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Dehydrogenation of Light Alkanes over Supported Pt Catalysts

by

Jason Wu

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

In

Chemical Engineering

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Alexis T. Bell, Chair
Professor Enrique Iglesia
Professor T. Don Tilley

Summer 2015

Dehydrogenation of Light Alkanes over Supported Pt Catalysts

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by

Jason Wu

Abstract

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Doctor of Philosophy in Chemical Engineering

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Professor Alexis T. Bell, Chair

The production of light alkenes comprises a 250 million ton per year industry due to their extensive use in the production of plastics, rubbers, fuel blending agents, and chemical intermediates. While steam cracking and fluid catalytic cracking of petroleum crude oils are the most common methods for obtaining light alkenes, rising oil prices and low selectivities toward specific alkenes have driven the search for a more economical and efficient process. Catalytic dehydrogenation of light alkanes, obtained from natural gas feedstock, presents an attractive alternative that offers high selectivity and greater flexibility in the alkene pool to address changing demands. Platinum is the most effective metal to catalyze the reaction, but by itself, suffers from catalyst deactivation due to the buildup of carbonaceous deposits. The addition of a secondary metal to form a bimetallic alloy has been of high interest due to its ability to suppress coking and increase selectivity. This dissertation has focused on developing a deeper understanding of promotion effects of various metals and elucidating the mechanism behind coking on Pt catalysts.

The use of Sn as a promoter was first investigated, and the effects of particle size and composition on the ethane dehydrogenation performance were determined using a colloidal method to prepare model catalysts. At high conversions, catalyst deactivation from coke formation was a strong function of particle size and Sn/Pt, in agreement with previous high resolution transmission electron microscopy studies (HRTEM) studies. Deactivation decreased significantly with decreasing particle size and increasing addition of Sn. For a fixed average particle size, the activity and selectivity to ethene increased with increasing content of Sn in the Pt-Sn particle. For Pt and Pt₃Sn compositions, the turnover frequency increased with increasing particle size, while the selectivity to ethene was not strongly affected.

For uncovering the mechanism by which Pt catalysts deactivate, carbon formation on MgO-supported Pt nanoparticles was studied by *in situ* HRTEM in order to obtain time-resolved images of a single nanoparticle during the dynamic coking process. An electron dose rate dependence on the rate of carbon growth was found, and a suitable imaging strategy was adopted in order to minimize beam-induced artifacts. Multi-layer carbon growth around the nanoparticle was investigated, and significant restructuring of the particle was also observed. In particular, step formation was captured in various images, supporting evidence that the nucleation and growth of carbon during coking on Pt catalysts often requires low coordination sites such as step sites. This

is in agreement with scanning tunneling microscopy (STM) experiments, which illustrate a slight preference for carbon atoms to nucleate at the step sites on a Pt(111) crystal.

Other promoters for light alkane dehydrogenation were then investigated. The thermal dehydrogenation of *n*-butane to butene and hydrogen was carried out over Pt nanoparticles supported on calcined hydrotalcite containing indium, Mg(In)(Al)O. The optimal In/Pt ratio was found to be between 0.33 and 0.88, yielding > 95% selectivity to butenes. Hydrogen co-fed with butane was shown to suppress coke formation and catalyst deactivation, with a ratio of $\text{H}_2/\text{C}_4\text{H}_{10} = 2.5$ providing the best catalytic performance. In addition, a Pt-Ir alloy was investigated for ethane and propane dehydrogenation. Following characterization to confirm formation of a bimetallic alloy, intrinsic rate measurements at low feed residence time revealed the following trend in activity: $\text{Pt}_3\text{Sn} > \text{Pt}_3\text{Ir} > \text{Pt}$. DFT calculations carried out on tetrahedral clusters (Pt_4 , Pt_3Ir , Pt_3Sn) show that this trend in activity can be attributed to variations in the HOMO-LUMO gap of the cluster.

*To family and friends
for continued support in work and life*

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List of abbreviations and symbols

σ^2	Mean square disorder
Å	Angstrom (10^{-10} m)
CN	Coordination number
C/Pt	Carbon per platinum ratio
DFT	Density Functional Theory
DR	Electron beam dose rate
e^-	Electron
EDX	Energy dispersive X-ray spectroscopy
EXAFS	Extended X-Ray Absorption Fine Structure
F	Feed flow rate
FCC	Fluid catalytic cracking
HAADF	High-angle annular dark field
HOMO	Highest Occupied Molecular Orbital
HRTEM	High-resolution transmission electron microscopy
ICP-AAS	Inductively coupled plasma-atomic absorption spectroscopy
ICP-OES	Inductively coupled plasma-optical emission spectroscopy
LUMO	Lowest Unoccupied Molecular Orbital
m	Mass of catalyst
PXRD	Powder X-ray diffraction
RRHO	Rigid rotor-harmonic oscillator
S_{product}	Selectivity to product
SEM	Scanning electron microscopy
STEM	Scanning transmission electron microscopy
STEM-EDS	Scanning transmission electron microscopy-energy dispersive spectroscopy
STM	Scanning tunneling microscopy
TEM	Transmission electron microscopy
TOF	Turnover frequency
W/F	Residence time
Wt%	Weight percentage
X	Conversion
XANES	X-ray Absorption Near Edge Structure

Acknowledgements

Throughout the five years I have spent at UC Berkeley, there are many people to thank who helped me arrive at Berkeley and also successfully leave Berkeley with a doctoral degree. I would like to first thank the faculty members at Purdue University whom I had the chance to interact with for driving and motivating my interest in chemical engineering. Though I spent many long nights on sometimes impossible problem sets, Purdue was where I cultivated a love for chemical engineering and problem solving. I would also like to thank Professor Dibakar Bhattacharyya of University of Kentucky for allowing me to work in his lab in the summer of 2009 and encouraging me to go to graduate school.

After I arrived at UC Berkeley, I chose to conduct research in the field of catalysis and join Professor Alexis T. Bell's group. Alex has been a tremendous advisor in guiding me in my research, and has always made himself available at all times for feedback and advice. He has not only taught me how to ask the right questions and presented me with opportunities to conduct novel experiments, but also shown me the importance of communicating science in a clear and concise manner, something that I will continue to strive for after I leave Berkeley. Through patience and meaningful collaboration, I am happy that Alex and I have pieced together results that tell a compelling story.

I would also like to express my gratitude towards Dr. Stig Helveg and Haldor Topsøe, the Danish catalyst company that I had the pleasure to collaborate with on *in situ* TEM experiments. Stig has been a tremendous collaborator and almost a second advisor, from halfway across the world, always making time to chat with me late in the evening to help guide me through my doctoral degree. His expertise in his field continues to astonish me, and I have learned the importance of paying meticulous attention to every detail of a complex experiment. His group members at Topsøe have also provided tremendous support for me, bringing about a successful collaboration. Everyone I had the chance to interact with at Topsøe always made my stays truly enjoyable.

Within the Bell group, countless people have helped me through tough times in lab. These wonderful co-workers include Amber, Anton, Bean, Chris, David, Ferenc, Greg, Joe, Lin, Rachel, Shaama, Shannon, Shylesh, and Zheng. I would like to especially thank Zhenmeng Peng, the post-doc who showed me the ropes when I first joined the group and really helped my project get on its feet without too much trouble. In addition, Kristin Stangl was instrumental in allowing me to focus on research and taking care of the logistical things that were associated with graduate school, with her skillful navigation through the bureaucracy of Berkeley.

Lastly, I would like to thank my family and friends for their continued support throughout graduate school. Sometimes science can be a little overwhelming, and to be able to focus on other aspects of life has made me a more well-rounded person. Whether it was collaborating in a musical chamber group or playing video games late at night, the people in my life who helped me participate in non-science things have really helped me to survive graduate school. The San Francisco Bay Area is truly a beautiful place – I am lucky to have enjoyed it with so many people, and I hope to call it home one day.

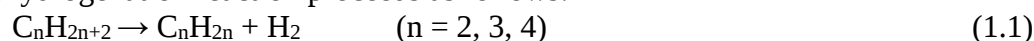
Chapter 1

Introduction

Light alkenes, such as ethene and propene, continue to be the most commercially important components of the petrochemical industry, with a forecasted demand of 260 million tons in 2016 [1]. They are extensively used as chemical building blocks for the production of a wide array of products, including polymers, fuel blending agents, chemical intermediates, and rubbers [2-4]. Figure 1.1 illustrates the most common uses of the light alkenes feedstock. The steadily growing demand for these products therefore has driven research to find an economical and selective process to produce light alkenes.

Steam cracking and FCC of naphtha or gas oil are the methods that have been used most extensively for obtaining ethene or propene. In 2007, more than 97% of the world's propene supply was produced by FCC or naphtha cracking, rather than using an on-purpose technique [5]. While these methods are convenient and well-documented, a typical product distribution from high-severity naphtha cracking exhibits 35% selectivity to ethene and 15% selectivity to propene, with substantial quantities of methane and coke as byproducts [6]. Low selectivities, combined with the rising cost of petroleum, have motivated the petrochemical industry to consider other more economical and efficient processes. The catalytic dehydrogenation of light alkanes to the corresponding alkenes is an attractive alternative, given the high selectivity of the reaction. The hydrogen produced as the principal byproduct of light alkane dehydrogenation is also desirable, since it can be used as a fuel to provide the energy needed for the endothermic dehydrogenation process and for heteroatom removal from petroleum. In addition, the recent natural gas boom in the U.S. driven by improvements in hydraulic fracturing technologies has made natural gas components, such as ethane and propane, very cheap and abundant [7].

The dehydrogenation reaction proceeds as follows:



This process is highly endothermic and thermodynamically-favored at high reaction temperatures and low alkane partial pressures, in order to achieve high conversions. In general, two types of catalysts are used for dehydrogenation of light alkanes: Pt-based catalysts and metal oxide catalysts such as CrO_x [8]. The majority of current research focuses on the Pt-based catalyst system, as will this dissertation, due to the excellent C-H bond activation characteristic of Pt. However, some challenges exist in formulating a selective and stable catalyst. Side reactions can often occur, which include hydrogenolysis and cracking. Hydrogenolysis involves the addition of hydrogen into a C-C bond of the alkane, resulting in the formation of two smaller alkanes [9]. Cracking can occur either thermally at high temperature and pressure or involve a Brønsted acid site that results in the formation of an alkene and an alkane, via a carbocation intermediate [10]. In addition to low selectivities, consequences of side reactions also include catalyst deactivation via carbon deposits on the catalyst surface, requiring regeneration of the catalyst by burning off coke deposits [11].

With thoughtful catalyst design however, product selectivity and catalyst stability can be maximized. Because it is known that large Pt ensembles have high activity for hydrogenolysis, impurities or inactive species on the surface may act as a site diluent and increase the overall selectivity towards dehydrogenation [12]. It is for this reason that Pt bimetallic alloys have been investigated extensively as effective catalysts for light alkane dehydrogenation. The addition of other metals, such as Sn, In, Ga, Ge, or Zn, can alter the properties Pt, enhance the activity towards

dehydrogenation, and suppress coking [13-15]. Previous work has focused on identifying the most effective promoters and elucidating the role of the promoter, both experimentally and theoretically [16, 17]. However, the effects of nanoparticle size and composition on the activity, selectivity, and stability of the reaction are largely unreported in the literature, only with a handful of studies on propane dehydrogenation [18, 19]. Additionally, the details behind the mechanism of coking on Pt and Pt bimetallic catalysts have not been characterized thoroughly.

The objective of this dissertation is to understand the effects of structure and composition of the catalyst for alkane dehydrogenation and elucidate the mechanisms behind catalyst deactivation via coking. In Chapter 2, supported catalysts of controlled particle size and composition were prepared to identify and quantify the effects of structure and composition for Pt-Sn bimetallic nanoparticles on the dehydrogenation of ethane. Of the promoting elements listed previously, the greatest attention has been given to Sn, given its effectiveness as a promoter. This work focused on the effects of catalyst parameters on the activity, selectivity, and stability of the catalyst. Pt and Pt-Sn nanoparticles were prepared ex-situ in solution, in the presence of capping agents, in order to control the size and composition of the particles before deposition onto Mg(Al)O, a calcined hydrotalcite support. To understand the true initial activity of un-deactivated catalysts, further experiments were run at low residence time conditions to limit ethene formation. This study illustrates the importance of synthesis methods to produce model catalysts of uniform size and composition in order to draw accurate structure-property relationships.

The findings from Chapter 2 definitively show that Sn suppresses coke formation and enhances catalyst stability dramatically. However, to better understand how promoters such as Sn inhibit coke formation, a clearer picture of how coke forms on monometallic Pt catalysts must first be established. In Chapter 3, carbon formation via ethene decomposition on MgO-supported Pt nanoparticles was studied by *in situ* HRTEM in order to monitor and understand the dynamics of coking on an atomic level. Catalysts were dispersed onto a grid to be inserted in the microscope, and then observed in 1 mbar ethene at 400-600°C in order to obtain time-resolved image series. The advantage of *in situ* HRTEM allows for the direct observation of the catalyst in the presence of reacting gases. Despite the wealth of information this technique may provide, careful considerations were taken to limit artifacts of the experiment that may be incurred by the high energy electron beam. After a suitable imaging strategy was adopted, greater focus was placed on understanding how multiple carbon layers encapsulate the nanoparticle and the result of any nanoparticle restructuring during the coking process. These findings are the first to demonstrate the *in situ* changes in catalyst structure during carbon growth on an atomic level. Insights from this study can not only enable further research in understanding how promoters might affect the coking mechanism, but also illustrate the viability of the technique in directly imaging catalysts at high temperatures in a 1 mbar gaseous environment. Supplementary experiments from STM can be found in Appendix A, which offer complementary atomic information regarding the nucleation and growth of carbon on the Pt surface.

Attention is then shifted to the properties and performance of other promoters for this reaction. In Chapter 4, catalysts for the alkane dehydrogenation have been prepared by dispersing Pt nanoparticles onto Mg(In)(Al)O, a calcined hydrotalcite-like support containing In and Al. Upon reduction at temperatures above 723 K, part of the In³⁺ cations present near the support surface and proximate to Pt are reduced and the resulting In atoms form a Pt-In bimetallic alloy with the supported Pt nanoparticles. The performance of Pt/Mg(In)(Al) catalysts for butane dehydrogenation reaction was then probed as a function of In/Pt ratio and reaction conditions. While butenes are not as in high demand compared to ethene and propene, they are still important

products that are used often to co-polymerize with ethene to produce plastics of varying flexibility. Parameters that were investigated include catalyst composition, hydrogen co-feed, and catalyst regeneration.

Finally, Chapter 5 examines the structure and performance of Pt-Ir catalysts for ethane and propane dehydrogenation. A recent computation study from within the group found Ir to be an effective promoter for propane dehydrogenation, and that Pt-Ir bimetallic particles should exhibit higher activity and greater stability than pure Pt [20]. In contrast to other promoting elements, Ir is unique in that it is capable of alkane activation and but by itself, suffers from low dehydrogenation activity and selectivity. Therefore, the focus of this work was to characterize the performance of the catalyst and compare it with Pt and Pt-Sn catalysts. Further DFT calculations were employed over Pt_3X ($\text{X} = \text{Pt}, \text{Sn}, \text{Ir}$) clusters in order to elucidate experimental trends. The findings of the theoretical analysis of ethane dehydrogenation on these clusters yielded the same trend observed experimentally, and revealed that both Pt and Ir atoms are capable of alkane activation, a characteristic not observed in the Pt-Sn system.

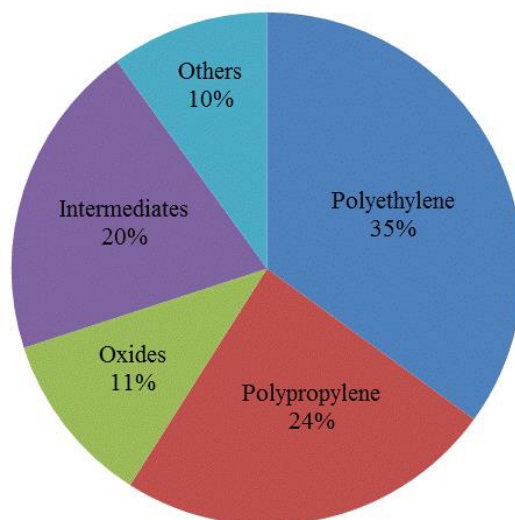


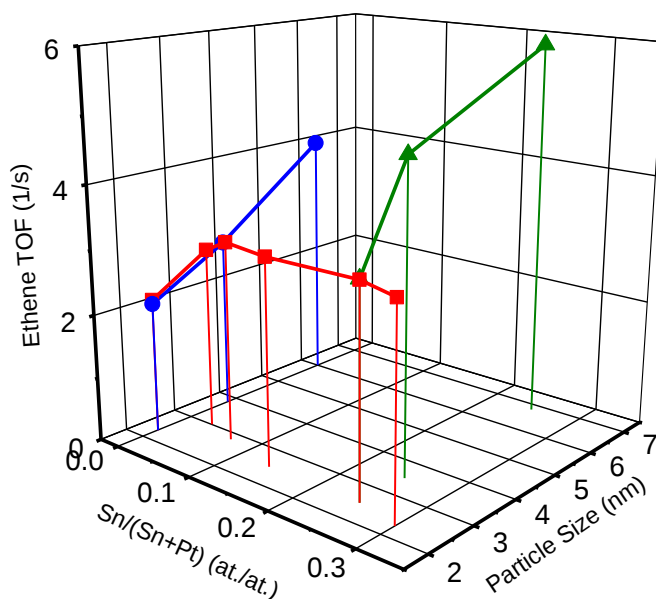
Figure 1.1 Product distribution from global light alkene consumption in 2010. Data from ref. 1.

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Chapter 2

Effects of Composition and Metal Particle Size on Ethane Dehydrogenation over $\text{Pt}_x\text{Sn}_{100-x}/\text{Mg}(\text{Al})\text{O}$ ($70 \leq x \leq 100$)



Abstract

The effects of composition and metal particle size of platinum catalysts on ethane dehydrogenation were investigated on $\text{Pt}_x\text{Sn}_{100-x}/\text{Mg}(\text{Al})\text{O}$ ($70 \leq x \leq 100$) catalysts prepared with average particle sizes between ~ 2 and 7 nm. At high conversions, catalyst deactivation from coke formation was a strong function of particle size and Sn/Pt. Deactivation rate decreased significantly with decreasing particle size and increasing Sn addition. To understand the true initial activity of un-deactivated catalysts, further experiments were run at low residence time conditions to limit ethene formation. For a given average particle size, ethane turnover frequency (TOF) and the selectivity to ethene increased with increasing content of Sn in the PtSn particle. For Pt and Pt_3Sn compositions, ethane TOF increased with increasing particle size, while the selectivity to ethene was not strongly affected. The observed effects of particle size and composition are attributed to a combination of geometric (size of active ensembles) and electronic (heat of ethene adsorption) factors.

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2.1. Introduction

The catalytic dehydrogenation of ethane has been widely investigated as an attractive alternative to steam cracking of naphtha for the production of ethene, a key building block for the production of chemicals and polymers [1, 2]. The principal co-product of ethane dehydrogenation is hydrogen, a vital commodity that can be used for a variety of applications in a refinery [3-5]. As discussed in Chapter 1, the most active catalyst for ethane dehydrogenation is platinum; however, in its pure form it exhibits low ethene selectivity and rapid coke deposition, which contributes to catalyst deactivation [6]. Isotopic studies have revealed that both methane formation and coke accumulation originate from ethene re-adsorption and dehydrogenation [6, 7]. The addition of a second metal, such as tin, indium, or gallium to platinum has been found to be effective in increasing ethene selectivity and suppressing coke formation [6, 8-11]. Both geometric and electronic effects of the second metals have been proposed to explain their roles in modifying the catalyst surface and changing the surface chemistry involved in ethane dehydrogenation [12-19].

While there is a considerable literature on the influence of additives on the activity, selectivity, and coke accumulation occurring on Pt bimetallic catalysts, a clear understanding of the separate effects of metal particle size and composition has not been previously reported [20-22]. The principal reason is that platinum catalysts are usually prepared via impregnation of metal precursors onto a support that are then reduced to form metallic particles. While such methods are simple and robust, they offer little control over particles composition and size. A typical product prepared in this way contains particles of different composition and size, the distribution of both variables depending upon the composition of the metal precursors and support and on the experimental procedure [23-25]. Moreover, not all of the metal forms an alloy with Pt, and consequently, a part of the additive is usually present in one form or another on the support [9, 23]. For these reasons, it is hard to separate the effects of particle size and composition on catalytic performance, since the effects of both parameters are usually entangled.

Furthermore, it has been observed that the initial deactivation on Pt for ethane dehydrogenation is very fast [6, 26]. Therefore, it is very difficult to measure the true initial activity of a pure Pt catalyst and compare it with a promoted Pt catalyst exhibiting lower initial deactivation. In order to determine if the initial rate of dehydrogenation on Pt is higher or lower than a bimetallic catalyst, the amount of coke formation must be reduced. Since Bell et al. have shown from previous isotopic studies that coke originates primarily from ethene, measuring rates at low conversions, or low residence time conditions, will offer a strategy for obtaining the true activity of Pt and Pt-bimetallic catalysts more accurately [6]. Similarly, measuring rates at low residence time conditions will provide insights on the true initial activity of catalysts with varying particle size, in the absence of significant deactivation.

The aim of the present work was to identify and quantify the effects of particle size composition for Pt-Sn bimetallic nanoparticles on the dehydrogenation of ethane to ethene. Particular attention was given to the influence of these variables on the rate and selectivity of ethene formation, the extent of coke accumulation, and the extent of catalyst deactivation. To compare the true initial activity of different catalysts, a low feed residence time was used. A synthetic method was employed to make Pt-Sn particles of uniform size that were then loaded onto a calcined hydrotalcite ($\text{Mg}(\text{Al})\text{O}$) support. Pt-Sn particles with similar size but different composition and with the same composition but different size were prepared by adjusting the synthetic parameters. The results of this study provide new insights into the roles of metal particle size and composition on the properties of Pt-Sn nanoparticles for ethane dehydrogenation.

2.2. Experimental

2.2.1 Synthesis of Platinum and Platinum-Tin Nanoparticles

Platinum nanoparticles were synthesized by reduction of a platinum acetylacetonate ($\text{Pt}(\text{acac})_2$, 97%, Aldrich) dissolved in octyl ether (OE, 99%, Aldrich) by 1,2-hexadecanediol (HDD, 90%, Aldrich) in the presence of oleylamine (OAm, 70%, Aldrich) and oleic acid (OA, 99%, Aldrich) [27]. In a typical procedure, all of the components were added to a 25 ml three-necked flask and the resulting solution was heated to 563 K at a rate of 5 K/min and maintained at this temperature for 30 min before cooling down to room temperature. To produce Pt-Sn bimetallic particles, tin acetylacetonate ($\text{Sn}(\text{acac})_2$, 99.9%, Aldrich) was added together with $\text{Pt}(\text{acac})_2$ at the start of the procedure. All the experiments were conducted under Ar using a standard Schlenk line. Pt particles with diameters ranging between ~ 2 and 8 nm, and composition, ranging in composition between Pt and $\text{Pt}_{70}\text{Sn}_{30}$, were obtained by adjusting the molar ratio of $\text{Sn}(\text{acac})_2/\text{Pt}(\text{acac})_2$, the amounts of OAm and OA, the temperature ramp rate, and the final reaction temperature. Upon completion of the nanoparticle preparation and cooling the reaction mixture to room temperature, a large amount of anhydrous ethanol was added in order to aid the separation of the Pt nanoparticles which was achieved by centrifugation at 3000 rpm for 5 min. The solid material produced in this manner was dispersed in anhydrous toluene to form a stable colloidal suspension. Details concerning the preparation of all samples are listed in Table S.2.1.

2.2.2 Preparation of $\text{Mg}(\text{Al})\text{O}$

Calcined hydrotalcite, namely $\text{Mg}(\text{Al})\text{O}$, was used as a support of the metal particles for its high thermal stability and moderate basicity. Previous studies have shown that $\text{Mg}(\text{Al})\text{O}$ suppresses thermal cracking of ethane and minimizes the formation of coke on the support [28-31]. Hydrotalcite was prepared by co-precipitation and subsequent thermal treatment [6, 20]. In a standard procedure, magnesium nitrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Alfa Aesar, 98-102%, 163.27 g) and aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Alfa Aesar, 98-102%, 23.8 g) were first dissolved in H_2O (deionized, 700 mL). Sodium carbonate (Na_2CO_3 , EMD Chemicals Inc., 99.5%, 3.36 g) and sodium hydroxide (NaOH , Fisher Scientific, 98.3%, 31.72 g) were dissolved in H_2O (700 mL) in a separate flask. The two solutions were mixed drop-wise at 333 K with constant stirring for 1 h. The precipitate was filtered and washed with excess H_2O till a neutral pH value was achieved. The resulting material was dried overnight at 383 K, and then heated to 973 K in air at a rate of 2 K/min and maintained at this temperature overnight.

2.2.3 Preparation of $\text{Pt}_x\text{Sn}_{100-x}/\text{Mg}(\text{Al})\text{O}$ ($70 \leq x \leq 100$)

All $\text{Pt}_x\text{Sn}_{100-x}/\text{Mg}(\text{Al})\text{O}$ ($70 \leq x \leq 100$) samples, except the 1.3 nm $\text{Pt}/\text{Mg}(\text{Al})\text{O}$, were prepared by dispersing $\text{Pt}_x\text{Sn}_{100-x}$ particles onto $\text{Mg}(\text{Al})\text{O}$. In a typical procedure, an appropriate volume of the toluene suspension of $\text{Pt}_x\text{Sn}_{100-x}$ ($70 \leq x \leq 100$) particles dispersed in toluene (containing around 0.02 g metal) was added to a suspension of 1.0 g $\text{Mg}(\text{Al})\text{O}$ in 5 mL anhydrous toluene. The mixture was stirred overnight before the resulting product was precipitated by adding three times the volume anhydrous ethanol and separated by centrifugation. The solid material was

heated at 723 K for 1 h in air to remove the surface capping agents and then reduced in an atmosphere of H₂ in Ar (10 vol.%) at 873 K for 1 h.

