, but also in branch type and branch frequency which is important to consider in PE upcycling, yet often poorly discussed.⁵² The influence of the starting PE type on the final LAB structure was investigated using two PEs with very different microstructures and higher molecular weights (closer to commercial-grade PEs). In addition to the low molecular weight PE (M_n 1,300 g mol⁻¹, M_w/M_n = 2.5), we investigated a higher molecular weight LDPE made by classical free-radical polymerization, with a higher molecular weight (M_n 8,100 g mol⁻¹) and dispersity (M_w/M_n = 9.4, Figure S9b). The overall branching frequency is slightly lower (18 br/1000C) than for the low molecular weight LDPE (23 br/1000C). Radical polymerization in absence of a chain transfer agent also results in long-chain branches. These differences in microstructure affect the viscoelastic behavior of the LDPE melt. A high-density polyethylene (HDPE, M_n 5,900 g mol⁻¹, M_w/M_n = 11.4), made by catalytic coordination polymerization, was also investigated. The HDPE chains are highly linear with only a small number of methyl branches (1.2 br/1000C) (see the Supporting Information for further PE characterization).

Both higher molecular weight PEs were depolymerized using Pt/F-Al₂O₃, under the reaction conditions optimized for the lower-molecular weight LDPE. The resulting crude hydrocarbon mixtures were similar in their liquid hydrocarbon yields, average carbon numbers, aromatic contents, and mono- vs. polyaromatic selectivity (Table S3, entries 2 – 4). Thus, the outcome of depolymerization is not significantly impacted by PE differences under the reaction conditions.

Slight structural variations are nevertheless observable by ¹H NMR after separation (Tables 1 and S7). The most significant difference is the overall branch frequency. Thus, HDPE and LDPE gave alkylbenzene products with, on average, half an alkyl branch per molecule, compared to one alkyl branch for products made from the model PE (Figure 5b and Table S7). This difference is likely caused by the difference in initial PE branching frequencies. Nevertheless, both HDPE and LDPE yield depolymerization products with branch densities 2x – 4x higher than in the PE starting

materials (Figure 5b and Table 1), confirming that even for these materials, most branches arise by acid-catalyzed skeletal isomerization during depolymerization.

Consistent with this origin, the distribution of branch length in the alkylbenzene products is nearly invariant (and mostly Me, with smaller amounts of Et, *n*-Pr and *n*-Bu, regardless of the type of PE, although there is a dependence on catalyst acidity (Figure 6 and Table S8). Notably, the amount of branching in the benzylic position changes little with the PE type. Nevertheless, PE molecular weight does affect the average extent of alkylbenzene substitution slightly (see the Supporting Information for detailed calculations). Specifically, alkylbenzenes derived from Pt/F-Al₂O₃-catalyzed depolymerization of higher molecular weight LDPE and HDPE show a slightly elevated ratio of longer (C_{≥2}) alkyl substituents to toluene-CH₃ substituents (2.4:0.6), compared to the lower molecular weight PE (2.1:0.9). This finding suggests that longer branches also promote cyclization. The higher molecular weight polymers also show a slight decrease in average alkyl chain length, which may be an artifact of the calculation since ¹H NMR resolves only toluene-CH₃ and averages the length of all C_{≥2} alkyl chains (both alkyl substituents directly attached to the phenyl ring and branches on these substituents). Aside from these minor variations, the aromatic substitution patterns in alkylbenzenes obtained by depolymerizing LDPE and HDPE share the same 3,4-dialkyltoluene core structure, with a *meta*-toluene-CH₃ relative to the neighboring alkyl chains (Table S9). The latter are predominantly *ortho* relative to each other, as shown by 2D NMR spectroscopy and by assignment (Figure S51) based on comparison with model compounds (3,5-diethyltoluene and 1,2-ethylbenzene, Figure S49).

Conclusions

Tandem catalytic PE hydrogenolysis-aromatization was scaled up, making purification of the alkane and alkylbenzene products by chromatographic separation possible. Detailed structural investigation of both isolated product types revealed lightly branched molecules whose branches arise predominantly by Brønsted acid-catalyzed skeletal isomerization. This reaction largely determines the number of branches in the resulting depolymerization product. The alkylbenzenes are largely dialkyltoluenes with ≤ 1 branch per molecule, and methyl as the major branch motif. Most (≥ 90 %) of the alkyl chains are unbranched at the benzylic carbon, which is important for their biodegradability.

Aromatization is initiated at an alkyl branch site, which stabilizes the tertiary carbocation. The precise cyclization mechanism depends on catalyst acidity, which determines the resulting aromatic substitution pattern. Thus, highly acidic Pt/F-Al₂O₃ yields dialkyltoluenes with the methyl group located mostly in the *meta*-position relative to the alkyl chains (i.e., 3,4-dialkyltoluenes), while less acidic Pt/γ-Al₂O₃ is selective for 2,3-dialkyltoluenes. This change in selectivity is consistent with a change in mechanism from indirect 1,5- to direct 1,6-ring closure. Catalyst design can therefore be used to control alkylbenzene structures to target surfactants for specific applications.^{22–24}

Finally, variability in the PE feedstock in terms of branching microstructure (e.g., HDPE vs. LDPE) and molecular weight exerts only a minor influence on the molecular architecture of the alkylbenzene products. Instead, their structures are determined by catalyst acidity due to its influence on hydrocarbon isomerization. The result is a consistent branch distribution regardless of PE grade, and a low prevalence of benzylic branching. This robustness of product selectivity regardless of the PE grade means it is not necessary to separate the different PEs prior to reaction to obtain consistent product characteristics. The depolymerization process therefore appears amenable to the use of realistic PE mixtures as feedstock, while still offering the flexibility to target specific structural characteristics in the surfactants *via* catalyst choice.