A sample of Pt/Mg(Al)O was prepared by incipient wetness impregnation. Pt(acac)₂ (0.02 g or 0.05 mmol) was dissolved in anhydrous toluene (1.5 mL) and added drop-wise onto the calcined Mg(Al)O support (1.0 g) with continuous stirring. The solid was dried under vacuum and then reduced in H₂/Ar (10 vol%) by raising the temperature to 723 K at 10 K/min and then maintaining it at 723K for 1 h.

2.2.4 Catalyst Characterization

Powder x-ray diffraction (PXRD) patterns were collected on a Siemens diffractometer (D 5000) equipped with a Cu K- α source (wavelength of 1.5418 Å). TEM images were taken using an FEI Tecnai 12 microscope with an accelerating voltage of 120 kV. HRTEM characterizations were conducted on the TEAM 0.5 high-resolution microscope operated at 80 kV at the National Center for Electron Microscopy (NCEM). STEM images were taken on a FEI Titan S80-300 microscope operated at 300 kV and under the HAADF mode. The alloy compositions of as-synthesized particles were measured by EDX on a Hitachi S-4300SE/N scanning electron microscope (SEM). The Pt and Sn contents of the catalysts were determined by ICP-AAS by Galbraith Laboratories, Knoxville, TN.

2.2.5 Catalyst Testing

Ethane dehydrogenation was carried out in a fixed-bed quartz reactor (7 mm internal diameter). In a standard procedure, the catalyst materials were first made into small pellets (250-500 μ m in diameter) by pressing, crushing, and sieving. Prior to testing, the pelleted catalyst was heated at 723 K overnight in air (UHP Praxair) to remove possible moisture from the support. The catalyst was heated to 873 K at a rate of 15 K/min in 1 atm 20% H₂ in He using a three-zone furnace. The catalyst was maintained at this temperature for 1 h to fully reduce the particles surface before exposing it to reactants. A feed containing ethane (99.95% Praxair), hydrogen (99.999% Praxair), and helium (UHP Praxair) was used to determine the activity, selectivity, and stability of all Pt_xSn_{100-x}/Mg(Al)O (70 $\leq$ x $\leq$ 100) samples for ethane dehydrogenation. The partial pressure of C₂H₆ and the H₂/C₂H₆ ratio were fixed at 0.2 bar and 1.25 respectively, if not otherwise specified. Internal mass transport limitations were not observed as evidenced by satisfaction of the Weisz-Prater criterion.

The reaction products were analyzed on-line by a gas chromatography – mass spectrometer (GC-MS, Varian, Model 320). A flame ionization detector (FID) was used to quantify the concentrations of all organic compounds eluting from the capillary column. TOF was estimated from Eq. (2.1):

$$\text{TOF} = (r_{\text{C}_2\text{H}_6} \cdot N_A) / (\text{SSA} \cdot x_{\text{Pt}} \cdot S_{\text{Pt}}) \quad (2.1)$$

where $r_{\text{C}_2\text{H}_6}$ is the rate of ethane consumption (mol/ [g_{metal} · s]) ; N_A is Avogadro's number; SSA is the specific surface area based on average size from TEM (cm²/g); x_{Pt} is the fraction of Pt relative to Sn content; S_{Pt} is the surface density of Pt atoms (1.31·10⁵ atoms/cm²) calculated from hydrogen chemisorption on polycrystalline platinum [32]. We assume a stoichiometry of one hydrogen atom per surface platinum and a surface composition identical to Sn/Pt of the bulk. While our previous

study has shown by XPS that surface enrichment of tin likely occur in PtSn alloys [27], we will discuss how our assumption may affect the results regarding effect of composition on TOF. The amount of accumulated coke was measured by burning the coke to CO₂ at 873 K in a mixture of 5% O₂ in He flowing at 60 cm³/min. The CO₂ signal was monitored as a function of time using a mass spectrometer and the signal integrated to determine the total amount of coke formed.

2.3. Results and Discussion

2.3.1 Catalyst Characterization

Figure 2.1 shows TEM images and particle size distributions for Pt and Pt-Sn nanoparticles prepared with average particle diameters of 2.3 to 3.0 nm. Most of the particles were spherical in shape and fell within a narrow size distribution around the mean diameter. Powder X-ray diffraction (PXRD) patterns of the as-synthesized particles, shown in Figure 2.2, suggest they have a face centered cubic (*fcc*) structure, with peaks assignable to (111), (200), (220), (311), and (222) planes. The positions of diffraction peaks for pure Pt metal (70-2057, JCPDS-ICDD) and Pt₃Sn alloy (or Pt₇₅Sn₂₅, 65-0958, JCPDS-ICDD) are included for reference. The diffraction peaks of all Pt-Sn samples fall between those for pure Pt and Pt₃Sn, suggesting the formation of alloys [33]. The peaks shift towards Pt₃Sn with increasing Sn content. The energy-dispersive X-ray (EDX) spectra indicate that both Pt and Sn are present in the particles and that the atomic percentage of Sn in the Pt-Sn alloy particles determined by EDX agrees closely with that determined by ICP-AAS (see Figure 2.3). The details of the ICP analysis are shown in Table S.2.2.

Nanoparticles of Pt and Pt₃Sn with particle sizes between ~ 1.3 and 6.0 nm were prepared in order to explore the effects of particle size on ethane dehydrogenation at constant particle composition. Smaller amounts of OA and OAm, together with slower heating rates and higher reaction temperatures, were used in combination for making larger particles [34]. Figure 2.4a and 2.4b show that the 3.8 nm and 6.0 nm Pt particles produced at 663 K appear to be more faceted in shape than the 2.3 nm particles produced at 413 K (see Figure 2.1a). By contrast, the 3.5 nm and 6.8 nm Pt₃Sn particles prepared at 663 K do not exhibit significant facets, and a small portion of the particles appear to have dumbbell or even wormlike structure (Figure 2.4c and 2.4d). Particles with such shapes may arise because of the lower melting temperature for Pt-Sn alloys, which have more mobile surfaces and tend to grow into each other when the surfaces are protected by an insufficient amount of capping agents [35, 36]. Figure 2.5 and 2.6 show the PXRD patterns for the Pt and Pt₃Sn nanoparticles as a function of the average particle size. The match between the positions of the reference peaks and those of the nanoparticles is consistent with these particles being pure Pt and Pt₃Sn. The diffraction peaks became sharper as the average particle size increased. It is also noted that the average particle size determined using the Scherrer equation is consistent with that determined by analysis of TEM images. Figure S.2.1 also show the TEM image of the Pt/Mg(Al)O catalyst prepared by incipient wetness impregnation with an average particle size of 1.3, in agreement with the result previously found using the same synthesis method [6].

2.3.2 Effects of residence time and deactivation

The effects of residence time on conversion for Pt/Mg(Al)O are shown in Figure 2.7. At higher residence times, or near equilibrium conversion, the extent of initial deactivation is severe. This agrees well with previous studies of Pt catalysts for ethane dehydrogenation. Therefore, the

initial data point at $25.0 \times 10^{-3} \text{ g} \cdot \text{s} \cdot \text{cm}^{-3}$ may already represent a deactivated catalyst, masking the true initial activity. Operating at a lower residence time ($3.75 \times 10^{-3} \text{ g} \cdot \text{s} \cdot \text{cm}^{-3}$), however, showed significantly less deactivation and stable conversion with time on stream.

Figure 2.8 shows a representative STEM image of fresh $\text{Pt}_3\text{Sn}/\text{Mg}(\text{Al})\text{O}$ prepared with mean diameter size of 3.5 nm. Oxidation and subsequent reduction of this and other samples of supported Pt and Pt-Sn showed no evidence for a change in the average particle size, nor was any change seen before and after use of these catalysts for ethane dehydrogenation at 873 K (compare Figures 3.8a and 3.8b). Therefore, it was concluded that the deactivation shown in Figure 3.7 originates from coke formation, rather than sintering of the catalyst. The extent of deactivation between 0.3 min and 10.3 min as a function of particle size for Pt and Pt_3Sn catalysts is shown in Figure 2.9. It is clear that both composition and size play an important role in coke formation, consistent with previous studies [8-10, 37]. With decreasing particle size and Sn addition, deactivation decreased significantly, an effect more pronounced at long residence time conditions. Figure 2.10 shows direct measurement of the accumulation of coke, measured as the moles of C per mole of surface Pt, as a function of particle size at high residence time condition. Coke formation rates increases as particle size increases for both Pt and Pt-Sn, a trend that is in full agreement with findings of a recent high-resolution TEM study [37]. Zhenmeng et al. [37] showed that particles less than about 2 nm in diameter demonstrate minimal coke accumulation after 2 h and a significant part of the coke accumulated on particles of this size migrate onto the support. For particles larger than about 6 nm in diameter coke deposition leads to complete encapsulation of the Pt particles by multiple graphene layers. The size dependency of carbon growth is attributed to the accommodation of strain energy generated in the graphene layers and the minimization of overall free energy in the carbon growth process [37, 38]. Figure 2.11 shows the effect of Sn/Pt on C/Pt at high residence time condition. The value of C/Pt measure after 2 h of reaction decreased very sharply with increasing Sn content. The strong decrease in coke formation upon the addition of Sn to Pt is fully consistent with results reported previously [6, 8, 10, 11] and is consistent with the lower deactivation on Pt_3Sn shown in Figure 2.9. TEM studies have also shown that Sn addition strongly reduces the accumulation of graphene layers even on larger Pt-Sn bimetallic particles. Zhenmeng et al. have previously proposed that the addition of Sn presents additional strain energy for the growth of graphene on Pt and in fact, may be blocking the steps for carbon nucleation [37].

2.3.3 Effects of particle size and composition

Reaction at low residence time reaction conditions was used to compare the effects of particle size and composition on ethane dehydrogenation performance. In all cases, 5 mg of catalyst was used and the reaction temperature was maintained at 873 K. Ethane was fed at a partial pressure of 0.202 bar together with hydrogen and helium. The total flow rate was kept at $80 \text{ cm}^3/\text{min}$ and the total pressure was maintained at 1 atm. Hydrogen was added to the feed in order to decrease coke formation [6]. Figure 2.12 shows the effect of $\text{H}_2/\text{C}_2\text{H}_6$ feed ratio on C_2H_6 conversion for 3.8 nm $\text{Pt}/\text{Mg}(\text{Al})\text{O}$ and 3.5 nm $\text{Pt}_3\text{Sn}/\text{Mg}(\text{Al})\text{O}$. Co-feeding hydrogen increased catalyst activity for dehydrogenation. However, as the $\text{H}_2/\text{C}_2\text{H}_6$ ratio was increased to 2.5, the conversion of ethane decreased due a downward shift in the equilibrium conversion. A $\text{H}_2/\text{C}_2\text{H}_6$ ratio of 1.25 was selected for the remaining experiments.

Figures 2.13 and 2.14 shows the effects of Sn content on ethane TOF and ethene selectivity for nanoparticles of nearly constant size ($\sim 2.5 \text{ nm}$) measured after 0.3 min from the onset of reaction. The TOF of ethane increased by about 40% and the selectivity to ethene increased from

85% to 95% as the fraction of Sn in the Pt-Sn nanopaticles increased from 0 to 0.42. As previously described, TOF values were calculated based on the assumption that the surface composition is identical to that of the bulk. We note, however, that our previous studies of unsupported PtSn nanopaticles prepared in the same manner as that used for the present study do show evidence for surface enrichment in Sn. This means that the TOF values for ethane consumption reported for PtSn/Mg(Al)O in Figure 2.13 represent a lower bound.

The effects of Sn promotion on the activity and selectivity of PtSn alloys is fully consistent with previous reports that have proposed that the addition of Sn to Pt affects the dehydrogenation of ethane as a consequence of both geometric and electronic effects [12-18]. Deposition of Sn on the surface of Pt particles reduces the size of Pt ensembles and thus the ability of Pt to cleave carbon-carbon bonds, a process leading to the formation of methane and coke [39-41]. In addition, the transfer of electronic charge from Sn to Pt reduces the heat of ethene adsorption, a critical step in coke formation [13, 15, 18]. Quantum chemical studies also suggest that the dissociative adsorption of ethane on surface Pt is enhanced by the presence of Sn [12, 13, 19], thereby promoting the rate-limiting step in ethane dehydrogenation. Our results show the same trend with Sn promotion but also suggest that even under conditions with little deactivation, Pt-Sn catalysts are intrinsically more active than Pt. We note, however, that even for low residence time conditions, there still exists a small amount of deactivation. Therefore, the addition of Sn suppresses coke formation, but does not eliminate it completely. We also note that since the extent of deactivation shown at low residence time conditions is significantly lower than what has been reported in the past [6, 8-10], we are able to measure closer to the intrinsic activity. Our results therefore suggest that Pt-Sn catalysts exhibit greater intrinsic activity than Pt catalysts.

The effects of particle size on ethane TOF and ethene selectivity for Pt/Mg(Al)O and Pt₃Sn/Mg(Al)O are illustrated in Figures 2.15 and 2.16. A sample of Pt/Mg(Al)O with average particle size of 8.5 nm was prepared to give an additional data point. Here we report what we believe is the first study of Pt and Pt₃Sn particle size dependence on ethane dehydrogenation. While selectivity to ethene remained nearly constant across all particle sizes for both Pt and Pt₃Sn, ethane TOF increased with increasing particle size. This suggests that ethane dehydrogenation favors flatter surfaces on large particles, which have a higher proportion of terrace sites versus corners and step sites. Low coordination Pt sites typically are more active for catalyzing C-C bond breaking [26]. Furthermore, binding energy calculations on Pt surfaces show that step edge atoms bind to ethene much stronger than terrace atoms [42]. The calculated binding energy difference between Pt(111) and Pt(211) for di- σ bonded ethene is 71 kJ/mol, a significantly stronger interaction with lower coordinated atoms. Therefore, larger particles may exhibit higher TOF for ethane dehydrogenation due to the ease with which nascent ethene is removed from the surface to the gas phase. The trend with particle size is identical for Pt and Pt₃Sn catalysts. While there is a 300% increase in ethane TOF from 1.5 nm to 8.5 nm for Pt/Mg(Al)O, the loss in specific surface area going to from 1.5 nm to 8 nm is about 500%. Therefore, while larger particles show higher TOF for dehydrogenation, it is still more favorable to use smaller particles for increased surface area. In addition, operating at high residence time to achieve industrially relevant conversions results in higher coke formation on larger particles.

2.4. Conclusions

The effects of composition and size of Pt-Sn particles on coke formation, rate of ethane dehydrogenation, and the selectivity to ethene were studied using Pt_xSn_{100-x}/Mg(Al)O ($70 \leq x \leq 100$)

nanoparticles dispersed onto Mg(Al)O. C/Pt decreased significantly with decreasing particle size and increasing Sn addition, trends consistent with our previous TEM study and explanations. A unique strategy was employed to make accurate comparisons of true initial activity. Operating at low residence time resulted in significantly lowered deactivation, attributable to lower coke formation from ethene, and allowed for measurement closer to the true initial activity. For a fixed average particle size, the TOF and selectivity of these catalysts for ethene production increased with the content of Sn. These trends are attributed to a combination of geometric and electronic effects brought about by the presence of Sn on the surface of Pt nanoparticles. TOF was also found to increase with increasing particle size, a trend attributed to differences in the fraction of lower-coordinated surface atoms and in the electronic properties of the particles. While ethane dehydrogenation may favor flatter surfaces, the gain in TOF is not significant enough to lose surface area by going to larger particles. Additionally, practical implementation of this system at high conversions suggests that small and Sn-promoted catalysts should be used to avoid coke formation.

2.5. Acknowledgements

This work was supported by a grant from Chevron Energy Technology Company. The authors acknowledge support of the National Center for Electron Microscopy, Lawrence Berkeley Lab, which is supported by the U.S. Department of Energy under Contract DE-AC02-05CH11231.

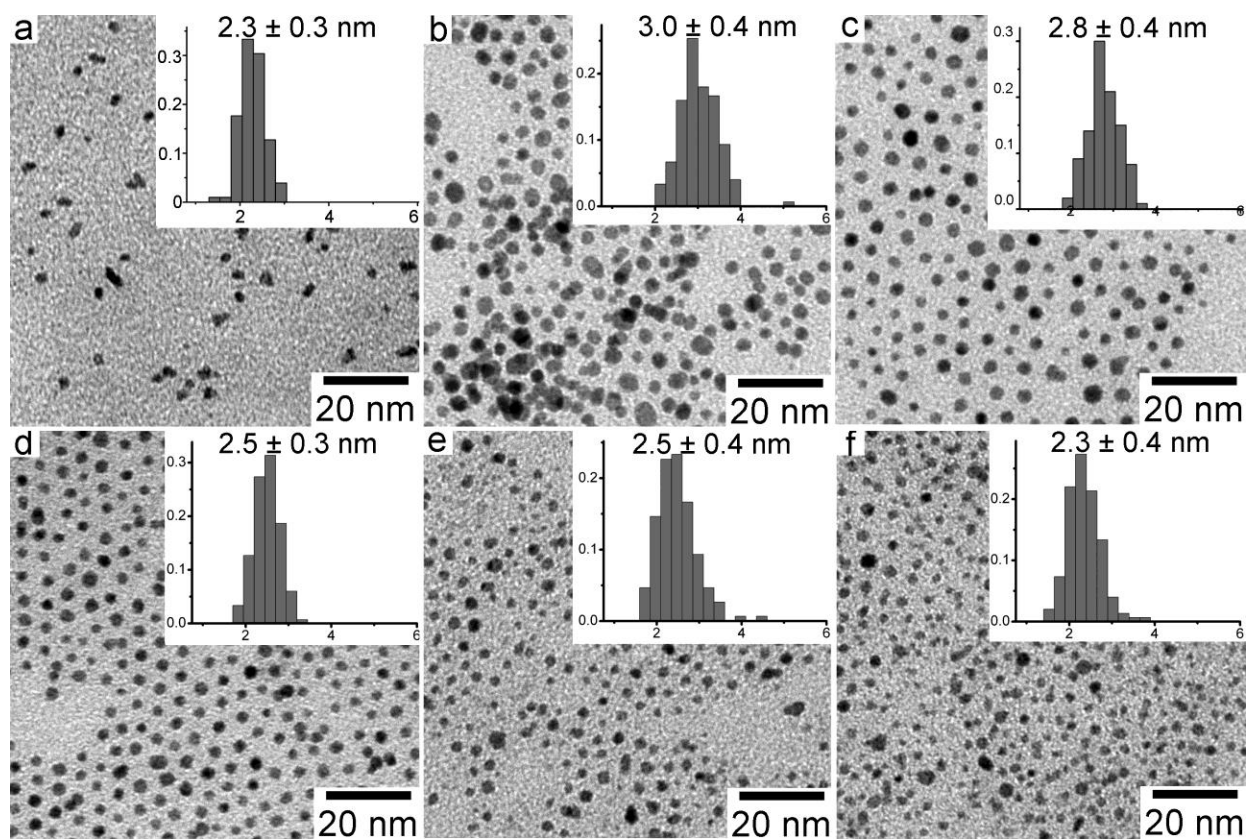


Figure 2.1. TEM images of as-synthesized (a) Pt, (b) Pt₉₇Sn₃, (c) Pt₉₃Sn₇, (d) Pt₈₆Sn₁₄, (e) Pt₇₅Sn₂₅, and (f) Pt₇₀Sn₃₀ nanoparticles.

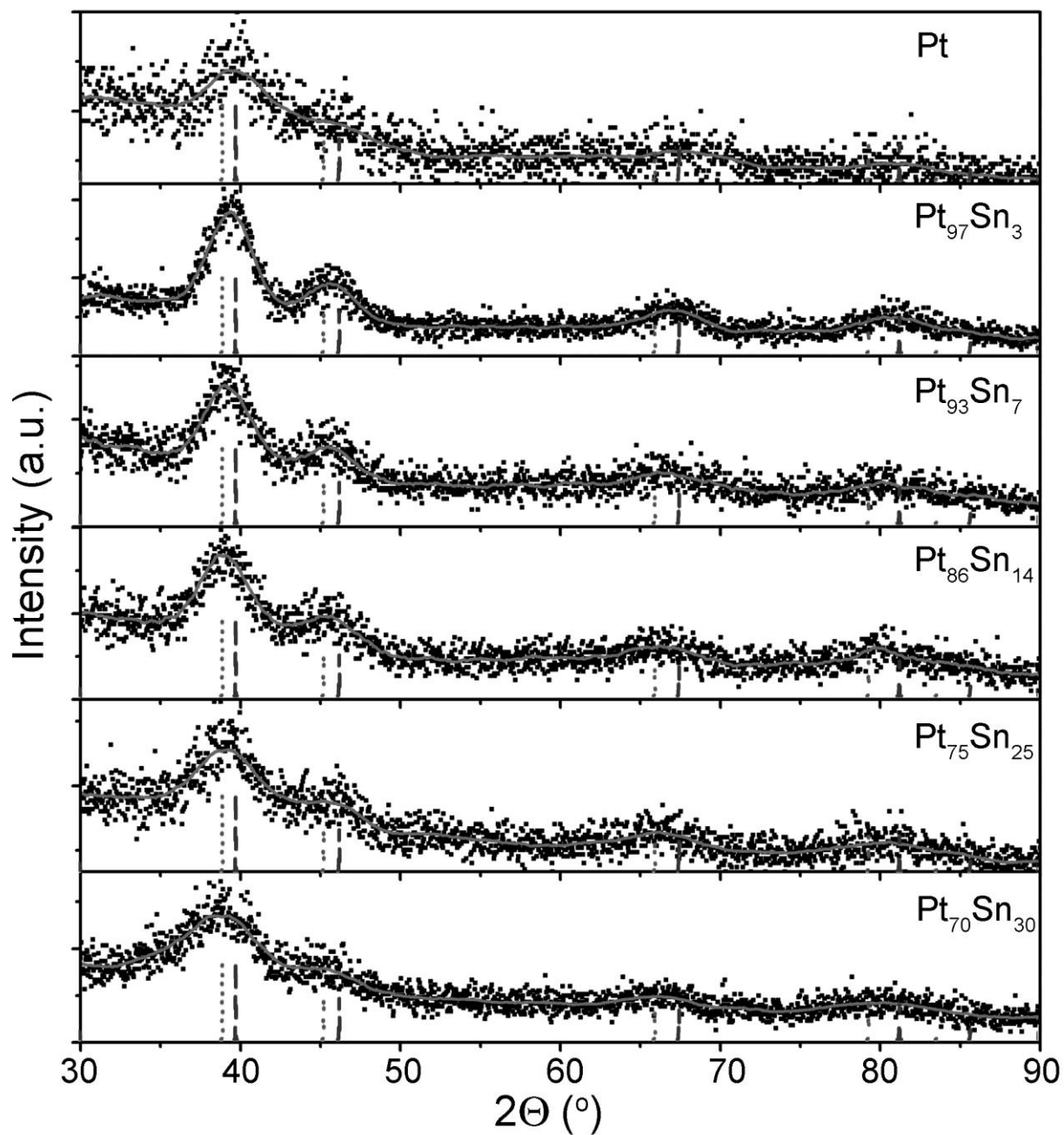


Figure 2.2. XRD patterns of as-synthesized Pt, $\text{Pt}_{97}\text{Sn}_3$, $\text{Pt}_{93}\text{Sn}_7$, $\text{Pt}_{86}\text{Sn}_{14}$, $\text{Pt}_{75}\text{Sn}_{25}$, and $\text{Pt}_{70}\text{Sn}_{30}$ nanoparticles. Reference Pt and Pt_3Sn peaks are shown by the dash lines and dot lines, respectively.

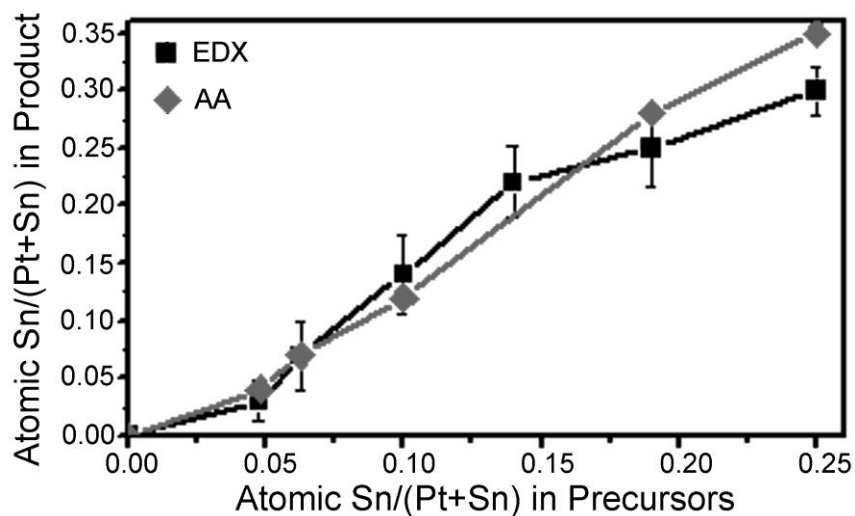


Figure 2.3. Relationship of Sn/(Pt+Sn) ratio in the products of particle synthesis, determined by EDX and ICP-AAS, to that of the metal precursors.

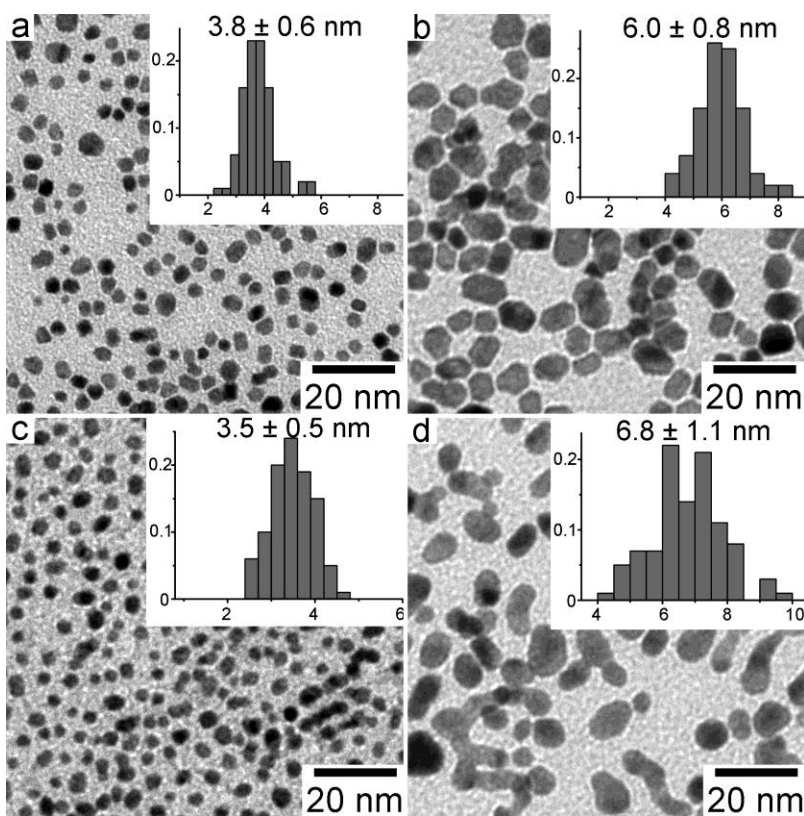


Figure 2.4. TEM images and particle size distribution of as-synthesized Pt nanoparticles with average diameters of (a) 3.8 nm and (b) 6.0 nm, and Pt₃Sn nanoparticles with average diameters of (c) 3.5 nm and (d) 6.8 nm.

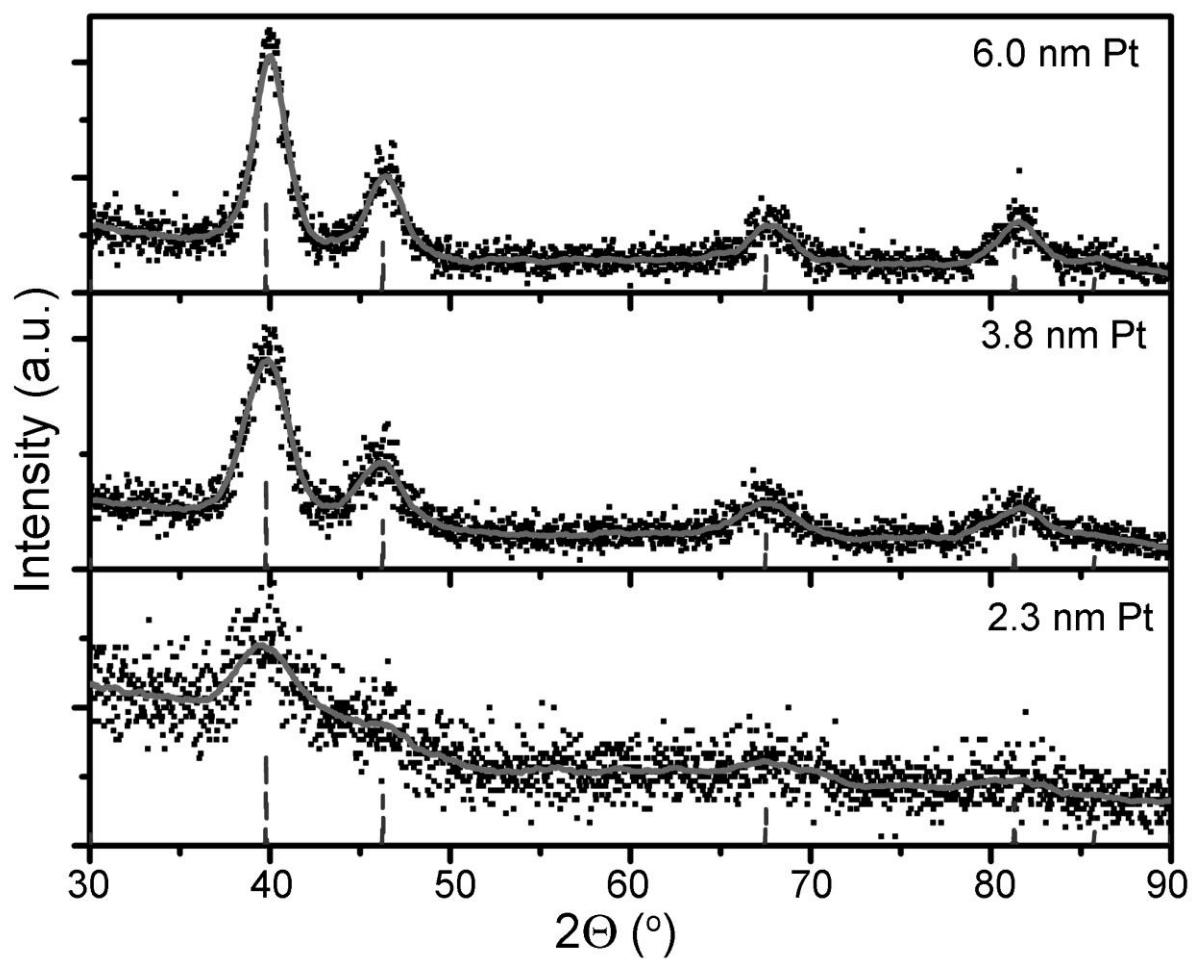


Figure 2.5. XRD patterns for as-synthesized Pt nanoparticles with average particle sizes of 2.3 nm, 3.8 nm, and 6.0 nm. Reference peaks for Pt are shown as dash lines.

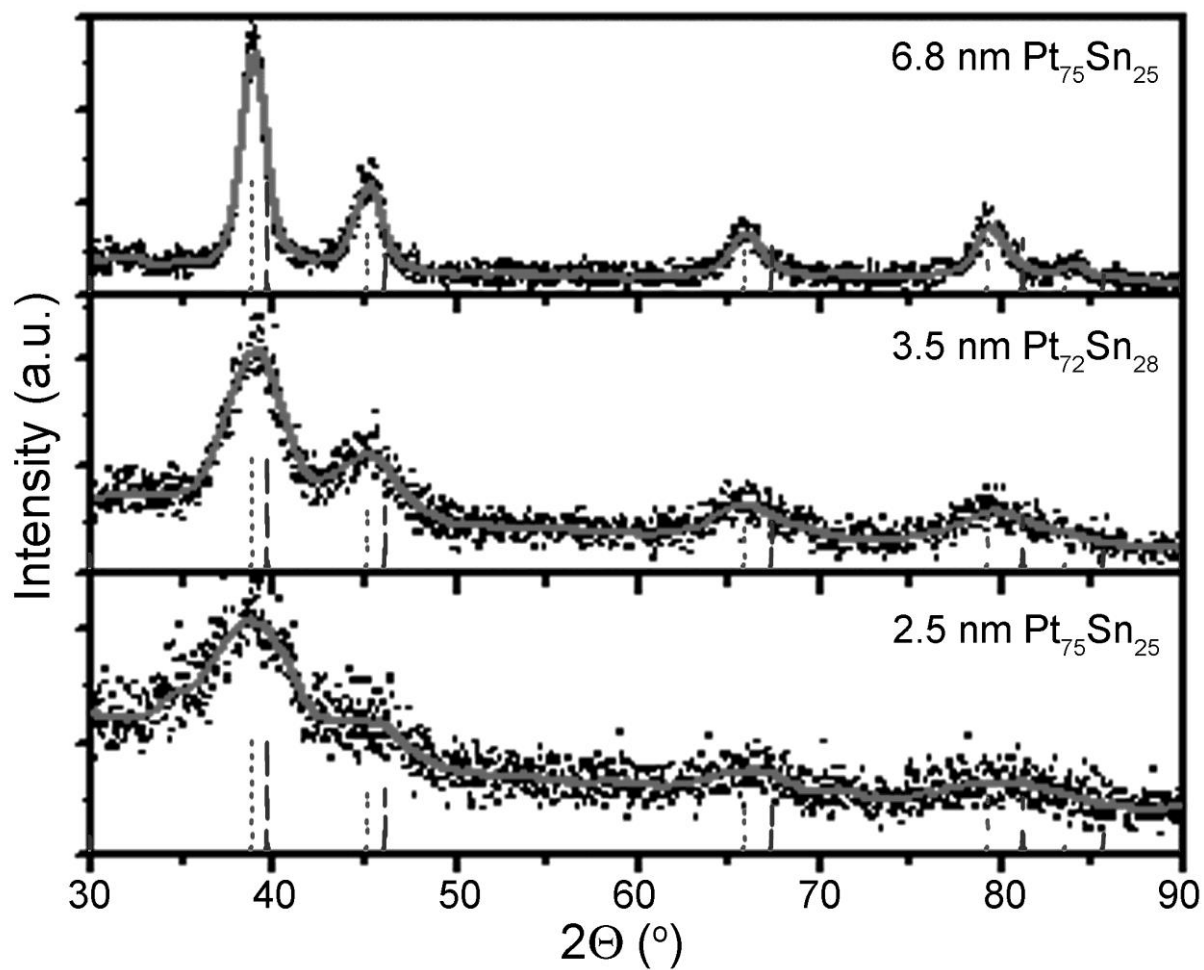


Figure 2.6. XRD patterns for as-synthesized Pt₃Sn nanoparticles with average particle size of 2.5 nm, 3.5 nm, and 6.8 nm. Reference peaks for Pt and Pt₃Sn are shown as dash lines and dot lines, respectively.

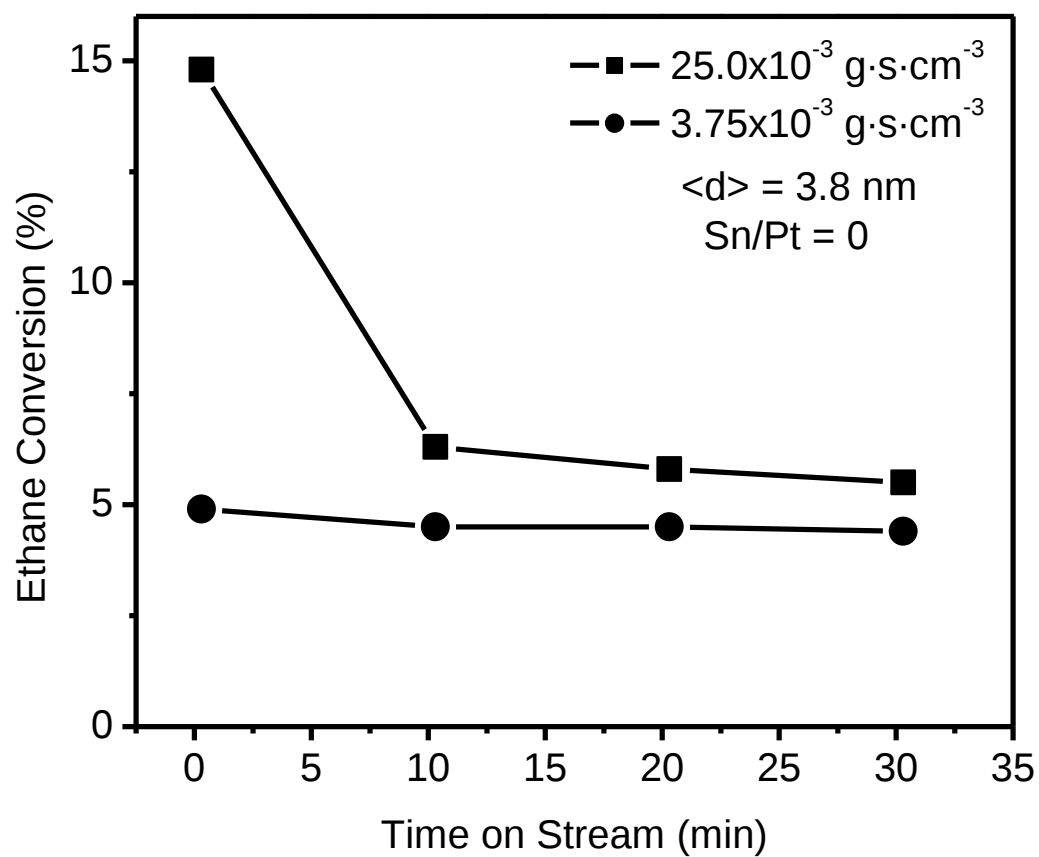


Figure 2.7. Effect of time on stream on conversion given for two different residence times for C_2H_6 dehydrogenation over Pt/Mg(Al)O . Reaction conditions: 873 K, 0.202 bar C_2H_6 , 0.252 bar H_2 , 0.556 bar He.

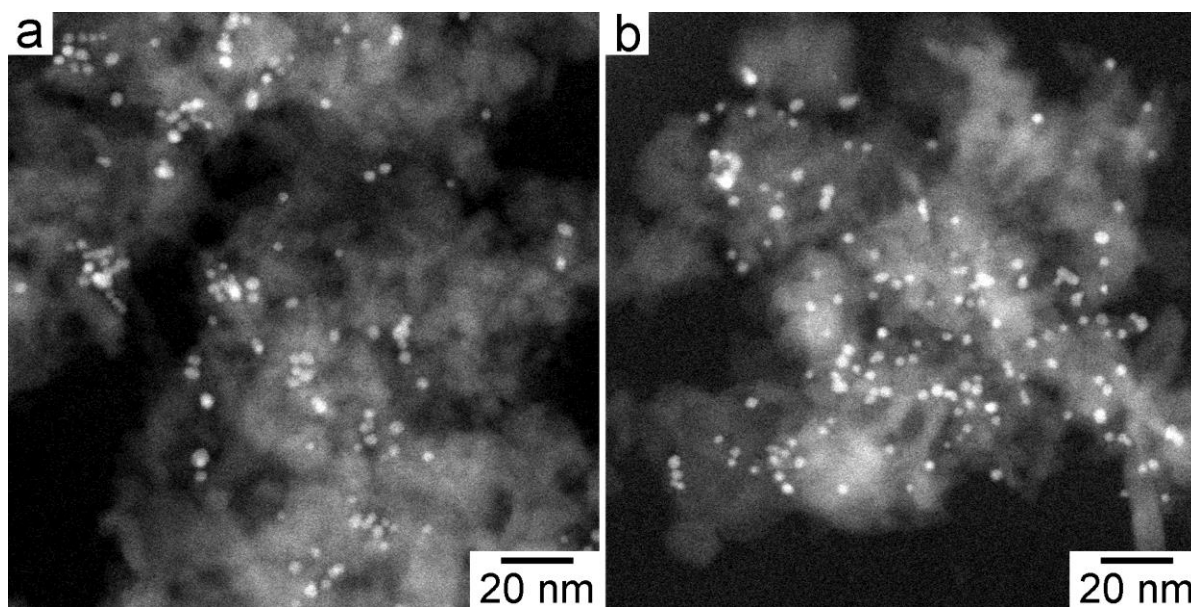


Figure 2.8. STEM images of 3.5 nm $\text{Pt}_3\text{Sn}/\text{Mg}(\text{Al})\text{O}$ catalyst (a) before and (b) after 120 min of ethane dehydrogenation. Reaction conditions: 873 K, 25 mg catalyst, 0.202 bar C_2H_6 , 0.252 bar H_2 , 0.556 bar He, total flow rate of $60 \text{ cm}^3/\text{min}$.

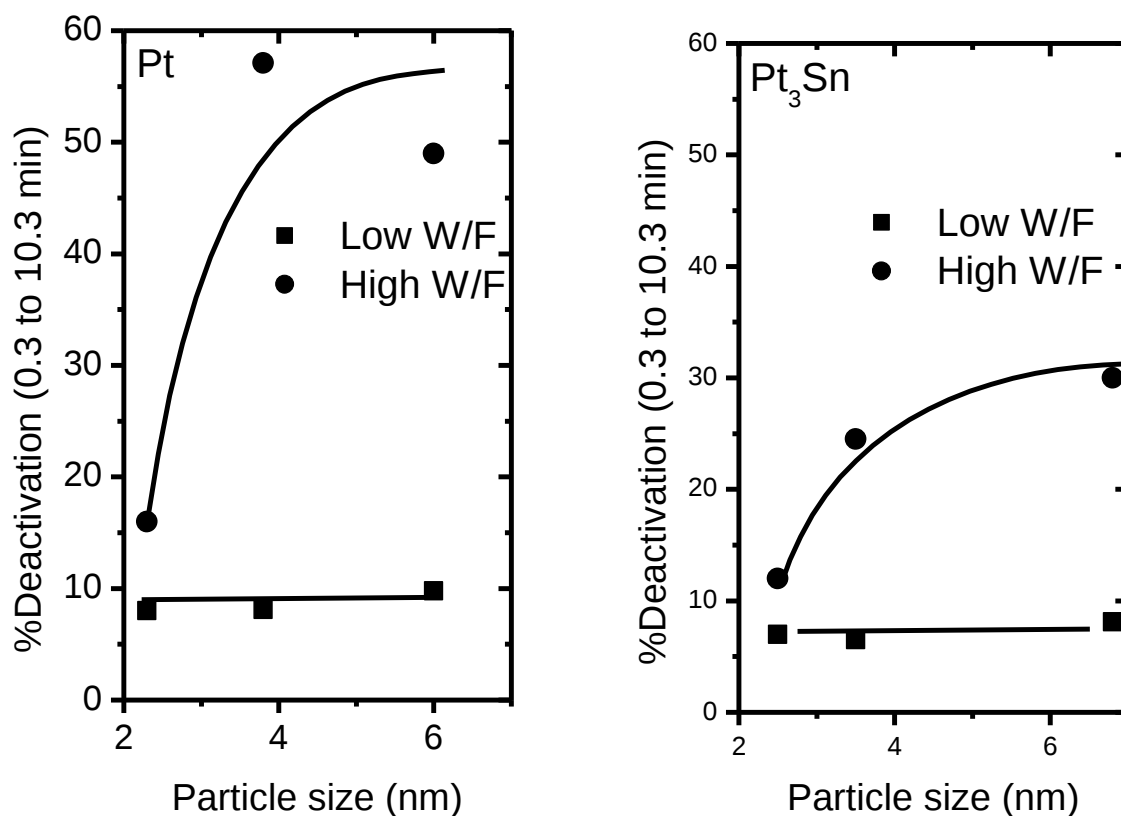


Figure 2.9. Effect of residence time (W/F) and composition on deactivation of C₂H₆ conversion between 0.3 and 10.3 min time on stream. Low W/F and high W/F experiments are at $3.75 \times 10^{-3} \text{ g} \cdot \text{s} \cdot \text{cm}^{-3}$ and $25.0 \times 10^{-3} \text{ g} \cdot \text{s} \cdot \text{cm}^{-3}$, respectively. Reaction conditions: 873 K, 0.202 bar C₂H₆, 0.252 bar H₂, 0.556 bar He.

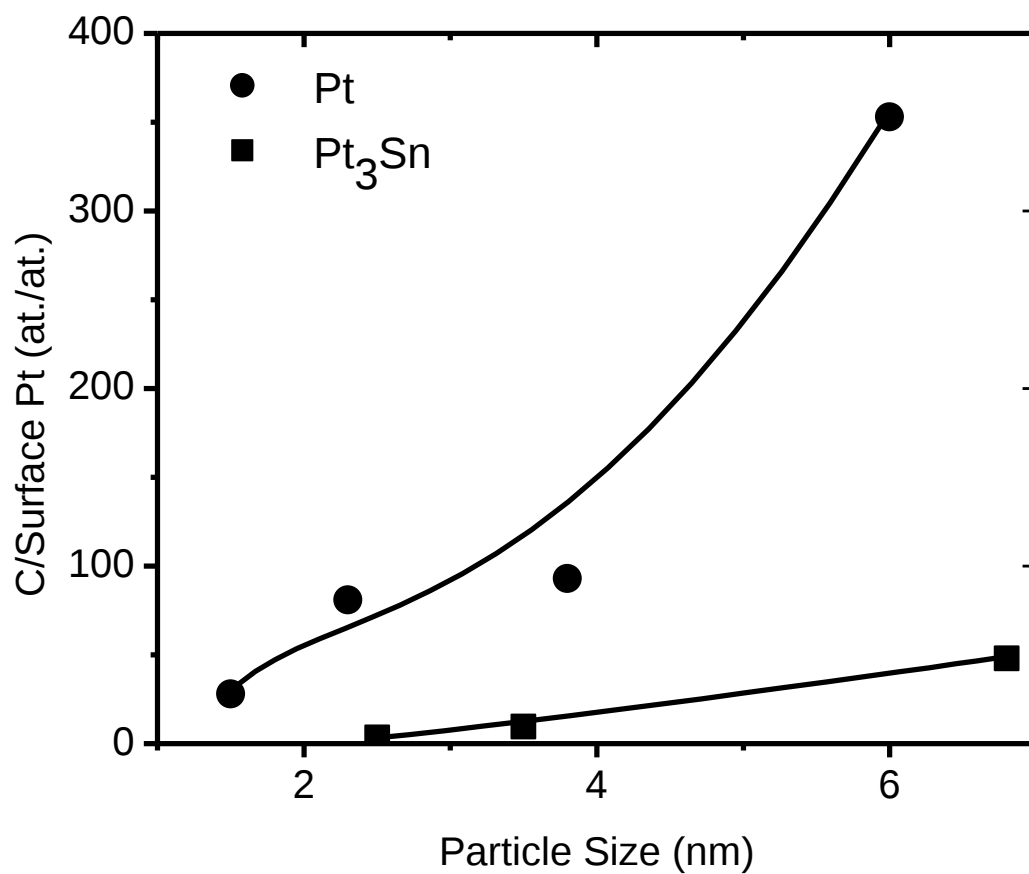


Figure 2.10. Effect of average size of Pt₃Sn and Pt particles on coke accumulation after 120 min of time on stream. Reaction conditions: 873 K, 25 mg catalyst, 0.202 bar C₂H₆, 0.252 bar H₂, 0.556 bar He, total flow rate of 60 cm³/min, W/F = 25.0x10⁻³ g·s·cm⁻³.

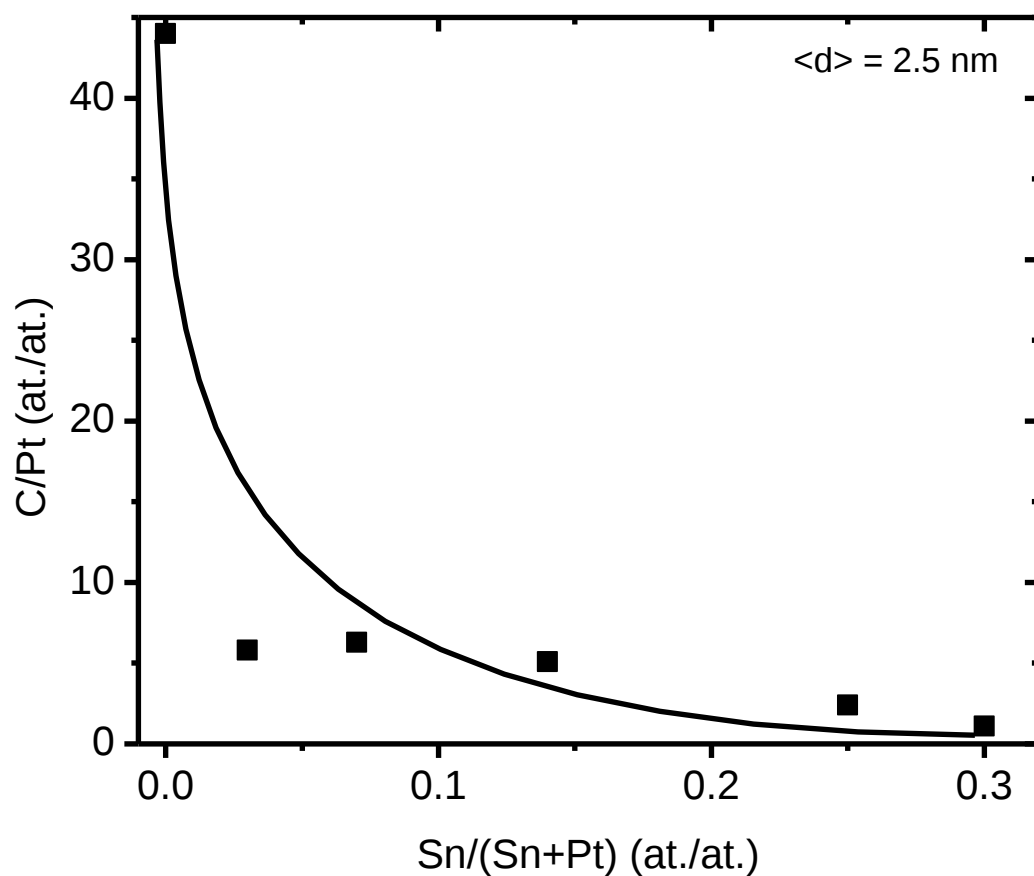


Figure 2.11. Effect of particle composition on coke accumulation after 120 min of time on stream. Reaction conditions: 873 K, 25 mg catalyst, 0.202 bar C_2H_6 , 0.252 bar H_2 , 0.556 bar He, total flow rate of $60 \text{ cm}^3/\text{min}$, $W/F = 25.0 \times 10^{-3} \text{ g} \cdot \text{s} \cdot \text{cm}^{-3}$.