Experimental methods

Materials and analytical methods

See the Supporting information for a detailed description of materials and analytical methods.

Preparation of catalyst support

F-Al₂O₃ with a nominal F-content of 0.8 wt% (measured: 0.6 wt%) was synthesized by incipient wetness impregnation of γ -Al₂O₃, according to a previous procedure.¹⁸ A solution of NH₄F (109 mg) in MilliQ H₂O (1.54 mL, corresponding to the pore volume) was added dropwise to calcined γ -Al₂O₃ (3.50 g, pore volume 0.44 mL g⁻¹) while stirring vigorously with a glass rod. The slurry was dried at 120 °C for 2 h, followed by heating to 550 °C (2 °C/min) and calcining in air at 550 °C for 5 h.

Synthesis of supported Pt catalysts

Catalysts were synthesized by incipient wetness impregnation to obtain materials with a nominal Pt loading of 1.6 wt% (see Table S1 for measured Pt contents). A solution of [Pt(NH₃)₄](NO₃)₂ (113 mg) in MilliQ H₂O (volume corresponding to the pore volume of the support) was added dropwise with vigorous stirring to 3.50 g of either γ -Al₂O₃ or F-Al₂O₃. The mixture was dried at 120 °C for 2 h before heating to 450 °C (2 °C/min) followed by calcination at 450 °C in air for 3 h. The resulting solids were reduced at 280 °C in a flow of 5% H₂ in Ar (temperature program: 2 h ramp to 280 °C, 2 h hold at 280 °C, cool to 120 °C), then evacuated at the same temperature (30 min, ca. 1 x 10⁻² mbar). Both catalysts were stored under an inert atmosphere (N₂ or Ar) prior to use.

PE depolymerization

Reactions were carried out in a Parr reactor (Series 4590 Micro) with a 25 mL stainless steel vessel, fitted with a safety burst valve and two manual valves. The reactor was equipped with a magnetically coupled crossed-blade impeller and a Pt100 internal temperature sensor connected to an electrical heating jacket (Figure S2). Typically, the reactor was loaded with 1.0 g polymer (low M_w PE, LDPE or HDPE) and 1.6 g catalyst (Pt/F-Al₂O₃ or Pt/ γ -Al₂O₃) inside an Ar-filled glovebox, then sealed. The reactor was removed from the glovebox, heated over 30 min to 280 °C, then held at that temperature for 4 h while maintaining stirring at 250 rpm. At the end of the reaction, the reactor was cooled to room temperature with an air jet, then gas products were

vented. Liquid and wax products were extracted with CH_2Cl_2 at room temperature. The solid residue was filtered and washed multiple times with CH_2Cl_2 (total volume 40 mL for both extraction and washing), then dried at 80 °C overnight in air. The solid residue was filtered and washed multiple times with CH_2Cl_2 (total volume 40 mL for both extraction and washing), then dried at 80 °C overnight in air. According to a previous TGA study, the solid consists of catalyst (86 – 93 wt%) and coke (7 – 14 wt%) as well as a small amount of unreacted polymer.¹⁸ The catalyst can be regenerated for further use by simple calcination, which causes minor Pt sintering in the first recycle.^{17,18} The solvent and other volatiles were removed using a rotary evaporator, followed by evacuation (ca. 1×10^{-2} mbar), to obtain the crude mixture of liquid hydrocarbons.

Alkylbenzene purification

Alkanes, alkylbenzenes, and polyaromatics were separated by combining four product batches for silica gel column chromatography (elution with hexanes). Alkylbenzenes ($0.81 \leq R_f \leq 0.90$) eluted after alkanes ($R_f \geq 0.91$) and before polyaromatics ($R_f < 0.8$).

Acid-catalyzed isomerization of model compounds

Attempted aromatic isomerizations were carried out in a 10 mL Parr reactor (Series 2500 Micro Batch Reactor System) equipped with a glass insert and a magnetic stirring bar, to mimic reaction conditions for depolymerization (temperature profile and hydrocarbon:catalyst ratio). The reactor was loaded with F- Al_2O_3 (100 mg) and an aromatic model compound (1,2-diethylbenzene, dodecylbenzene, or 2-octyltoluene, 60 mg) in a N_2 -filled glovebox. The sealed reactor was heated over 30 min to 280 °C, then held at that temperature for 4 h while stirring at 250 rpm. After cooling the reactor to room temperature using an air jet, the hydrocarbons were dissolved in CH_2Cl_2 . The solids were removed by filtration and washed (ca. 10 mL CH_2Cl_2 for extraction and washing). The solvent was removed using a rotary evaporator (40 °C, ≤ 400 mbar) and the liquid residue analyzed by NMR spectroscopy.

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Author contributions

D.J.B. conducted scaleup experiments; M.B. performed all other experiments and polymer/product characterization. M.B. and S.L.S. wrote the manuscript. All authors have given approval to the final version of the manuscript.

Notes

UC Santa Barbara filed a patent application on catalytic conversion of PE to alkylbenzenes.

Supporting Information

The Supporting Information is available free of charge at <https://.....>

Detailed experimental methods, catalyst characterization, additional reaction data, 1D and 2D NMR spectra, GC-FID chromatograms (PDF).

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