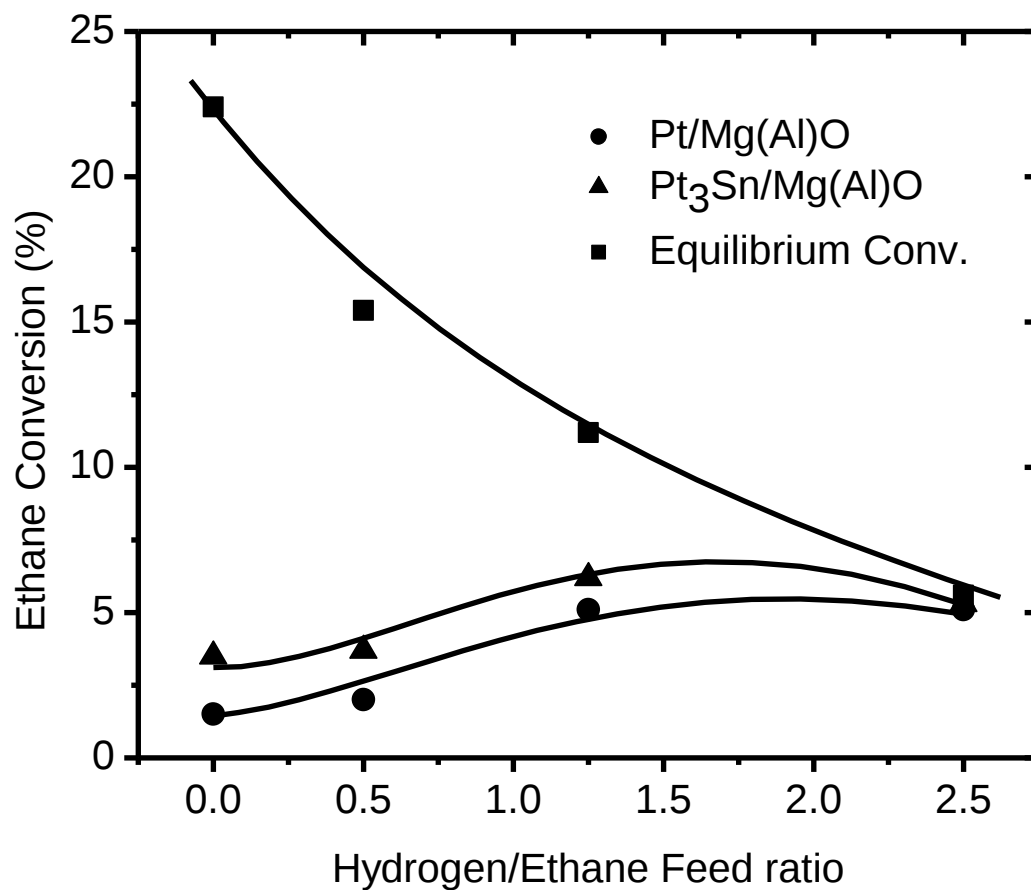


Figure 2.12. Effect of H_2/C_2H_6 feed ratio on C_2H_6 conversion for Pt/Mg(Al)O and Pt₃Sn/Mg(Al)O. Reaction conditions: 873 K, 5 mg catalyst, 0.202 bar C_2H_6 , total flow rate of 80 cm^3/min . $W/F = 3.75 \times 10^{-3} \text{ g} \cdot \text{s} \cdot \text{cm}^{-3}$.

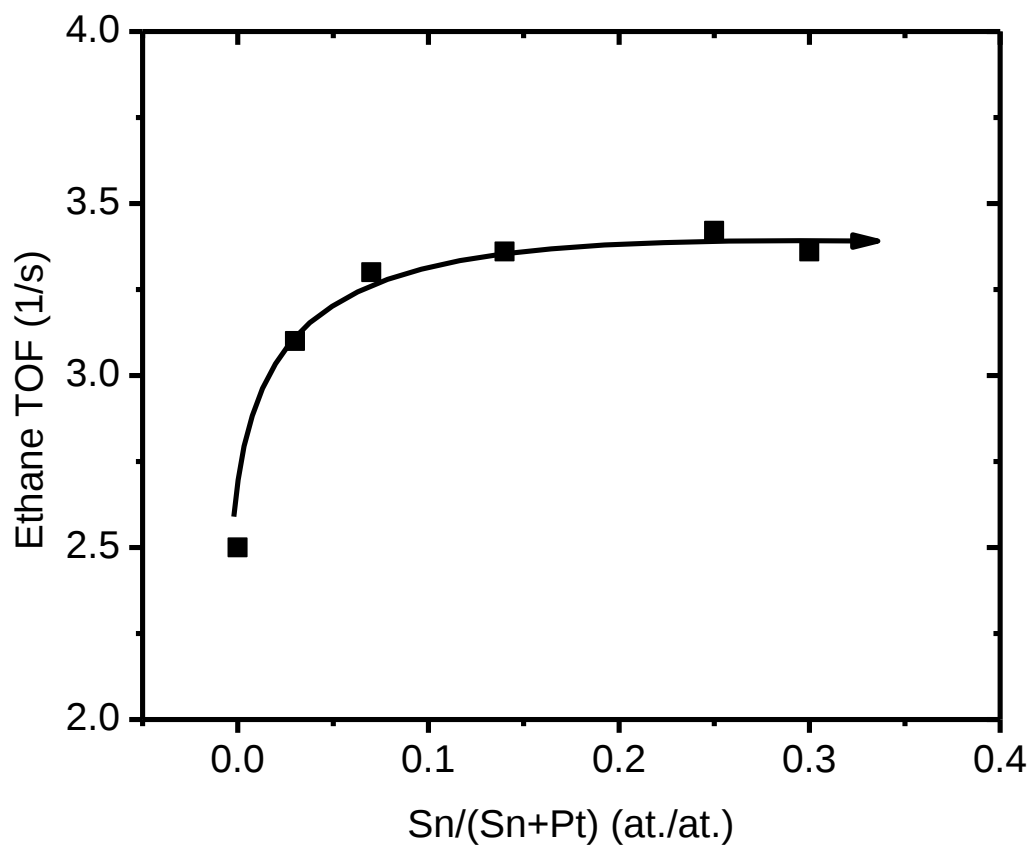


Figure 2.13. Effect of particle composition on TOF of C_2H_6 consumption. Reaction conditions: 873 K, 5 mg catalyst, 0.202 bar C_2H_6 , 0.252 bar H_2 , 0.556 bar He, total flow rate of $80 \text{ cm}^3/\text{min}$, $W/F = 3.75 \times 10^{-3} \text{ g} \cdot \text{s} \cdot \text{cm}^{-3}$, time on stream: 0.3 min, $\langle d \rangle = 2.5 \text{ nm}$.

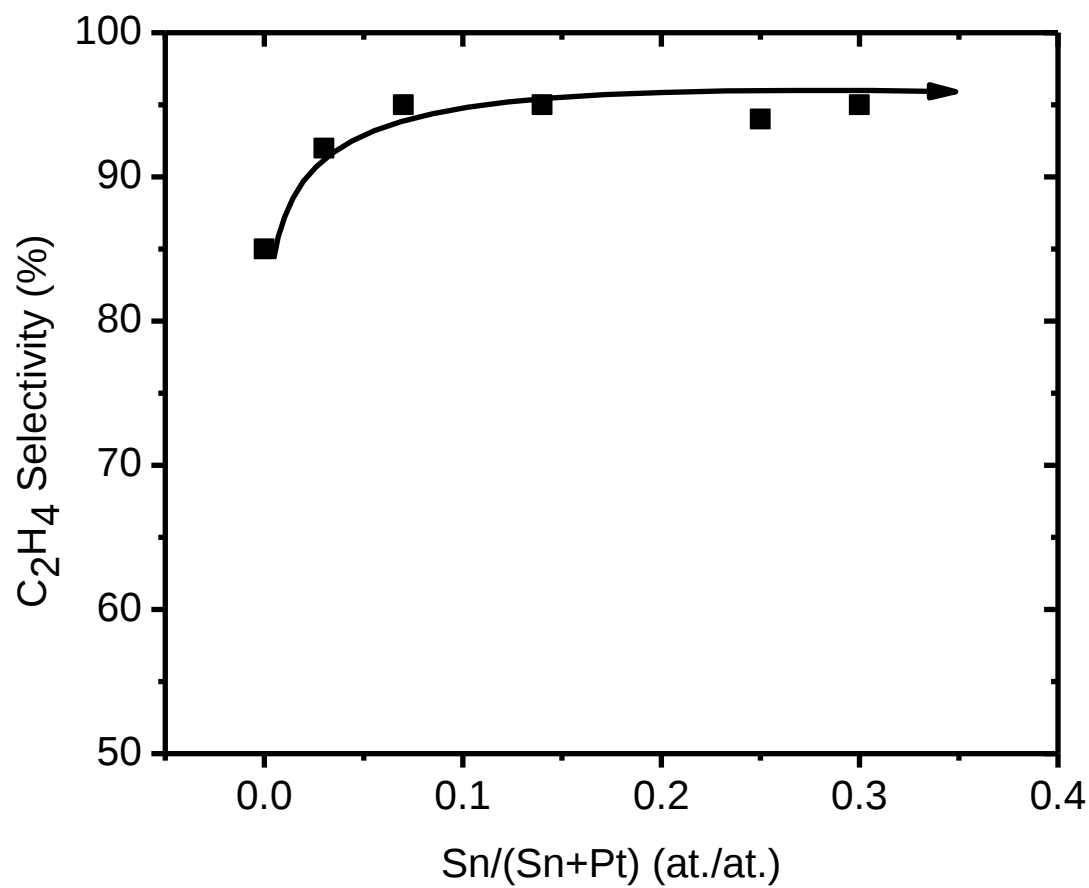


Figure 2.14. Effect of particle composition on the selectivity to C₂H₄. Reaction conditions: 873 K, 5 mg catalyst, 0.202 bar C₂H₆, 0.252 bar H₂, 0.556 bar He, total flow rate of 80 cm³/min, W/F = 3.75x10⁻³ g·s·cm⁻³, time on stream: 0.3 min, <d> = 2.5 nm.

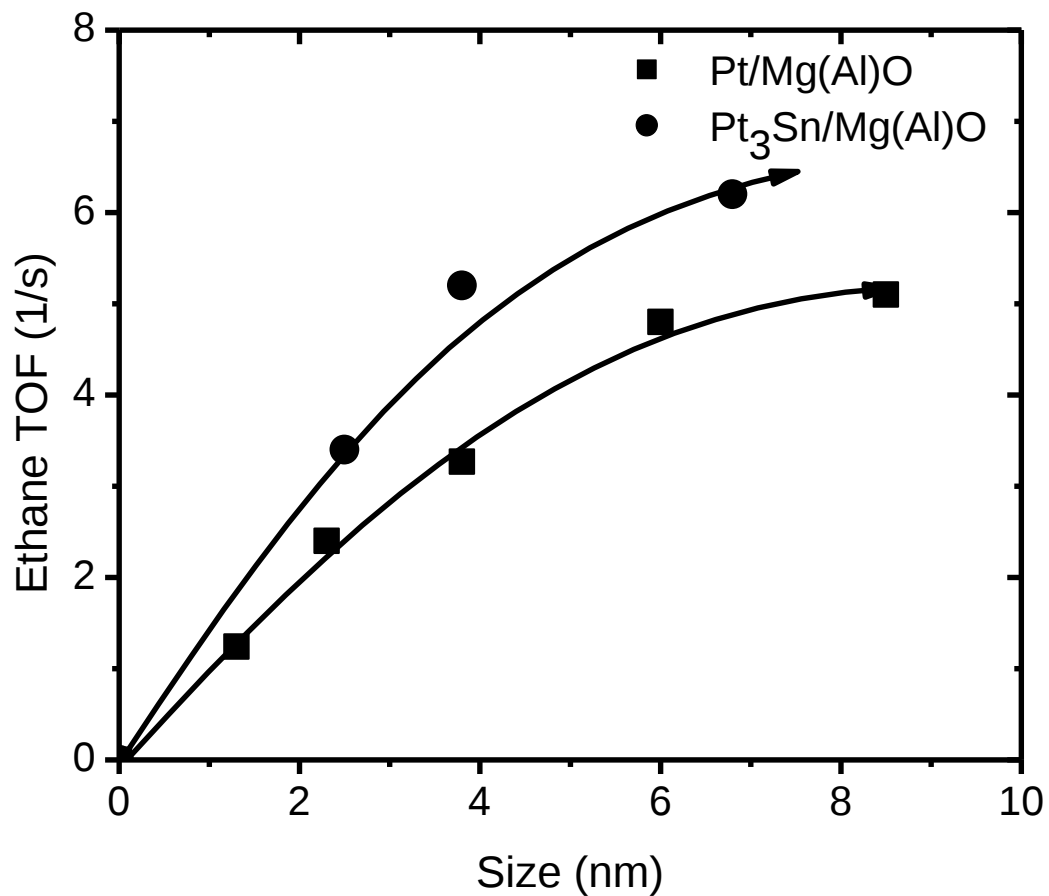


Figure 2.15. Effect of average particle size (Pt₃Sn, Pt) on the TOF of C₂H₆ consumption. Reaction conditions: 873 K, 5 mg catalyst, 0.202 bar C₂H₆, 0.252 bar H₂, 0.556 bar He, total flow rate of 80 cm³/min, W/F = 3.75x10⁻³ g·s·cm⁻³, time on stream: 0.3 min.

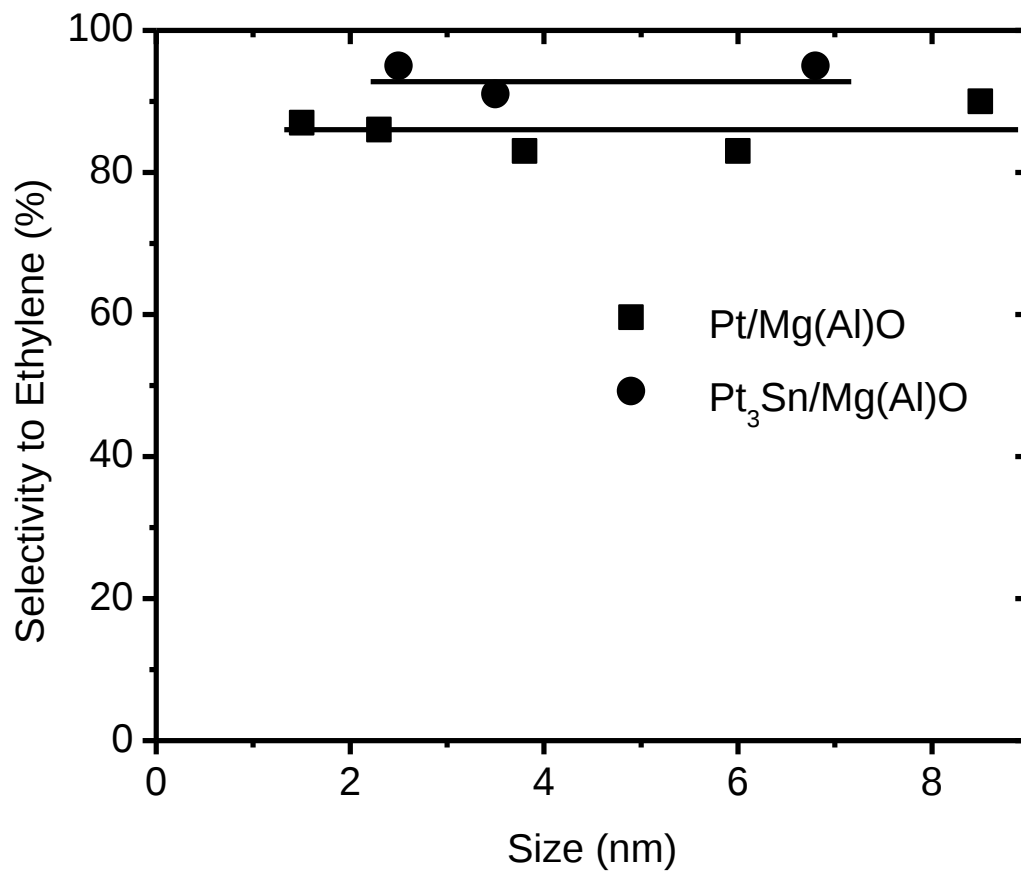


Figure 2.16. Effect of average size particle size (Pt₃Sn, Pt) on the selectivity to C₂H₄. Reaction Condition: 873 K, 5 mg catalyst, 0.202 bar C₂H₆, 0.252 bar H₂, 0.556 bar He, total flow rate of 80 cm³/min, W/F = 3.75x10⁻³ g·s·cm⁻³, time on stream: 0.3 min.

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2.6 Supporting Information

Table S.2.1. Synthetic parameters for making Pt_xSn_{100-x} nanoparticles and the compositions in the final products based on EDX. 5.0 mL of OE, 0.20 g of HDD, and 30 min of reaction time were used in all the experiments.

Sample #	Pt(acac) ₂ (μmol)	Sn(acac)) ₂ (μL)	OAm (mL)	OA (mL)	Ramp Rate	T (°C)	Product (EDX Data)
6.0 nm Pt	125	0	0.05	0.05	2	290	Pt
3.8 nm Pt	125	0	0.1	0.1	2	290	Pt
2.3 nm Pt	125	0	0.5	0	5	140	Pt
3.0 nm Pt ₉₇ Sn ₃	125	1	0.5	0.5	5	200	Pt ₉₇ Sn ₃ ± 1.8
2.8 nm Pt ₉₃ Sn ₇	125	2	0.5	0.5	5	200	Pt ₉₃ Sn ₇ ± 3.0
2.5 nm Pt ₈₆ Sn ₁₄	125	3	0.5	0.5	5	200	Pt ₈₆ Sn ₁₄ ± 3.5
2.5 nm Pt ₇₅ Sn ₂₅	125	7	0.5	0.5	5	200	Pt ₇₅ Sn ₂₅ ± 3.4
2.3 nm Pt ₇₀ Sn ₃₀	125	10	0.5	0.5	5	200	Pt ₇₀ Sn ₃₀ ± 2.1
3.5 nm Pt ₇₂ Sn ₂₈	125	10	0.5	0.5	5	290	Pt ₇₂ Sn ₂₈ ± 2.0
6.8 nm Pt ₇₅ Sn ₂₅	125	10	0.1	0.1	2	290	Pt ₇₅ Sn ₂₅ ± 3.0

Table S.2.2. Data of metal loadings and compositions from ICP-AAS measurements.

Sample #	Pt content (wt. %, ICP-AAS)	Sn content (wt. %, ICP-AAS)	Particle Composition
6.0 nm Pt/Mg(Al)O	2.40	N/A	Pt
3.8 nm Pt/Mg(Al)O	1.84	N/A	Pt
2.3 nm Pt/Mg(Al)O	1.11	N/A	Pt
1.3 nm Pt/Mg(Al)O	0.824	N/A	Pt
3.0 nm Pt ₉₇ Sn ₃ /Mg(Al)O	1.75	0.0415	Pt ₉₆ Sn ₄
2.8 nm Pt ₉₃ Sn ₇ /Mg(Al)O	1.85	0.0821	Pt ₉₃ Sn ₇
2.5 nm	1.78	0.150	Pt ₈₈ Sn ₁₂
2.5 nm	1.51	0.364	Pt ₇₂ Sn ₂₈
2.3 nm	1.35	0.452	Pt ₆₅ Sn ₃₅
3.5 nm	1.63	0.418	Pt ₇₀ Sn ₃₀
6.8 nm	1.98	0.401	Pt ₇₅ Sn ₂₅

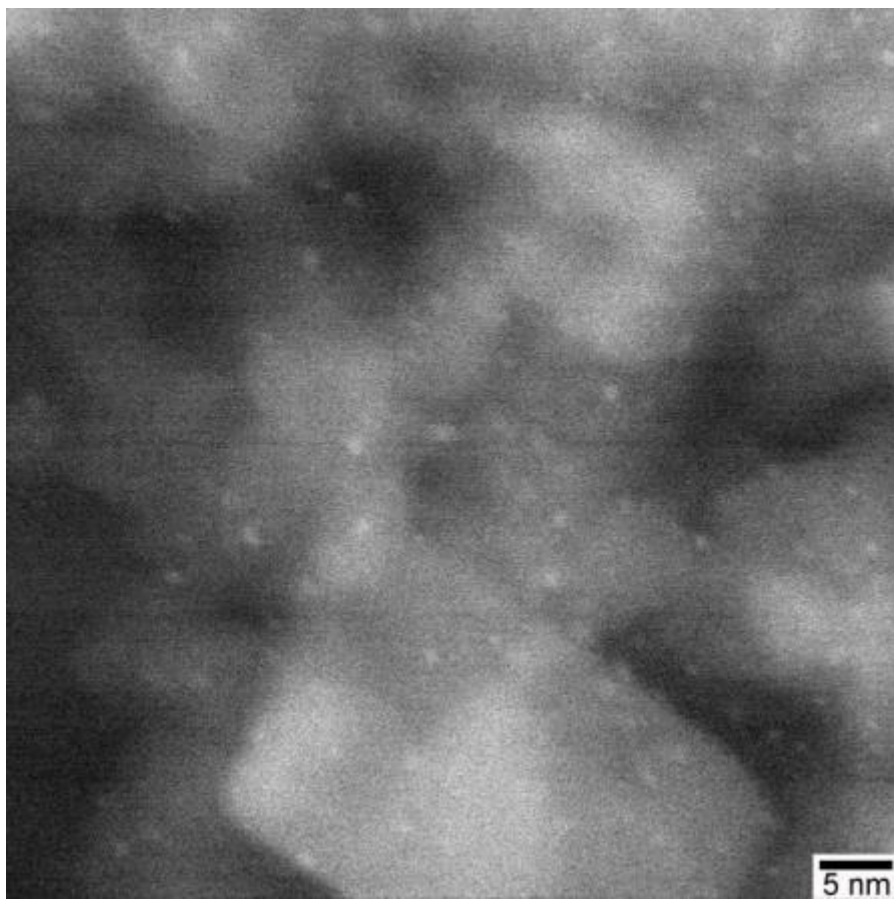
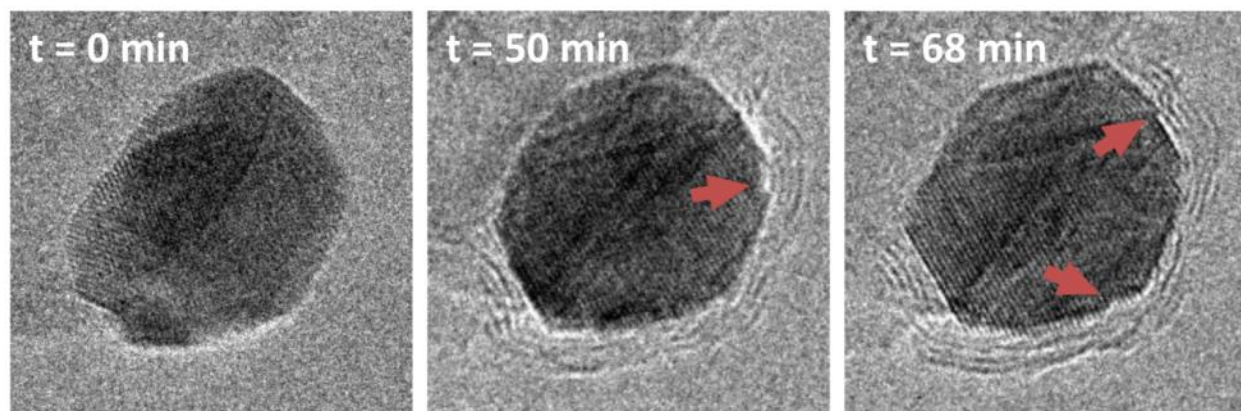


Figure S.2.1. STEM image of as-prepared 1.3 nm Pt/Mg(Al)O using an incipient wetness method.

Chapter 3

Understanding the coking mechanism on supported Pt nanoparticles by *in situ* HRTEM



Abstract

Carbon deposition on MgO-supported Pt nanoparticles from ethylene decomposition was studied by *in situ* TEM (TEM) in order to elucidate the mechanism behind coking of Pt catalysts at the atomic level. To study this process, an imaging strategy was established for controlling beam-gas-sample interactions in order to minimize beam-induced changes. Hereby, we could observe how carbon encapsulation occurred on Pt nanoparticles and the role of the Pt surface. The mode by which multiple carbon layers grew around the nanoparticle was observed and the evidence suggests that multiple partial layers are capable of growing simultaneously prior to full encapsulation of the nanoparticle. Furthermore, significant shape change was observed on all Pt nanoparticles that grew carbon and a circularity analysis indicated particles became rounder as the coking process continued. Due to the formation of more low-coordinated sites, a closer examination at the surface structure revealed that in some cases, step formation accompanied carbon growth, in agreement with previous *in situ* carbon growth studies on other transition metals and *ex situ* TEM studies on Pt nanoparticle coking. This observation provides direct evidence of Pt restructuring during coking, and offers a guide for future understanding of designing stable catalysts.

3.1. Introduction

Supported platinum nanoparticles are used extensively to promote the transformation of alkanes to a variety of products via reactions such as dehydrogenation [1-5], dehydroaromatization [6, 7], and isomerization [8, 9]. The processes are often accompanied by formation of carbonaceous deposits that lead to blockage of the active sites and ultimately to catalyst deactivation [2, 10-12]. Extensive research had been undertaken to minimize the deposition of carbon, in an effort to improve the stability of supported Pt nanoparticles. For example, the addition of elements, such as Sn or In, to form a bimetallic catalyst has been found to be effective in inhibiting the formation of coke [1-3, 13, 14]. In addition, selection of a support free of acidic sites is also important in preventing polymerization of dehydrogenated hydrocarbon species catalyzed by the metal to form coke [15, 16]. Many spectroscopic techniques are available to characterize the structure and composition of coke post-mortem [17-19] and theoretical calculations have also been undertaken to understand hydrocarbon decomposition pathways on Pt surfaces [20-22]. However, to improve the understanding on the mechanism of coking on supported Pt nanoparticles detailed observations of the surfaces are needed to address the role of the active sites on the carbon growth. This, in turn, may help to better design future catalysts with greater resistance to deactivation.

Transmission electron microscopy (TEM) has proven to be a highly informative technique for elucidating carbon growth on transition metals, providing a direct visualization of the surface structure and shape of nanoparticles at the atomic level. Furthermore, electron micrographs of nanoparticles at atomic-resolution can be obtained in the presence of reactive gas atmospheres and elevated temperatures, through the use of differential pumping of the microscope's vacuum system [23-25]. Direct imaging of a working catalyst, referred to as in situ TEM or environmental TEM, is a promising method for capturing carbon growth as a function of time [26-30]. Because nanoscale carbon has been recognized as a class of materials with interesting physical and chemical properties [31], the majority of carbon deposition studies utilizing in situ TEM have focused on metal substrates, such as Ni, Fe, and Co, that favor the formation of graphene [27-30, 32-34]. In contrast, only a few in situ studies have been reported for Pt [26, 35, 36]. Because of the low solubility of carbon in Pt [37], it has been speculated that carbon deposition on Pt proceeds via a surface diffusion mechanism rather than a dissolution and bulk diffusion mechanism [38]. Carbon atoms are first produced by the adsorption and subsequent dehydrogenation or C-C bond cleavage of hydrocarbons on the metal. It has then been proposed that the transport of carbon atoms is mediated by the surface, and that step sites act as preferential growth centers. This phenomenon has been observed experimentally by in situ TEM on Ni nanoparticles [27] and supported by density functional theory (DFT) calculations [39]. However, to date, we are not aware of any efforts to make in situ observations of the onset of carbon deposition and the effects of this process on the structure of Pt nanoparticles. In particular, the aim of this paper is to address how multiple carbon shells grow upon particle encapsulation, in contrast to nanofiber growth, and what is the role of the nanoparticle surface.

In the present study, in situ TEM was employed to study Pt nanoparticles in the presence of ethylene at elevated temperatures. Time-resolved images were acquired in order to directly observe the formation of multiple carbon layers encapsulating the nanoparticle and characterize the dynamic changes of the nanoparticle in the gaseous environment. Despite the impressive capability of in situ TEM to monitor carbon formation on working catalysts, beam-induced processes compared to ex situ TEM remain challenges. Both elastic and inelastic scattering of electrons is prominent in the presence of gas molecules, and contributes to a loss in spatial

resolution as well as changing the property of the catalyst particles and altering reaction kinetics of carbon growth [25, 40]. Therefore, a careful investigation of the carbon deposition reaction was carried out in which the electron illumination was systematically optimized to establish an approach allowing for conducting the experiment with suppressed electron beam-induced changes while elucidating the mechanism by which Pt nanoparticles coke.

3.2. Experimental

3.2.1 Preparation of MgO-supported Pt catalysts

Platinum nanoparticles were prepared by the method described in 2.2.1. Magnesium oxide (MgO) nanocubes were used as a support in the experiments and were made by re-crystallizing MgO nanopowders (<50 nm, Aldrich) in air at 1333 K for 30 min. A suspension of Pt particles in anhydrous toluene, containing 0.01 g Pt metals in 5 mL of anhydrous toluene was mixed with a suspension of 0.2 g of MgO in 10 mL of anhydrous toluene. The mixture was stirred overnight under a N₂ atmosphere before the resulting product was precipitated out by adding an excess amount of anhydrous ethanol followed by centrifugation. The solid material was calcined in air at 573 K for 1 h to remove residual organic agents involved in the synthetic procedure and then treated in an atmosphere of 10% H₂/Ar (UHP Praxair) at 873 K for 1h to fully reduce the Pt surface.

An additional sample of Pt/MgO was prepared by wet impregnation in order to obtain a sample with larger particle size. Platinum acetylacetonate (Pt(acac)₃, 97%, Aldrich) was dissolved in toluene and added to a slurry of MgO in toluene to achieve a Pt content of 3.5 wt%. The mixture was then stirred at room temperature for 2 h and then set in a rotary evaporator overnight to remove the solvent. After drying, the catalyst was reduced at 723 K for 2 h (5 K/min ramp) in a flow of 10% H₂/Ar (UHP Praxair) to form the final catalyst.

3.2.2 Ex-situ TEM characterization and reactor testing

Samples were first examined by *ex situ* TEM to characterize particle size and loading. Images were taken using a FEI Tecnai 12 microscope with an accelerating voltage of 120 kV at the Electron Microscope Laboratory of the University of California, Berkeley. High-resolution TEM (HRTEM) characterizations of the sample were conducted on the TEAM 0.5 high-resolution microscope operated at 80 kV at the National Center for Electron Microscopy (NCEM) in Berkeley, CA.

A portion of the catalysts was used for ex-situ carbon deposition in a reactor system in order to provide a reference point for optimizing electron beam illumination. In a typical procedure, 25 mg of catalyst was loaded into a quartz tube reactor and heated to 873 K at 15 K/min in 20% H₂/He (UHP Praxair) using a three-zone furnace at 1 atm. The catalyst was maintained at this temperature for 1 h before being exposed to a feed of 40% C₂H₆/He (99.95% Praxair), at a flow rate of 40 cm³/min. The reaction was then stopped by cooling the sample down to room temperature in the gas flow, and the coked catalyst was stored in a vacuum desiccator.

3.2.3 In-situ HRTEM

In situ TEM experiments were carried out using an image aberration-corrected Titan 80-300 ETEM microscope equipped with a differentially pumped gas cell [40]. The microscope was

operated in TEM mode at an acceleration voltage of 300 kV, with the spherical aberration coefficient in the range of -10 to -20 μm and electron dose rates of 100-2000 $\text{e}^-/\text{\AA}^2\text{s}$ in the magnification range allowing for the resolution of Pt(111) and Pt(200). Specimens were prepared by crushing the dry catalyst powder for 3 min and dispersing it in anhydrous ethanol. The mixture was sonicated for 5 min, followed by 30 s of centrifugation. The supernatant was then isolated and sonicated again for 5 min, before dispersing onto either a plasma-cleaned stainless steel grid or a Protochips e-chip. Stainless steel grids were mounted in a Gatan 628 Inconel single-tilt heating holder with an isotropic information transfer out to at least 0.14 nm. The temperature was measured by a thermocouple attached to the furnace of the holder [41]. The e-chips were loaded into the Protochips MEMS-based heating holder. The e-chips were operated at elevated temperatures using a constant-resistance mode [42].

In any experiments, the specimens were first reduced by heating in 1 mbar H_2 to 773 K for 30 min, after which specific particles were selected for time-resolved observations. The deposition of carbon was initiated by the removal of hydrogen and introduction of 1 mbar ethene, at a specified sample temperature. Time-lapsed TEM image series were acquired of samples during the exposure to ethene once the sample drift had subsided. Low electron doses were used for *in situ* observations in order to minimize beam-induced artifacts, and the beam was shut off in between successive images to further minimize the total accumulated dose for each experiment. In addition, the amount of time spent illuminating each nanoparticle was recorded in order to estimate the total accumulated electron dose. The TEM images were acquired at 0.1-0.5 s exposure using a CCD camera. Following the experiment, the reaction gas was removed from the microscope and a post-mortem examination of the sample was conducted at a pressure below 1×10^{-5} mbar.

3.3. Results and Discussion

Fig. 3.1a shows a TEM image of the as-synthesized Pt nanoparticles, together with the particle size distribution. Most of the Pt particles were faceted in shape and had an average diameter of 5.85 ± 1.55 nm. A TEM image is shown in Fig. 3.1b taken after deposition of the nanoparticles onto the support followed by calcination in order to remove the capping agents and *in situ* reduction in 1 mbar H_2 at 773 K for 30 min. Little evidence of nanoparticle sintering was found (5.89 ± 1.2 nm), indicating the catalyst is thermally stable in the microscope. The high-resolution TEM image of one representative particle taken *in situ* shows a clean surface with distinct facets, suggesting that all organics involved in the synthesis of the catalyst had been successfully removed. A second sample was synthesized by wet impregnation with the aim of attaining a larger average particle size and is shown in Fig. S3.1a. Similarly, Fig. S3.1b shows an image of a representative particle after *in situ* reduction. It is evident that Pt particle is terminated by well-defined facets. Throughout this study, no significant difference in carbon growth between the two samples was observed. Fig. 3.2 shows a graphical illustration of the imaging strategy adopted, as outlined previously in the Experimental section.

First, in order to address carbon deposition inherently related to the Pt/MgO catalyst, a blind experiment was conducted. In this experiment, the catalyst was first exposed to 1 mbar C_2H_4 for 15 min without beam exposure at a specified temperature, followed by evacuation of the gas and lowering of the temperature to 523 K for imaging. Fig. 3.3 shows a clear temperature dependence on the extent of coke formation in the microscope. Below 623 K, no observable carbon was present on the Pt particles (Fig. 3.3a). However, coke formation was observed as the temperature was raised, as evidenced by growing number of encapsulating carbon layers around

the Pt particle. To conduct the carbon growth in a reasonable time window, a reaction temperature of 773 K was selected for the majority of the experiments reported here. In addition, using the present condition (1 mbar C₂H₄, 773 K) yields a multilayer carbon structure in which we aim to elucidate the growth mechanism.

Next, to address the onset of the electron beam effect on growth, experiments were conducted under varying electron illumination conditions. Fig. 3.4 reveals the effect of dose rate on the rate of carbon growth at the reaction conditions chosen. The highest dose rate used (2000 e⁻/Å²s) provided images with the highest signal-to-noise ratio but at the cost of inducing beam effects. After 16 min of reaction time at 2000 e⁻/Å²s, the observed nanoparticle accumulated 4 layers of encapsulating carbon. However at lower dose rates (500 e⁻/Å²s and 1000 e⁻/Å²s), significantly fewer layers formed at reaction times longer than 16 min. Therefore, selection of the dose rate plays an important role in balancing image quality and minimizing beam-accelerated carbon growth. This qualitative effect observed in Fig. 3.4 can be quantified as shown in Fig. 3.5, where the number of full or partial layers of carbon is plotted as a function of reaction time for varying dose rates. Again, it is clearly evident that using a dose rate of 2000 e⁻/Å²s significantly alters the rate of carbon growth compared to the lower dose rates tested. The reference points indicate that on particles previously unexposed by the beam, there is roughly the same number of layers of carbon as there were on the particles that were continuously imaged at both 1000 and 500 e⁻/Å²s, whereas the reference point for 2000 e⁻/Å²s shows less carbon compared to the particles illuminated under the beam through the experiment. Therefore, the two lower rates were suitable for optimizing image signal while reducing beam-induced artifacts. In addition to the beam capable of accelerating carbon deposition, it was observed also that extended beam illumination on grown carbon structures in vacuum could sputter off carbon layers. This effect is documented in Fig. 3.6 and it can be seen that during post-mortem analysis, a period of 9 min at 1000 e⁻/Å²s is enough to sputter off two carbon layers. Therefore it is important to limit the amount of beam exposure when observing carbon, both during growth and in vacuum.

To address the mechanism of carbon growth, the first issue investigated was the growth mode of multiple carbon layers around the nanoparticle. From the two time series shown Fig. 3.7, it is clear that multiple partial layers are capable of forming without the necessity of full particle encapsulation by the first layer. Examination of Fig. 3.7b and Fig. 3.7c (and similarly Fig. 3.7e to Fig. 3.7f) show that additional layers of carbon have nucleated and grown from the surface of the observed nanoparticle, without the nanoparticle being full encapsulated. Therefore, the formation of additional layers of carbon can precede the encapsulation of a Pt particle by a single graphitic sheet. No previous experimental evidence has directly addressed this issue, to the best of our knowledge. Interestingly, molecular dynamics (MD) simulations have shown that during the growth of the initial carbon layer on Fe nanoparticles it is more thermodynamically favorable for new carbon atoms precipitating from the nanoparticle to join the edge of the existing graphene layer, rather than to precipitate between the existing layer and the metal nanoparticle surface and thereby initiate a new graphene layer [43]. To address the differences in the findings for Pt and Fe, a closer examination was undertaken of whether the Pt nanoparticle restructures over the course of carbon deposition.

A survey of three representative particles is shown in Fig. 3.8. It is clear that in each case particles evolved in shape over time, and became rounder as the coking continued. While slight particle rotation during the course of the experiment could affect the profile shape of the particles, the “rounding” effect that accompanied carbon growth was consistently observed through the study. To quantify this effect, the particle circularity was calculated for 15 different particles over

reaction time and the difference in circularity between the final coked particle and the initial reduced particle are plotted in Fig. 9. The circularity was calculated using Eq. 3.1.

$$\text{Circularity} = 4\pi \times (\text{area}/\text{perimeter}^2) \quad (3.1)$$

With this definition, a circularity of 1.0 is expected for a perfect circle and a circularity of zero is expected for an infinitely elongated polygon. While the difference in circularity was not uniform among all particles, it was clear from a quantitative analysis that the particles examined became rounder as a function of reaction time, in agreement with Fig. 3.9. An increase in circularity implies the formation of more low-coordinated sites such as kinks, corners, and possibly steps. Because of evident restructuring of the nanoparticle, a greater focus was placed on the dynamics of the surface structure.

Fig. 3.10 shows a time series illustrating the effect of carbon growth on the surface morphology of the Pt nanoparticle. At $t = 3$ min, we observe the formation of a partial layer on the topside of the nanoparticle, accompanied by the formation of a small step, and at $t = 12$ min, the formation of a second step appears at the bottom side of the nanoparticle together with the formation of another carbon layer. This effect becomes more pronounced over time as the step becomes enlarged at $t = 20$ min, allowing the formation of a second layer. This effect of step formation is in agreement with previous *in situ* studies of carbon nanotube growth occurring on Ni [27-29]. However, for Pt we see the formation of steps during carbon encapsulation. The formation of steps as a function of reaction time is also illustrated in Fig. 3.11 for longer time scales and to illustrate more statistical significance. It is clear from both time series that not only does the shape of the nanoparticle change over time, but also new steps are formed that can nucleate the formation of new carbon layers. Therefore, if steps become enlarged over time (Fig. 10) or multiple steps form on the surface of the nanoparticle (Fig. 3.11), this could present multiple new sites for carbon atoms assembly into multiple new carbon layers. The availability of multiple nucleation locations would explain why multiple partial layers grow simultaneously. The question remains as to what is the driving force behind the restructuring of the Pt nanoparticle to form steps. While to the best of our knowledge there is no literature pertaining to Pt, DFT calculations for Ni suggest that nucleation near a metal step edge is more likely than on a terrace site [44, 45] and that the gain in energy by binding carbon atoms to a step compared to a terrace is enough to compensate the energy cost for Ni step formation. A similar explanation might be extended to the Pt, though more detailed DFT calculations for carbon growth on Pt are needed. While both Ni and Pt both exhibit surface restructuring, carbon layers on Ni tend to slough off the particle and form a nanotube, whereas Pt and other noble metals tend to exhibit carbon encapsulation [46]. In both cases, carbon layers tend to contour the surface of the nanoparticle. However, Ni particles may be dynamic such that the nanoparticle elongates and carbon contouring the surface leads to the formation of a tube that is more stable. In the case of Pt, a less dynamic metal surface implies less new active step sites and hence carbon contouring the nanoparticle leads to particle encapsulation.

Previous *ex situ* TEM studies of carbon formation on Pt/MgO [26] have shown that the formation of graphene layers initiates at low-coordination number sites located at steps on the surface of Pt nanoparticles. Also of note, a recent study on the nucleation and growth of graphene on Pt(111) surfaces using scanning tunneling microscopy (STM) suggests that graphene islands nucleate slight more favorably at metal step edges than on terraces [47]. Therefore, a possible explanation for why bimetallic Pt catalysts are effective at suppressing coke deposition is that the second element (Sn, In, Ga, etc.) increases the strain at the Pt step edge and suppresses the nucleation of carbons at the steps. It is important to note, however, that not all particles observed in the present study exhibited step formation in conjunction with carbon growth. This could either

be a result of carbon nucleating on a terrace site, or a step site that is hidden from a 2-D projection view of a 3-D nanoparticle. It is evident, though, that the nanoparticle is not static during coking deposition (Fig. 3.8), and in some cases, step formation facilitates the nucleation and growth of additional carbon layers (Figs. 3.10, 3.11).

Despite the “pressure gap” between experiments done in a reactor system and inside the microscope, similarities in step formation and carbon nucleation are striking, as shown in Fig. 3.12. In Fig. 3.12a, a sample of Pt/MgO had been exposed to a pressure of 0.4 bar of ethane for 2 h at 873 K and imaged by HRTEM. The graphene layers can be traced back to the step that has formed on the concave side of the nanoparticle. Nanoparticles that had been exposed to 1 mbar of ethene for 20 min at 773 K (Fig. 3.12b) exhibited almost identical characteristics, with multiple carbon layers nucleating from the step edge. Therefore, despite the low pressures of hydrocarbon used in the *in situ* TEM experiment, similarities in carbon growth mechanisms can be observed, proving *in situ* TEM is a valuable tool for imaging catalysts at work.

3.4. Conclusions

In situ HRTEM experiments were done to investigate the formation of carbon layers on MgO-supported Pt nanoparticles upon exposure of the catalyst to ethene at elevated temperature inside the microscope. A careful imaging strategy was adopted in order to minimize beam effects and a proper electron beam dose rate was selected to suppress beam-assisted carbon growth. *In situ* TEM also revealed that multiple partial layers of graphene can form, without the Pt particle being completely encapsulated by the first carbon layer. Additionally, particles became rounder as a function of reaction time, as measured by circularity factor, suggesting that coking causes significant restructuring on Pt nanoparticles. A closer look at the surface of the nanoparticles revealed that in some cases, step formation was observed in conjunction with coking, supporting previous evidence that step sites may play a major role in nucleation and growth of carbon. These insights into the coking mechanism on Pt nanoparticles may pave the way for better understanding on why bimetallic catalysts are more durable than their monometallic counterparts.

3.5. Acknowledgements

The authors express their appreciation for the opportunity to obtain *in situ* HRTEM images at Haldor Topsøe A/S. The authors also acknowledge efforts from Juan Salvador Martinez Espin and Pablo Beato for fruitful discussions and experimental support. This work was supported by a grant from Chevron Energy Technology Company. *Ex situ* microscopy experiments were conducted at the UC Berkeley Electron Microscopy Lab and the Molecular Foundry, Lawrence Berkeley National Lab, which is supported by the U.S. Department of Energy under Contract # DE-AC02-05CH11231.

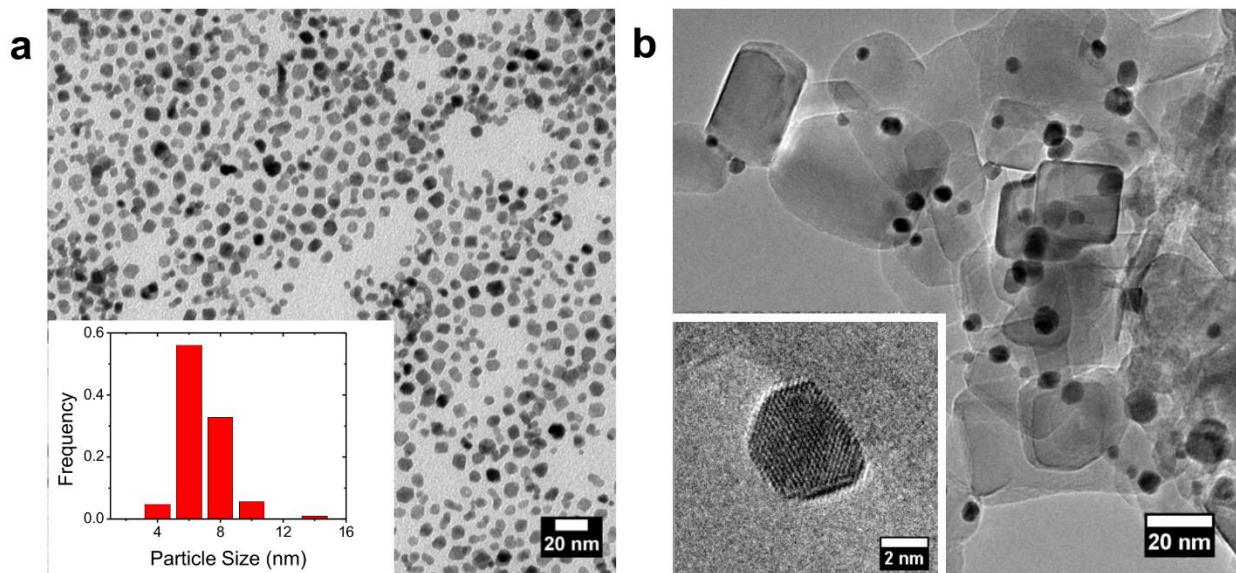


Figure 3.1. TEM of a) as-synthesized Pt nanoparticles and their particle size distribution, and b) *in situ* TEM of MgO supported Pt after being reduced in the microscope in 1 mbar H₂ at 773 K for 30 min. Inset of (b) shows one representative Pt particle taken at high resolution with dose rate 2000 e⁻/Å²s.

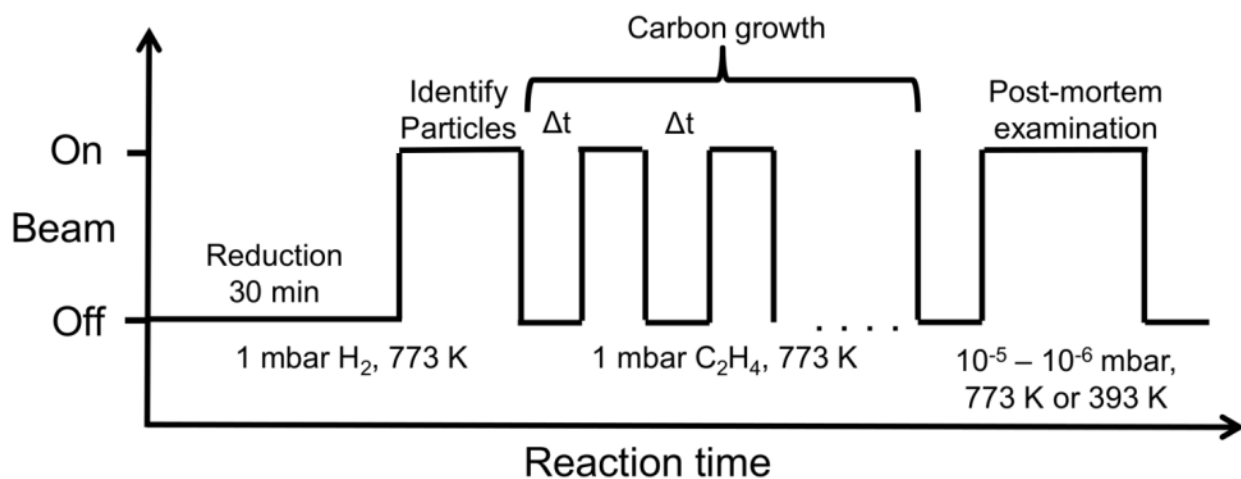


Figure 3.2. Schematic of the experiment conducted on the Titan 80-300 ETEM microscope, operated at 300 kV.

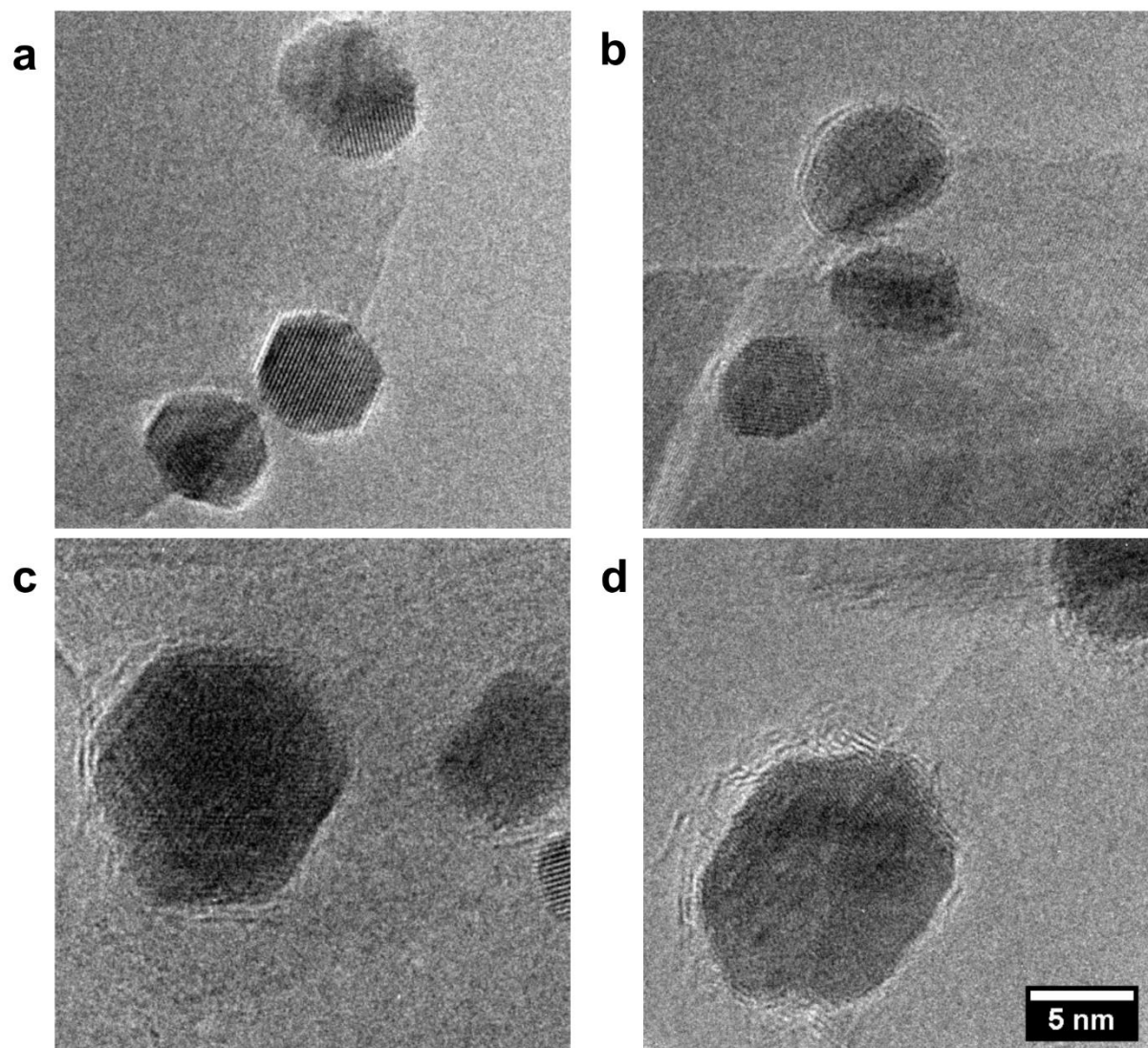


Figure 3.3. *In situ* TEM images of Pt/MgO after 15 min exposure in 1 mbar C₂H₄ at (a) 623, (b) 673, (c) 723, (d) 773 K taken at 2000 e⁻/Å²s, with the beam shut off during the growth process.

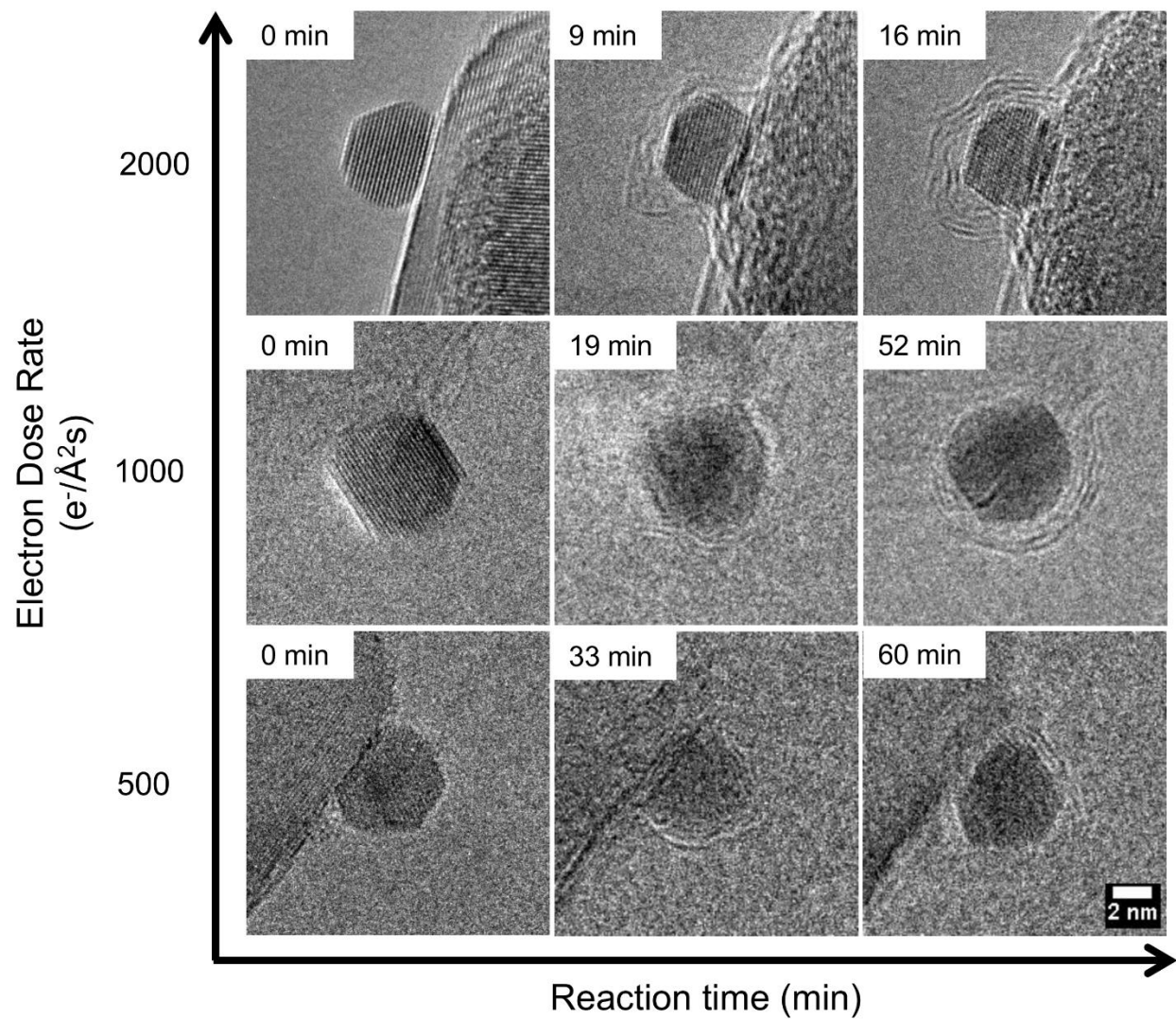


Figure 3.4. Effect of beam dose on carbon growth (1 mbar C_2H_4 , 773 K) on Pt/MgO as a function of reaction time.

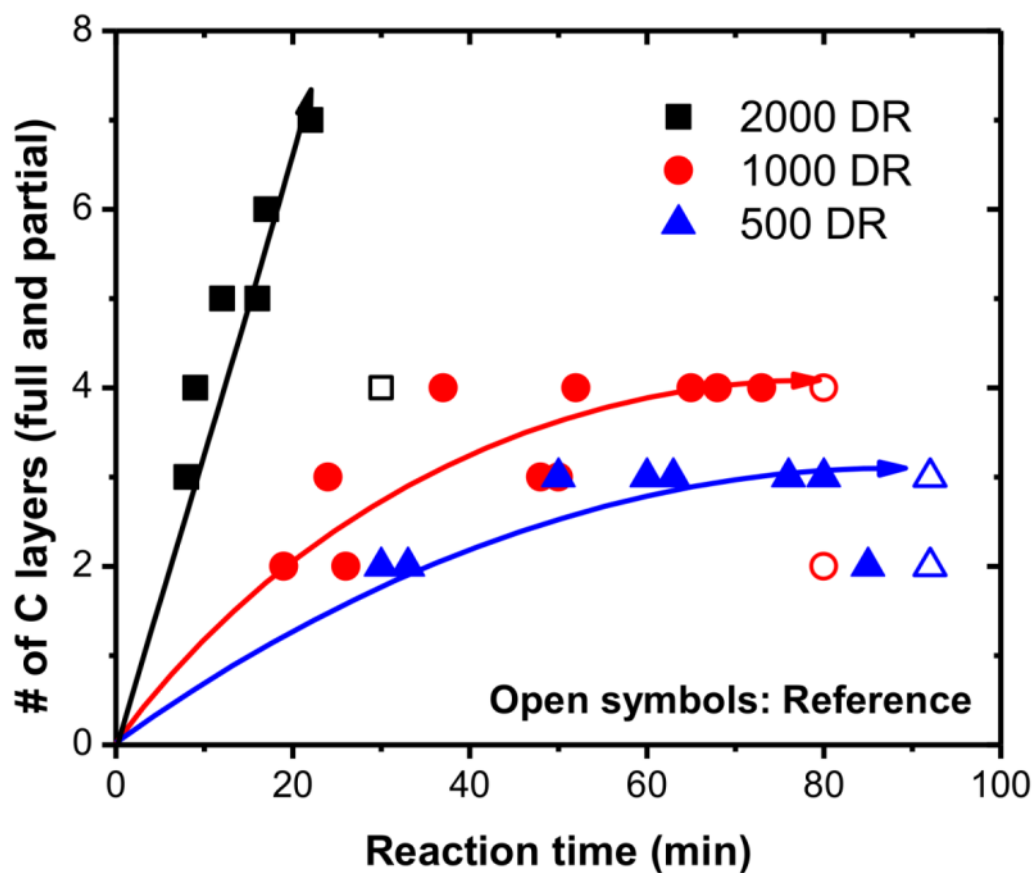


Figure 3.5. The number of carbon layers (full + partial) as a function of reaction time and 3 different dose rates. Open symbols refer to particles serving as a reference that were observed post-mortem, without any prior beam exposure. Growth conditions: 1 mbar C_2H_4 , 773 K

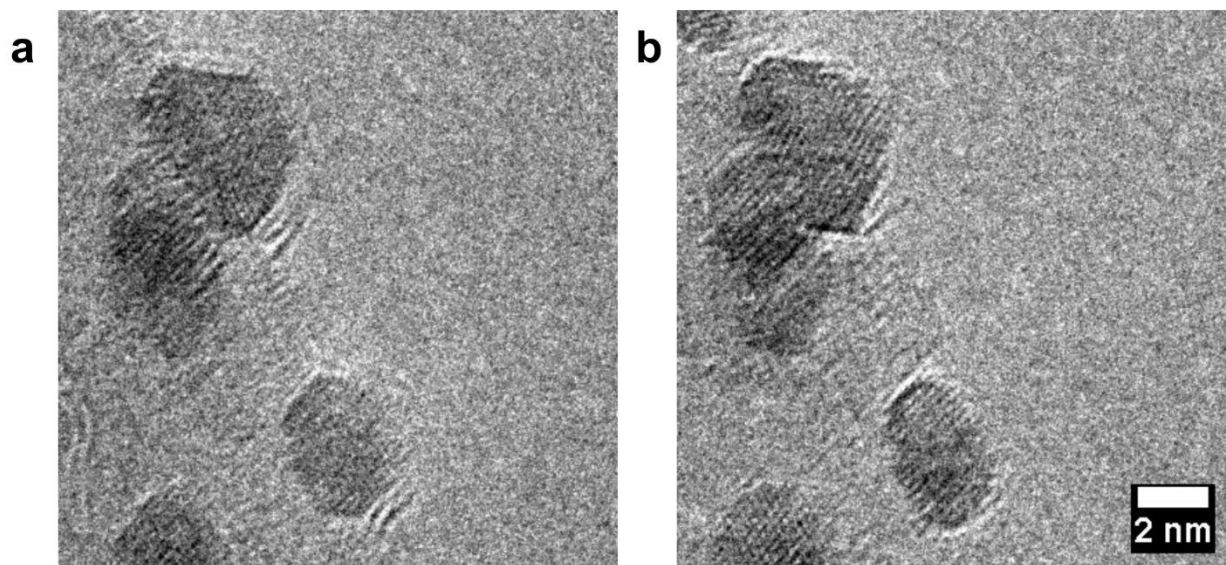


Figure 3.6. Effect of beam illumination time during post-mortem analysis on carbon deposited *in situ*. The a) original carbon layers were sputtered off by the electron beam after b) 9 min of illumination at $1000 \text{ e}^-/\text{\AA}^2\text{s}$, $1.2\text{e-}5 \text{ mbar}$.

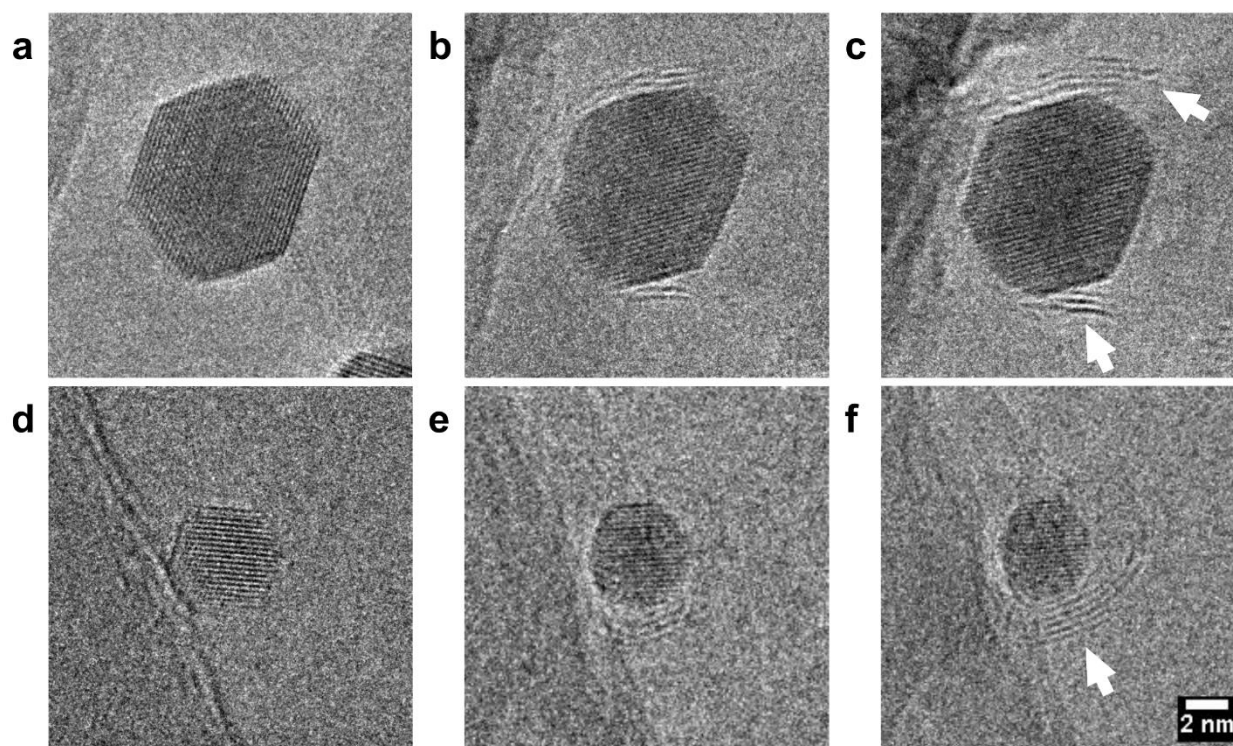


Figure 3.7. Two series of time-resolved TEM images Pt nanoparticles (a – 0 min, b 24 min, c – 37 min, and d – 0 min, e 40 min, f – 71 min) acquired *in situ* to illustrate multi-layer carbon growth. The images are recorded at $1000 \text{ e}^-/\text{\AA}^2\text{s}$ (a-c) and $500 \text{ e}^-/\text{\AA}^2\text{s}$ (d-f). Growth conditions: 1 mbar C_2H_4 , 773 K. The white arrows indicate the location of partial layer formation.

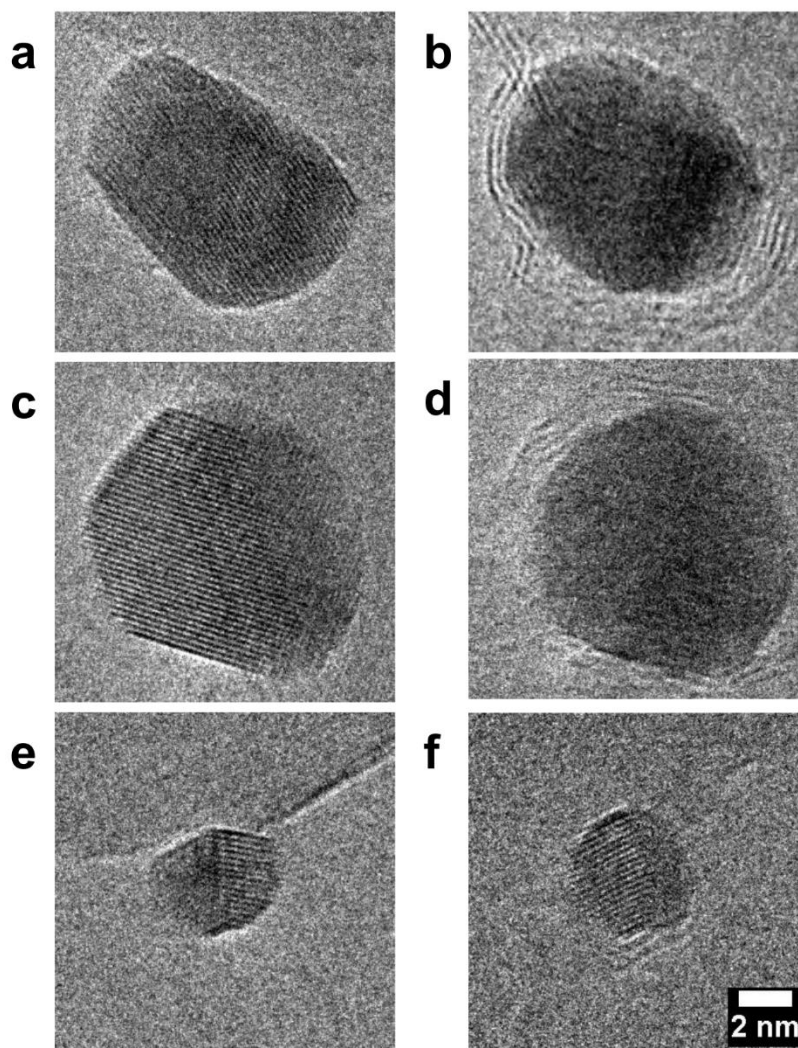


Figure 3.8. *In situ* TEM images of three representative particles as a function of reaction time (a-c – 0 min, b – 58 min, d – 37 min, f – 22 min) illustrating shape change, taken at $1000 \text{ e}^-/\text{\AA}^2\text{s}$. Growth conditions: 1 mbar C_2H_4 , 773 K

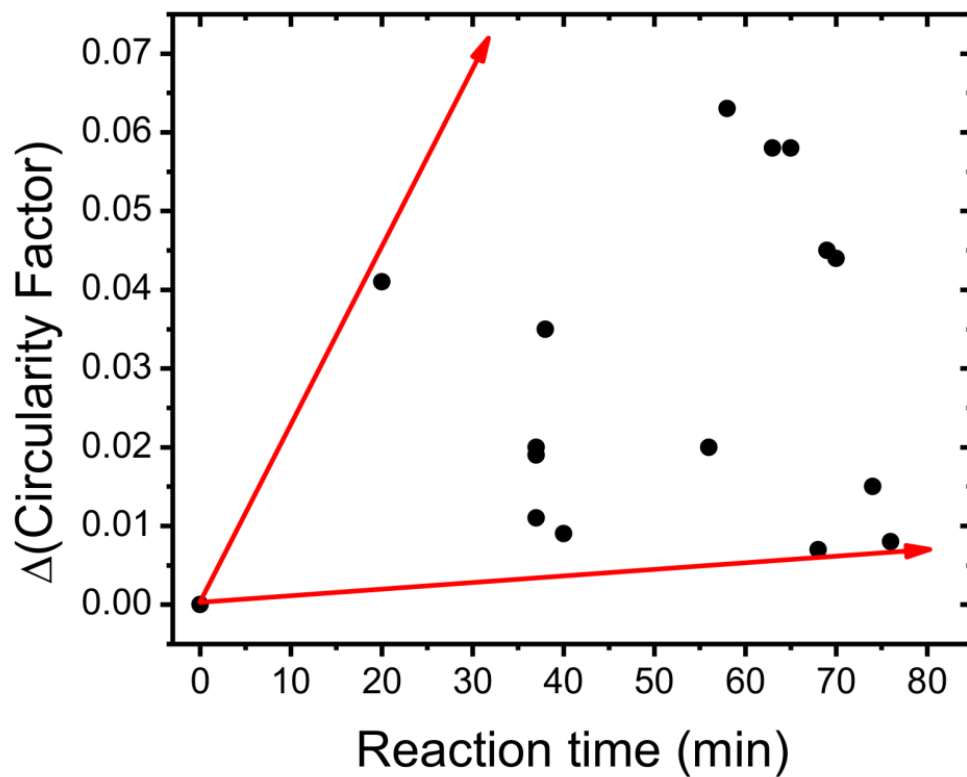


Figure 3.9. Circularity factor (as calculated in Eq. 1) as a function of reaction time for 15 different particles, taken at $1000 \text{ e}^-/\text{\AA}^2\text{s}$ and $500 \text{ e}^-/\text{\AA}^2\text{s}$. Growth conditions: 1 mbar C_2H_4 , 773 K

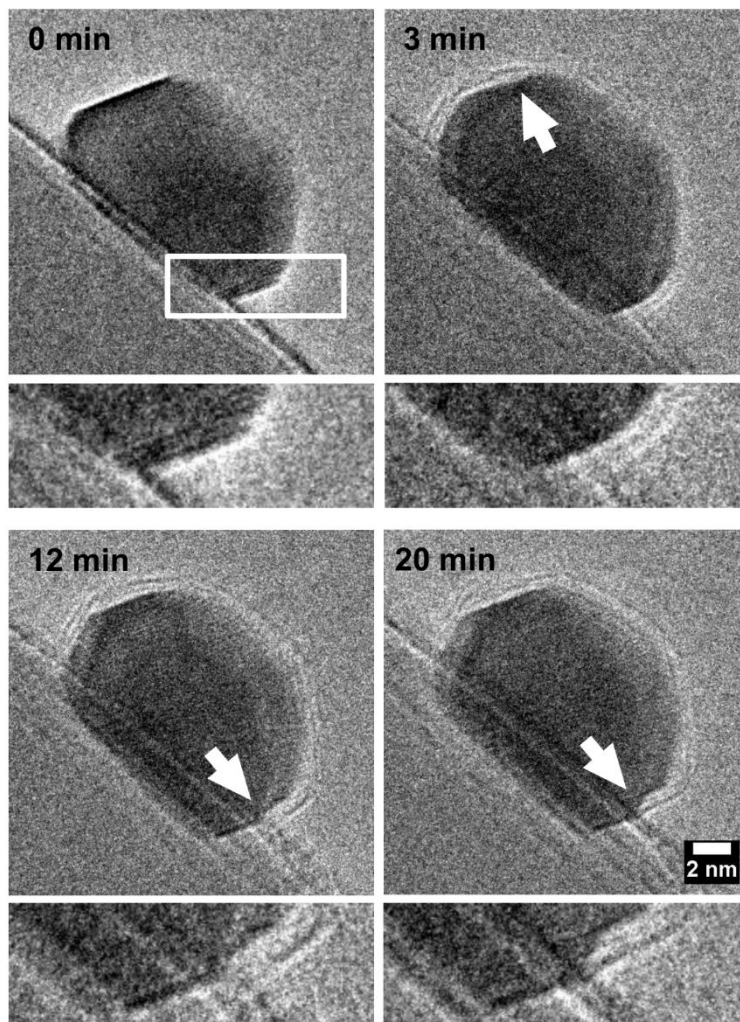


Figure 3.10. Time-lapsed *in situ* TEM images of a Pt nanoparticle over the course of 20 min under 1 mbar C₂H₄ at 873 K, taken with a dose rate of 500 e⁻/Å²s. White arrows indicate the formation of a step accompanying carbon deposition with inset of region of interest on bottom.

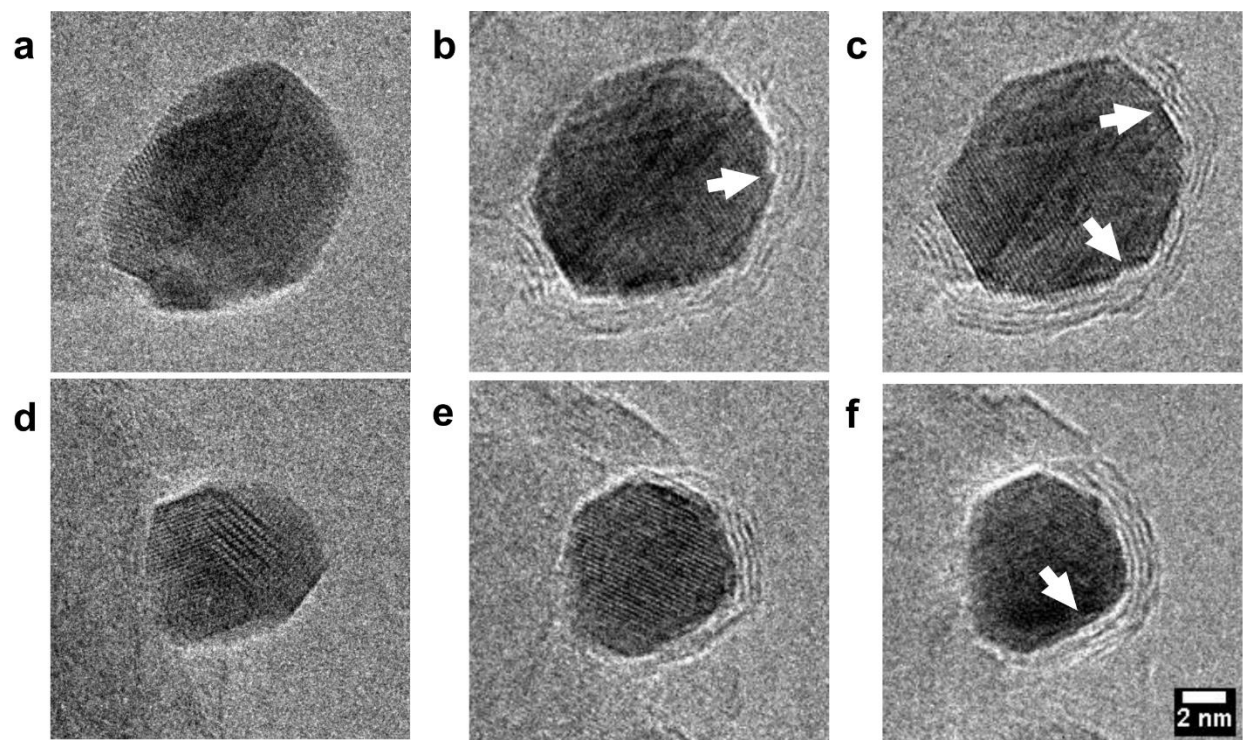


Figure 3.11. 2 time lapsed series (a – 0 min, b – 50 min, c – 68 min, and d – 0 min, e – 61 min, f – 76 min) of Pt nanoparticles during carbon growth (1 mbar C_2H_4 , 773 K), taken at a dose rate of $1000 \text{ e}^-/\text{\AA}^2\text{s}$. White arrows indicate the location of step formation as carbon layers encapsulate the nanoparticle.

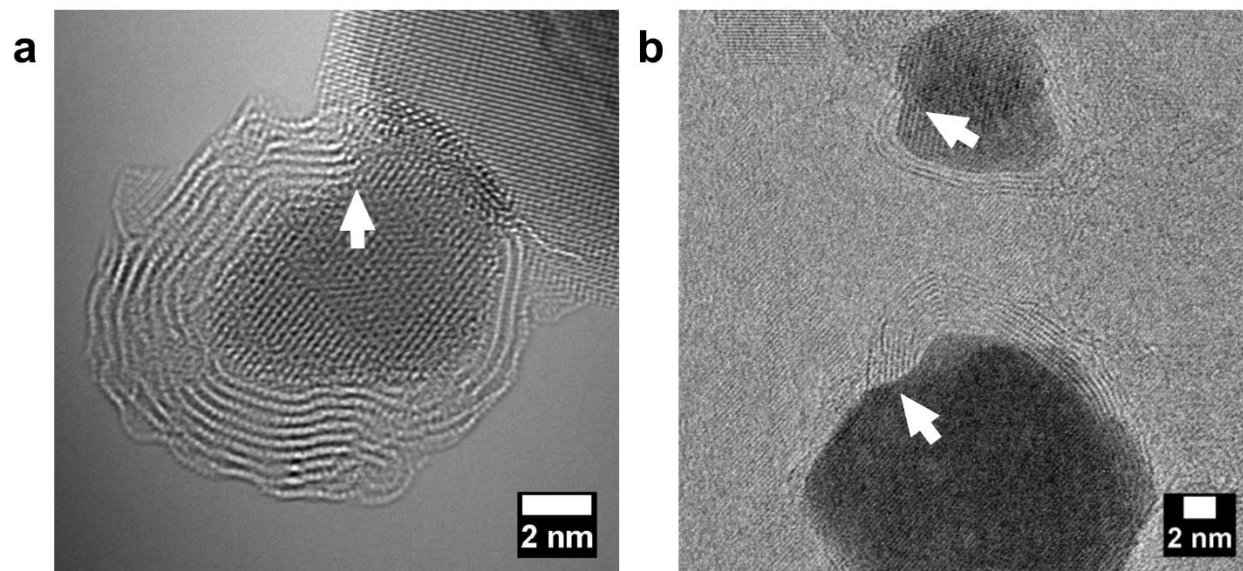


Figure 3.12. An *ex situ* TEM image of (a) Pt/MgO carburized in a reactor system under 0.2 bar ethane at 873 K for 1 h. For comparison, an *in situ* TEM image of (b) Pt/MgO carburized in the microscope under 1 mbar C₂H₄ at 773 K for 20 min, taken at 500 e⁻/Å²s.

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3.6 Supporting Information

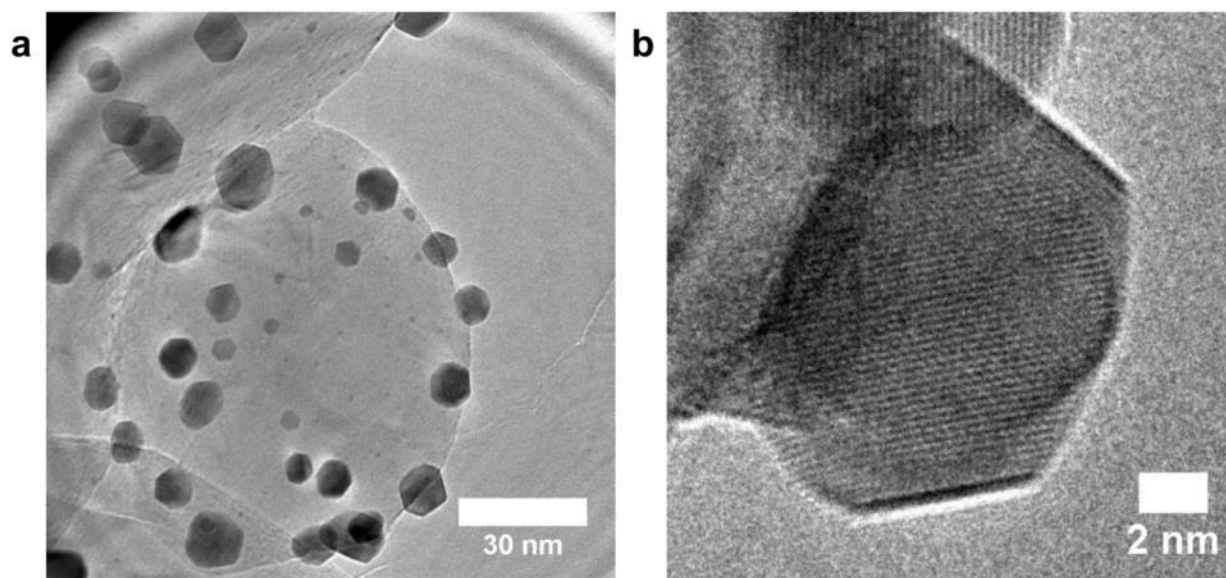
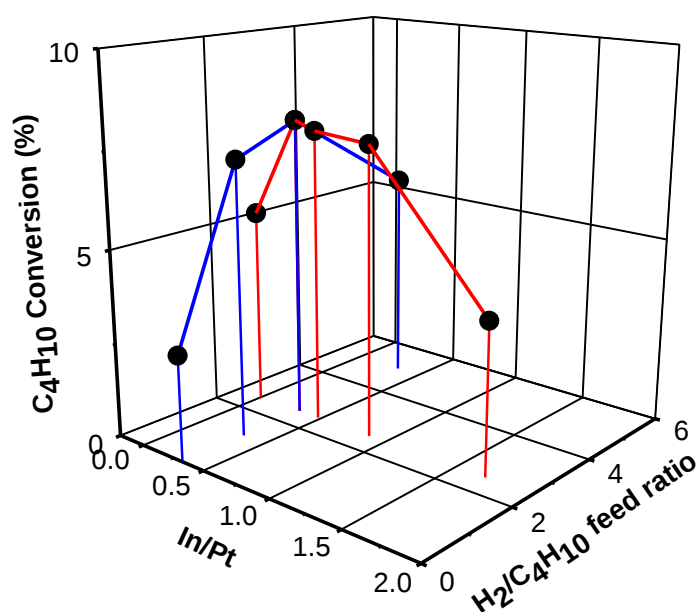


Figure 3.S.1 (a) *Ex situ* TEM of Pt/MgO and (b) *in situ* TEM of MgO supported Pt after being reduced in the microscope in 1 mbar H₂ at 773 K for 30 min.

Chapter 4

n-Butane dehydrogenation over Pt/Mg(In)(Al)O: A Parametric Study



Abstract

The catalytic dehydrogenation of butane to butene and hydrogen was investigated over Pt nanoparticles supported on calcined ex-hydrotalcite containing indium, Mg(In)(Al)O. Prior work has shown that upon reduction in H_2 at temperatures above 673 K, bimetallic Pt-In particles are formed, as evidenced by X-ray Absorption Near Edge Structure (XANES) and Extended X-Ray Absorption Fine Structure (EXAFS). The performance of Pt/Mg(In)(Al)O for butane dehydrogenation was found to be highly dependent on the bulk In/Pt ratio. The optimal ratio was found to be between 0.33 and 0.88, yielding > 95% selectivity to butenes. Hydrogen co-fed with butane was shown to suppress coke formation and catalyst deactivation, a ratio of $H_2/C_4H_{10} = 2.5$ providing the maximum catalytic performance. Regeneration of catalysts after removal of accumulated carbon and reduction in H_2 restored the original catalyst activity and selectivity. Butane dehydrogenation above 803 K resulted in higher formation of butadiene, a known precursor to coke. No evidence for butane cracking was found to occur on Pt/Mg(In)(Al)O due to moderately basic nature of the support.

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4.1. Introduction

Light alkenes are currently produced by steam cracking of alkanes or naphtha at high temperatures. However, these processes exhibit low alkene selectivity and produce significant amounts of methane and coke. Catalytic dehydrogenation of C_2 - C_5 alkanes offers an attractive alternative because it utilizes low-cost reactants and can be carried out with high selectivity [1, 2]. Since the dehydrogenation of alkanes is endothermic, high temperatures are required to achieve reasonable conversions. The heat required for alkane dehydrogenation can be supplied externally through the combustion of methane or, alternatively, through the combustion of a portion of the hydrogen generated by alkane dehydrogenation [3].

Platinum is known to be the most effective transition metal for dehydrogenation of light alkanes. However, in the absence of a promoting element, platinum catalysts exhibit low alkene selectivity and deactivate rapidly due to coke formation. Addition of a modifying element, such as Sn, Zn, Ge, Ga, or In, to form a bimetallic alloy with Pt [4-12], increases the alkene selectivity and decreases the formation of coke [13-17]. Studies of Pt bimetallic alloys suggest that the promoting element enhances the dissociative adsorption of the reacting alkane and reduces the adsorption of the product alkene, the process that initiates coke formation [18-21]. The support composition can also affect the sintering of the supported metal and the formation of coke. Studies have shown that metal oxide supports free of acid sites, such as K-L zeolite, spinels, alkali-doped alumina, and calcined hydrotalcite, reduce coke formation [13, 22-28]. $Mg(Al)O$, or calcined hydrotalcite-like material, is particularly attractive because it is moderately basic and thermally stable. The Al cations in the support help to maintain the dispersion of Pt [29].

As discussed in Chapter 1 and 2, the modifying element studied most extensively is Sn [17, 30-37]. Supported Pt-Sn catalysts are commonly synthesized by coimpregnation of Pt and Sn precursors into a metal oxide support. Properties of the PtSn catalyst depend heavily on composition of precursors and synthesis procedure [17]. Pt-In catalysts, however, have been found to have narrower particle size distributions and more uniform composition than Pt-Sn catalysts [38, 39]. Sun et al. have recently shown a novel approach for producing Pt-Ga and Pt-In bimetallic nanoparticles supported on calcined hydrotalcite containing Ga or In [40, 41]. These catalysts exhibit high activity and selectivity for ethane and propane dehydrogenation. Characterization of these catalysts by XANES and EXAFS has shown that during H_2 reduction at 873 K, a part of the Ga^{3+} or In^{3+} cations at the surface of the support is reduced and the resulting zero-valent Ga or In forms Pt-Ga or Pt-In bimetallic particles [40, 41, Supporting Information 4.5]. Additional details can be found in the supporting information.

While butenes are valuable products, the production of butenes by butane dehydrogenation has not been studied as extensively and systematically as the production of C_2 or C_3 alkenes by dehydrogenation of the corresponding alkanes. Table 2.1 lists previous studies of n-butane dehydrogenation over Pt-containing bimetallic catalysts under various reaction conditions. It is notable that some of the previous studies [42, 43] were carried out under conditions close to thermodynamic equilibrium. Consequently, it is not possible to gauge the intrinsic activity of the catalysts reported or the effects of time on stream on catalyst activity. Here, we report the performance of Pt/Mg(In)(Al)O catalyst for the dehydrogenation of n-butane. Reaction conditions were chosen such that the catalyst operated away from thermodynamic equilibrium, enabling us to investigate the effects of In/Pt ratio on the intrinsic activity, butene selectivity, stability, and coking of Pt/Mg(In)(Al)O.

4.2. Experimental

4.2.1 Catalyst Preparation

The support, Mg(In)(Al)O, was prepared by the following procedure. 58.31g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, 98-102%), appropriate amounts (depending on the desired In/Al ratio) of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Alfa Aesar, 98-102 %) and $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (Alfa Aesar, 99.9%), were dissolved in 250 mL of deionized water. A second solution containing 1.2 g of Na_2CO_3 (EMD Chemicals Inc, 99.5%) and 11g of NaOH (Fisher Scientific, 98.3%) was prepared in 250 ml deionized water. The two solutions were mixed drop-wise with stirring held at 333 K for 20 min, and aged at room temperature for 18 h. The resulting suspension was filtered, and the solid product dried in air overnight at 383 K. This product was then heated in air to 973 K at 2 K/min and maintained at this temperature for 10 h to obtain the calcined ex-hydrotalcite support, Mg(In)(Al)O.

Pt was dispersed onto 1 g of Mg(In)(Al)O by incipient wetness impregnation, using a solution containing 21 mg of Pt(acetylacetonate)₂ (Sigma Aldrich, 99.99%) dissolved in 1.5 mL toluene. The mixture was then left at room temperature in air for 2 h, and dried overnight at 383 K in an oven. After drying, the catalyst was reduced at 723 K for 2 h in 10% H_2/Ar (60 cm³/min). The content of Pt, Mg, Al and In was determined by Galbraith Laboratories (Knoxville, TN) using inductively coupled plasma optical emission spectroscopy by dissolving samples in hydrofluoric acid.

4.2.2 Catalyst Testing

Reactions were carried out in a quartz reactor with an inner diameter of 7 mm. Prior to testing, the catalyst (0.005 g, 0.25-0.5 mm particle size, diluted with quartz particles of the same particle size in a 1:4 ratio) was heated at 10 K/min to 873 K in 20% H_2 (UHP Praxair) in He (100 cm³/min) and then maintained at this temperature for 1 h. The catalyst bed was heated by a three-zone furnace (Applied Test System, Inc.) controlled by Watlow 998 controllers. The temperature of the catalyst bed was measured by two thermocouples centered axially inside the reactor, one at the top and one at the bottom of the catalyst bed. Brooks mass flow controllers were used to deliver each gas. All experiments were performed in the kinetic regime, confirmed by varying the flow rate at constant residence time. The absence of intra-particle- mass transport effects was evidenced by a linear Arrhenius plot and was further confirmed using the Weisz-Prater criterion.

Catalysts were regenerated by oxidization in a flow of 5 vol.% O_2 (99.999% Praxair) in He (100 cm³/min) for 15 min followed by reduction in a flow of 20 vol.% H_2 (UHP Praxair) in He (100 cm³/min). Prior the changing gas composition, the reactor was flushed with helium. The amount of coke deposited during 2 h of butane dehydrogenation was determined in the following manner. Upon termination of an experiment, the catalyst was purged in flowing He (60 cm³/min) at 273 K for 30 min, after which it was exposed to a mixture of 5% O_2 in He flowing at 60 cm³/min. The CO_2 generated was monitored by online mass spectrometry and the amount of coke deposited on catalyst was calculated from the amount of generated CO_2 .

Reactants and products were analyzed online using a gas chromatograph-mass spectrometer (Varian, Inc., Model 320) equipped with a 14-port sampling valve and three sample loops. One sample loop was injected into an Alumina PLOT column for flame ionization detection of eluted products. The second sample loop was injected into a second Alumina PLOT column

and analyzed by mass spectrometry. The third sample loop was injected into a Haysep N column connected in series with a Mol Sieve 5A packed column, and eluted products were detected by thermal conductivity.

4.3. Results and Discussion

4.3.1 Effect of Addition of In

A list of samples investigated is presented in Table 4.2. The Pt content was between 0.7 – 0.8 wt%. The Mg/(Al+In) ratio for the support was maintained at 5, and the In/Al ratio was varied from 0 to 0.083. For all of the catalysts examined, the bulk In/Pt ratio (labeled in the sample name) was between 0 and 1.7. STEM images of Pt/Mg(In)(Al)O show small metal particles about 1 nm in diameter even distributed across the support, as shown in Figure S.4.2. Furthermore, similar particle size distributions were previously observed for all catalysts with In/Pt ratio from 0 to 1.7, suggesting that the presence of In in the support does not affect the metal particle size [41].

Prior to catalyst testing, empty reactor tests were conducted with reacting gases flowing through reactor without catalyst. It was found that effluent C₁-C₃ (CH₄, C₂H₆, C₂H₄, C₃H₈, C₃H₆) products concentrations formed in the empty reactor were nearly identical to the effluent concentrations observed with a Pt-In catalyst in the reactor from 773 K to 873 K. Therefore, all C₁-C₃ products are taken to arise from the reactor and not the catalyst. This is likely due to the absence of acid sites on Mg(Al)O that would contribute to cracking side reactions. The concentration of these products never exceeded 4% of all products formed at 803 K with H₂/C₄H₁₀ = 2.5. The selectivities to butenes (1- and 2-butene) were therefore determined from Eq. (4.1) where [X] is the molar concentration of X:

$$S_{C_4H_8} (\%) = [C_4H_8]/([C_4H_8] + [C_4H_6]) \cdot 100\%, \quad (4.1)$$

The effects of In/Pt ratio on conversion and selectivity are shown in Figure 4.1. The conversion of n-butane goes through a maximum in the area between the In to Pt ratios of 0.33 and 0.88, while butene selectivity remains above 95% for In/Pt $\geq$ 0.33. The effect of In/Pt ratio observed in Figure 4.1 is similar to that observed for ethane and propane dehydrogenation at 873 K over Pt/Mg(In)(Al)O and Pt/Mg(Ga)(Al)O [40, 41]. The occurrence of a maximum in conversion with increasing In/Pt ratio suggests that for In/Pt ratios between 0.33 and 0.88, In incorporation enhances the activity of the catalyst from bimetallic alloy formation. The decrease in rate for In/Pt ratios above 0.88 is very likely due to a progressive loss in Pt atoms at the particle surface resulting from an increasing fraction of surface In atoms, rather than from varying particle size distributions across In/Pt ratios. Previous hydrogen chemisorptions experiments show that the percentage of Pt on the surface for In/Pt = 0.33, 0.48 and 0.88 are 84%, 94%, and 65% respectively [41]. However at In/Pt = 1.7, the percentage of exposed Pt sites drops to 35%, supporting the drop in butane conversion observed here. The increase in selectivity for In/Pt $\geq$ 0.33 also suggest that the presence of In contributes to the desorption of butenes to prevent the formation of butadiene.

The turnover frequency for butane dehydrogenation was determined based on measurements of H₂ chemisorption [41]. Figure 4.2 shows that the TOF for butane dehydrogenation increases by a factor of two as In/Pt increases from 0 to 1.7. This trend is in agreement with TOF measurements for ethane and propane dehydrogenation over Pt/Mg(In)(Al)O and similar to that observed for ethane dehydrogenation on bimetallic PtSn/Mg(Al)O catalyst [46].

Even though higher In/Pt ratios were not tested beyond 1.7, we surmise that the TOF will eventually decrease beyond In/Pt = 1.7 due to increasing Pt-In coordination on the surface, as was seen for ethane and propane dehydrogenation over Pt/Mg(In)(Al)O [41]. Figure 2.2 also shows that the distribution of butene isomers was roughly 40% cis-2-butene, 35% 1-butene, and 25% trans-2-butene and was nearly constant across the In/Pt ratios examined.

Carbon accumulation after 2 h of reaction is also a strong function of In/Pt ratio of the catalyst, as shown in Figure 4.3. Increasing the In/Pt ratio from 0 to 0.33, causes the C/Pt ratio to decrease by 40%. Similar effects have been observed for ethane and propane dehydrogenation over Pt/Mg(In)(Al)O [41]. The suppression of coke formation by supported bimetallic catalysts, such as Pt-Sn or Pt-In, has been attributed to both geometric and electronic effects. For Pt-Sn catalysts, the presence of Sn at the surface reduces the number of adjacent Pt atoms, hence decreasing the number of Pt atoms in ensembles required to form coke precursors [47]. This same explanation has been proposed for Pt-In catalysts [41]. Since it has been shown that Sn reduces the heat of adsorption of the formed alkene [18-21], it is also reasonable to suggest that In reduces the heat of adsorption of butene, and hence, the extent of coke formation. Butadiene is a well-known precursor to coke [48], and therefore can contribute to deactivation of catalyst [49]. It is notable that while the thermodynamic driving force for graphite formation per unit of carbon is very similar for n-butene and ethene, we observe a greater extent of deactivation under identical conditions for n-butane than ethane dehydrogenation over Pt/Mg(In)(Al)O (In/Pt = 0.33). This is very likely due to the higher thermodynamic potential of butadiene to form coke.

4.3.2 Effect of Co-Feed Hydrogen

Figure 4.4 illustrates the effects of H_2/C_4H_{10} feed ratio on conversion and butene selectivity for Pt/Mg(In)(Al)O-0.33. Previous studies have shown that catalyst deactivation can be inhibited by addition of H_2 , CO_2 , H_2/O_2 , or H_2O to the feed [50-53]. Raising the ratio of H_2 to C_4H_{10} from 0.5 to 2.5 causes a significant increase in butane conversion while selectivity was nearly constant. However, increasing the ratio above 2.5 caused a decrease in conversion. A similar effect has been observed previously in studies of ethane and propane dehydrogenation on Pt/Mg(Al)O, Pt/Mg(Ga)(Al)O, and Pt/Mg(In)(Al)O [40, 41, 46]. In all the cases, the rate of alkene formation increases with increasing H_2 /alkane ratio and then decreases beyond the maximum. Siddiqi et al. have previously proposed that at low H_2 /alkane, adsorbed H atoms on the catalyst surface contribute to the removal of the second hydrogen atom of the adsorbed alkyl species, resulting in a higher rate of alkene formation [40]. Increased butene production can also be attributed to hydrogen inhibiting deactivation by coke formation, as will be discussed. However, at higher surface concentrations of hydrogen, the conversion will decrease due to lowering of the equilibrium conversion as the H_2/C_4H_{10} feed ratio increases.

The amount of carbon accumulated in 2 h of reaction over Pt/Mg(In)(Al)O-0.33 is shown in Figure 4.5, as a function of H_2/C_4H_{10} feed ratio. Without hydrogen in the feed ($H_2/C_4H_{10} = 0$), the accumulated carbon is very high. After 2 h of time on stream, the absence of hydrogen in the feed produces almost four times more coke than when $H_2/C_4H_{10} = 2.5$. This trend has been observed previously with PtSn/Mg(Al)O for ethane dehydrogenation [47]. In the presence of hydrogen, the formation of coke precursors, such as butadiene, is suppressed by inhibiting further dehydrogenation of butenes. In addition, it has been shown by TEM for Pt/MgO nanoparticles that graphene layers form rapidly in the first 10 min under ethane dehydrogenation, but reach a plateau afterward [54]. We observe a qualitatively similar behavior during n-butane dehydrogenation in

that the C/Pt ratio increases rapidly during the first 30 min but then levels off. It is also evident that since the C/Pt ratio is much greater than unity, the majority of the accumulated coke migrates to the support and only a small fraction remain on the surface of the metal particles, allowing access to the surface of the Pt-In nanoparticles.

4.3.3 Catalyst Regeneration

Figure 4.6 shows conversion and selectivity for three cycles of butane dehydrogenation over Pt/Mg(In)(Al)O-0.33. After removal of accumulated carbon and H₂ reduction at 873 K, the original conversion and selectivity for butane dehydrogenation is restored close to those seen in the original cycle. The loss of dehydrogenation activity is minimal between cycles, as also seen for ethane and propane dehydrogenation over Pt/Mg(In)(Al)O [41]. Furthermore, deactivation over time on stream is attributed to coke formation rather than sintering. STEM images of reacted Pt/Mg(In)(Al)O show similar particle size distributions after 2 h of ethane and propane dehydrogenation at 873 K [41]. Therefore, we reasonably conclude that sintering is also minimal for butane dehydrogenation, particularly since butane dehydrogenation was carried out at 803 K, instead of 873 K. During each cycle, the selectivity to butenes is above 95% after 2 h of time on stream.

4.3.4 Effects of Residence Time and Temperature

The effects of residence time on the conversion of Pt/Mg(In)(Al)O are shown in Figure 4.7. At high residence times, the conversion plateaus near 30%, close to that corresponding to equilibrium conversion for the reaction conditions used. All of the data presented in Figs. 1-5 were all performed at 3.75×10^{-3} g s /cm³, for which the conversion is 13%. At this residence time, the intrinsic rate of n-butane consumption is 206 $\mu\text{mol/g}\cdot\text{s}$ and the turnover frequency for n-butane dehydrogenation is 5.53 s^{-1} , based on H₂ uptake measurements made on Pt/Mg(In)(Al)O (In/Pt = 0.33) [41] to determine the concentration of surface Pt sites. Notably, the selectivity to butenes is constant with residence time.

The effect of temperature on butane conversion and butene selectivity are shown in Figure 4.8. While overall conversion increases with increasing temperature, the selectivity to butenes decreases from 97% at 773 K to 85% at 873 K, the remaining products being butadiene. As noted previously, butadiene is a known precursor to coke, so therefore operation at 873 K leads to significant coke formation and deactivation.

The apparent first-order rate coefficient for butane dehydrogenation, k_f , was determined from the measured rate of reaction corrected for the approach to equilibrium. Figure 4.9 shows an Arrhenius plot for k_f . The apparent activation energy determined from this plot is 129.4 kJ/mol, which is similar to the value of 117.2 kJ/mol reported for butane dehydrogenation over PtSn/ γ -Al₂O₃ [55].

4.4. Conclusions

Catalysts for the dehydrogenation of n-butane were prepared by dispersing Pt nanoparticles onto a calcined hydrotalcite-like support containing In, Mg(In)(Al)O. Upon reduction at temperatures above 723 K, we have shown previously (Supporting Information 4.5) that a part of the In³⁺ cations present near the support surface and adjacent to Pt are reduced and the resulting In

atoms form a Pt-In bimetallic alloy with the supported Pt nanoparticles. Performance of Pt/Mg(In)(Al)O for butane dehydrogenation was a strong function of the bulk In/Pt ratio. Between In/Pt = 0.33 and 0.88, the catalyst activity for butane dehydrogenation reached a maximum and the butene selectivity reaches ~ 95%, with primary products being cis-2-butene and 1-butene. Alloying In with Pt also caused a significant decrease in the accumulation of C during butane dehydrogenation, compared to pure Pt catalyst. We attribute these trends to the geometric and electronic effects from the presence of In, as previously proposed for PtM alloys (M = In, Sn, Ga, Zn, Ge) [4-12, 40, 41, 47]. Addition of hydrogen to the feed also inhibited catalyst deactivation and reduced carbon accumulation, as seen for both ethane and propane dehydrogenation over Pt/Mg(In)(Al)O [41]. Catalyst regeneration by removal of accumulated carbon and subsequent H₂ reduction at 873 K restored the original activity and selectivity. The temperature chosen for butane dehydrogenation was 803 K, above which butadiene formation became increasingly important, resulting in a strong increase in catalyst deactivation due to coking.

4.5. Acknowledgements

This work was supported by Chevron Energy Technology Company. The author thanks Pingping Sun et al. for synthesis and characterization of the catalyst.

Table 4.1. N-butane dehydrogenation by Pt-containing bimetallic catalysts. Comparison between conversion at t = 10 min, 2 h and total initial selectivity to all butenes, including butadiene.

<i>Second Metal</i>	<i>Support</i>	<i>Pt wt%</i>	<i>Size (nm)</i>	<i>T (K)</i>	<i>W/F (g s / cm³)</i>	<i>%C₄H₁₀ Feed</i>	<i>H₂/C₄H₁₀</i>	<i>Initial Rate (μmol/g·s)</i>	<i>X at t = 10 min</i>	<i>X at t = 2 h</i>	<i>S_{Butenes}</i>	<i>Estimated Equil. Conv.</i>	<i>Ref.</i>
Sn	MgAl ₂ O ₄	0.3	1-3	803	0.67	44.4	1.25	9.5	32	28	97	22.9	42
Pb	MgAl ₂ O ₄	0.3	1-3	803	0.67	44.4	1.25	3.9	13	11.3	92	22.9	42
Sn	γ - Al ₂ O ₃	0.3	-	803	0.67	44.4	1.25	8.9	30	28	94.4	22.9	43
Ge	γ - Al ₂ O ₃	0.3	-	803	0.67	44.4	1.25	8.0	27	18	90.4	22.9	43
Sn	SAPO-34	0.5	1.4-2.5	858	2.5	80	0.25	5.1	36.1	13.2	44	58.6	44
Sn	CMgO	1	2.8	773	0.2	33.3	1	74.4	17.9	15	95.7	21.5	45
In	Mg(Al)(In)O	0.89	1	803	0.00375	13.3	2.5	206	13	7.5	98	35.4	-
In/Sn	MgAl ₂ O ₄	0.3	-	803	0.67	44.4	1.25	8.9	30	29	95	22.9	22

Table 4.2. Catalyst Composition. (*) as determined by ICP-OES.

<i>Sample Name</i>	<i>Pt wt %</i>	<i>In wt %</i>	<i>Starting ratio Mg:Al:In</i>	<i>Mg/(Al+In)*</i>	<i>In/Al*</i>	<i>In/Pt*</i>
Pt/Mg(Al)O	0.70	0	100:10:0	5.09	0	--
Pt/Mg(Al)(In)O-0.33	0.89	0.171	100: 9.95:0.05	5.13	0.0047	0.33
Pt/Mg(Al)(In)O-0.48	0.71	0.201	100: 9.9: 0.10	4.82	0.0065	0.48
Pt/Mg(Al)(In)O-0.88	0.83	0.428	100: 9.86: 0.14	4.90	0.010	0.88
Pt/Mg(Al)(In)O-1.7	0.67	0.674	100: 9.75: 0.25	4.60	0.021	1.7

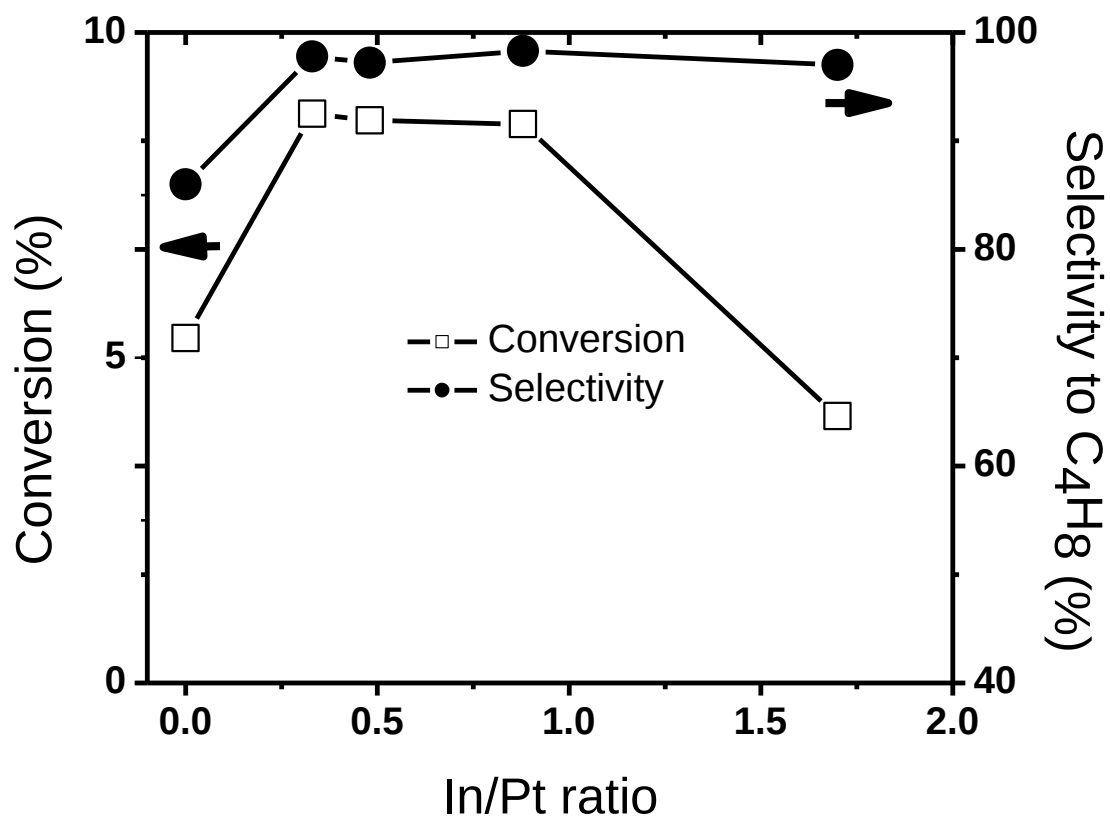


Figure 4.1. Effect of In/Pt ratio on butane conversion and butene selectivity after 25 min of time on stream. Reaction conditions: $T = 803\text{ K}$, catalyst mass = 5 mg, C_4H_{10} : 13%, total flow rate: $80\text{ cm}^3/\text{min}$, $\text{H}_2/\text{C}_4\text{H}_{10} = 2.5$

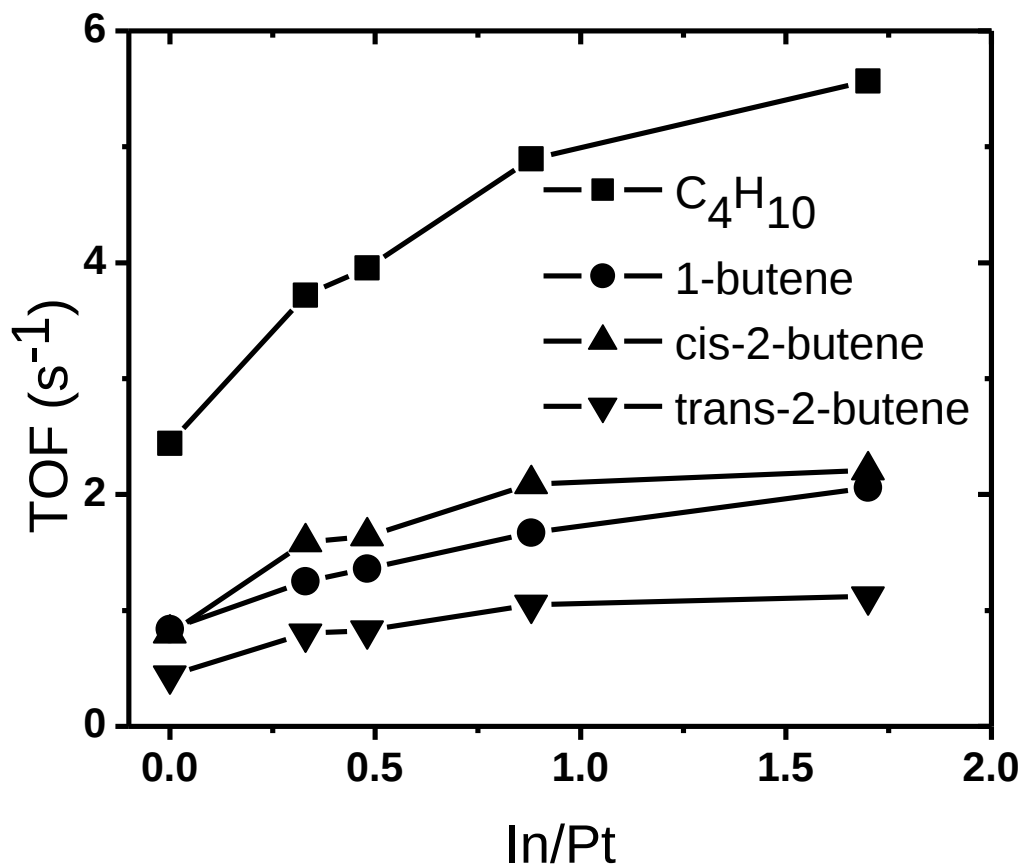


Figure 4.2. Effect of In/Pt ratio on butane and butene TOF's after 25 min of time on stream. Reaction conditions: $T = 803 \text{ K}$, catalyst mass = 5 mg, C_4H_{10} : 13%, total flow rate: $80 \text{ cm}^3/\text{min}$, $\text{H}_2/\text{C}_4\text{H}_{10} = 2.5$

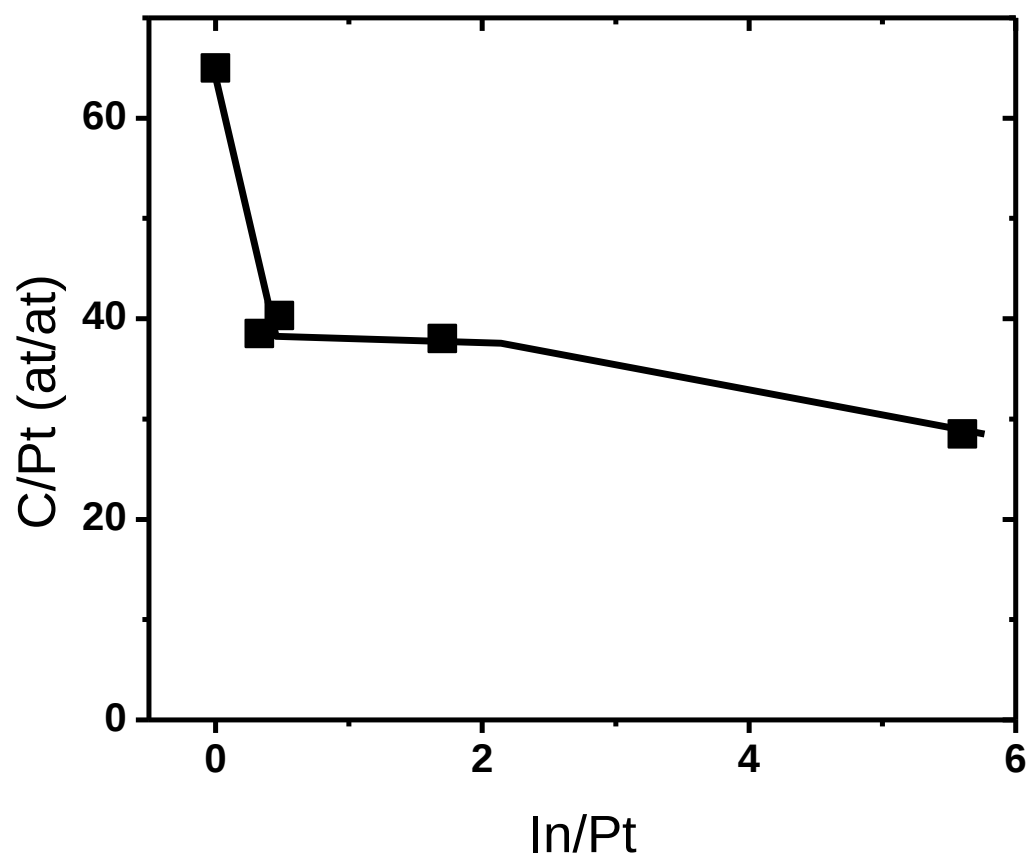


Figure 4.3. Dependence of C/Pt ratio on bulk In/Pt ratio measured for 2 h time on stream for butane dehydrogenation on Pt/Mg(In)(Al)O. Reaction conditions: $T = 803\text{K}$, catalyst mass = 5 mg, C_4H_{10} : 13%, total flow rate: $80\text{ cm}^3/\text{min}$, $\text{H}_2/\text{C}_4\text{H}_{10} = 2.5$

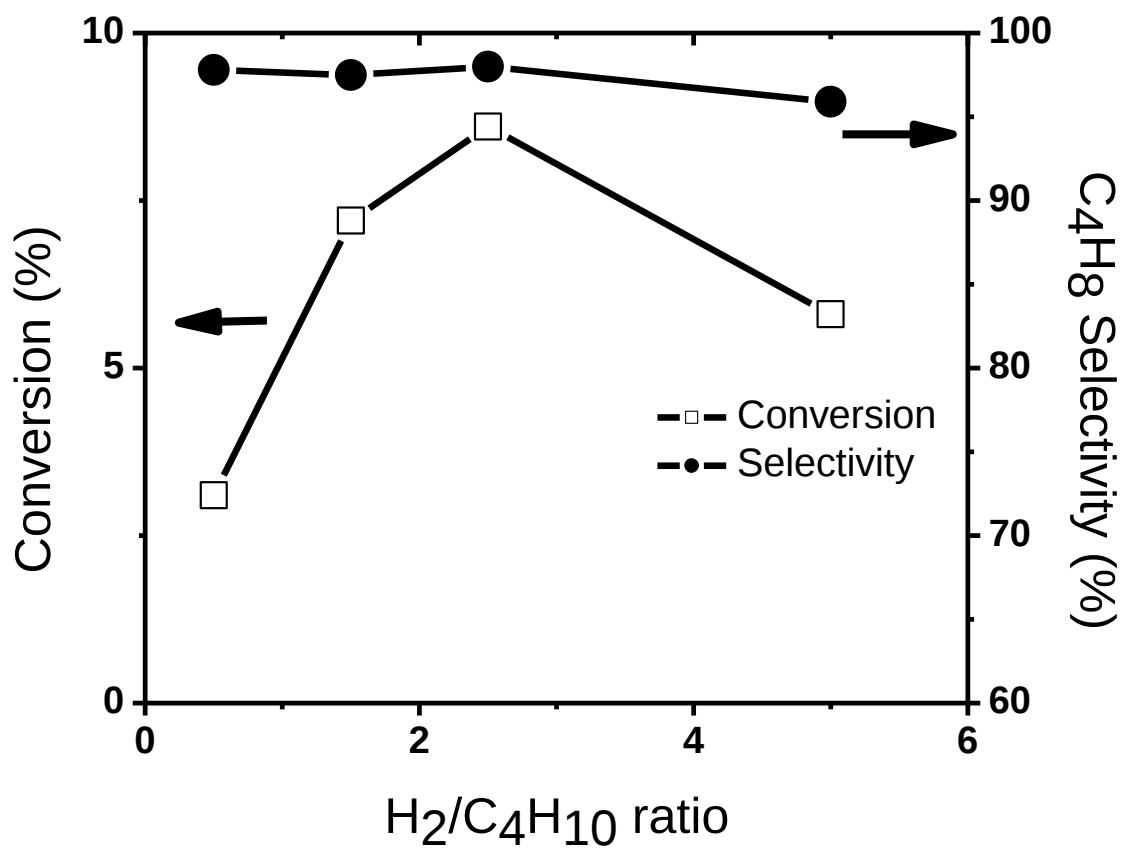


Figure 4.4. Effect of hydrogen to n-butane feed ratio on butane over Pt/Mg(In)(Al)O (In/Pt = 0.33) measured after 25 min of time on stream. Total flow kept constant at 80 cm³/min by adding a balance of He, T = 803 K, catalyst mass = 5 mg, C₄H₁₀: 13%.

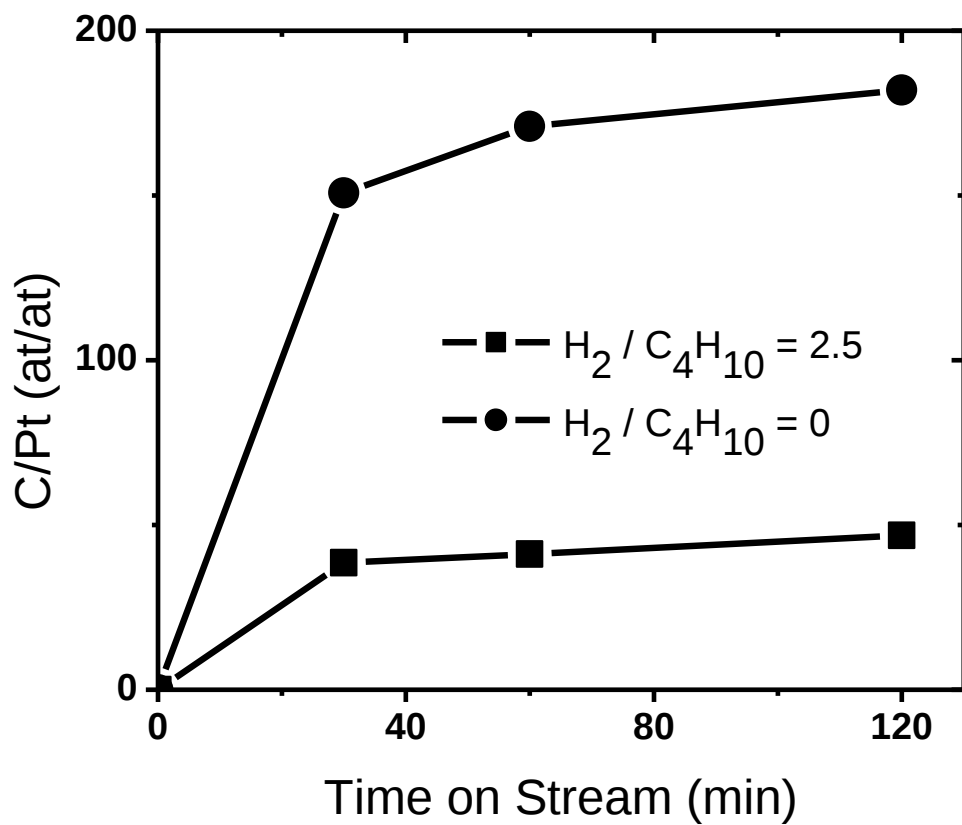


Figure 4.5. Amount of coke accumulation with time on stream during butane dehydrogenation on Pt/Mg(In)(Al)O (In/Pt = 0.33) for hydrogen to n-butane feed ratios of 0 and 2.5. Reaction conditions: T = 803K, catalyst mass = 5 mg, C₄H₁₀: 13%, total flow rate: 80 cm³/min

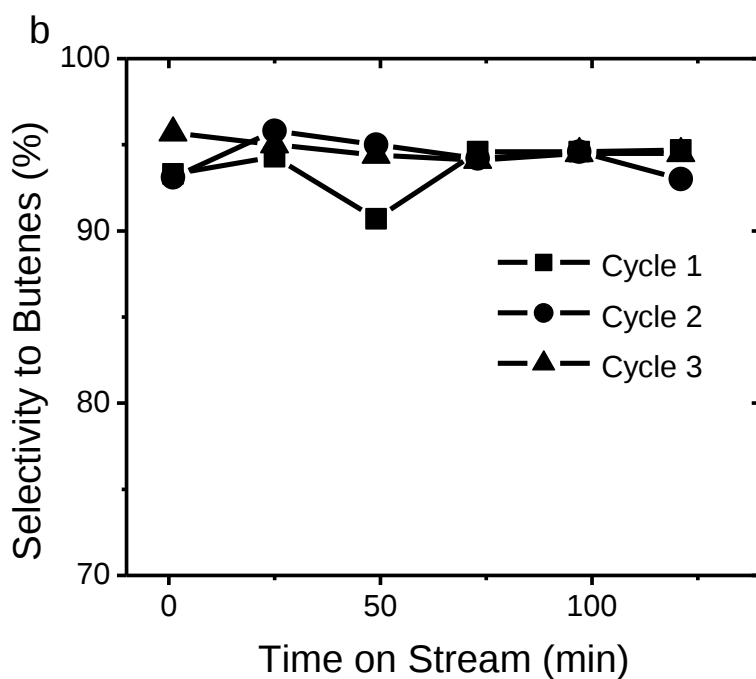
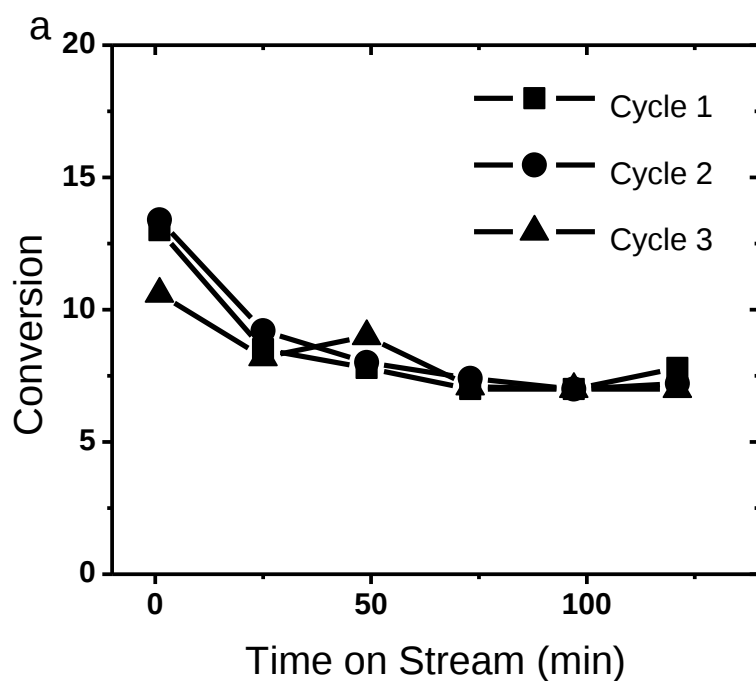


Figure 4.6. Effects of catalyst recycling on (a) butane conversion and (b) butene selectivity for butane dehydrogenation over Pt/Mg(In)(Al)O (In/Pt = 0.33). Each cycle consists of reduction-reaction-oxidation steps. Reaction conditions: $T = 803\text{ K}$, catalyst mass = 5 mg, C_4H_{10} : 13%, $\text{H}_2/\text{C}_4\text{H}_{10} = 2.5$, total flow rate: $80\text{ cm}^3/\text{min}$

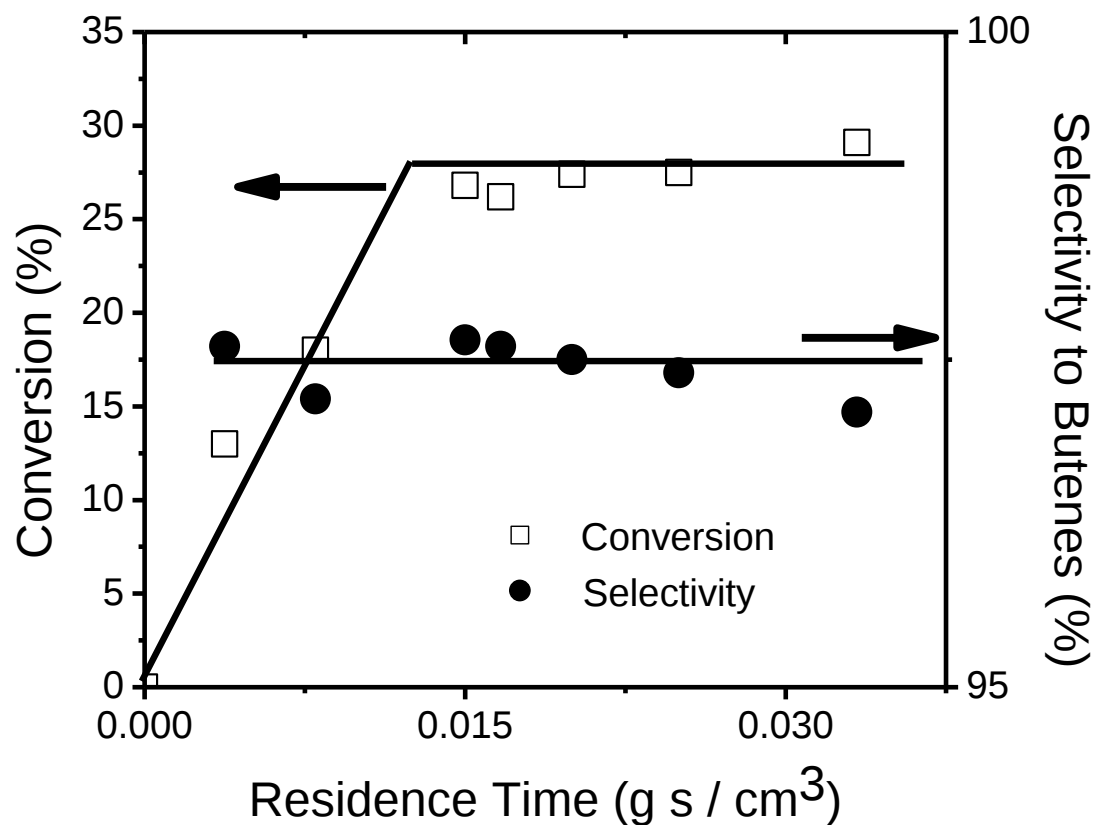


Figure 4.7. Effects of residence time (W/F) on n-butane conversion and butene selectivity during butane dehydrogenation over Pt/Mg(In)(Al)O (In/Pt = 0.33) measured after 1 min of time on stream. Reaction conditions: T = 803 K, C₄H₁₀: 13%, H₂/C₄H₁₀ = 2.5

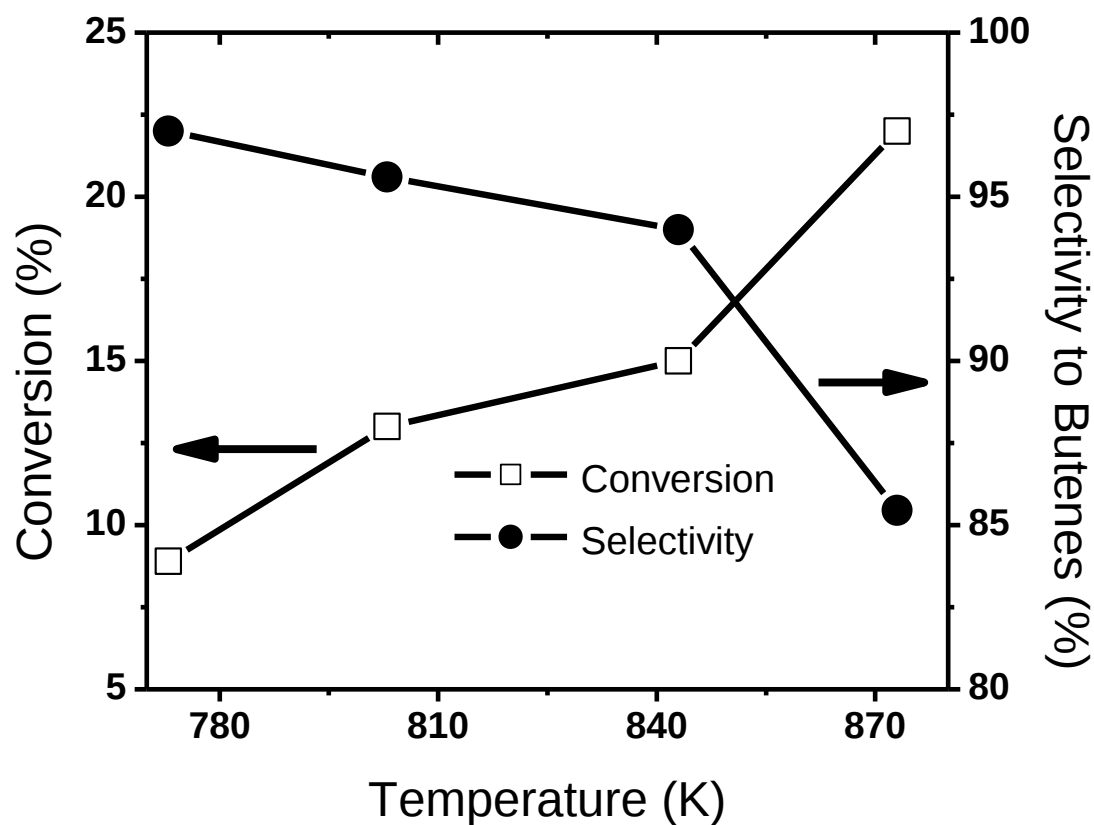


Figure 4.8. Effects of temperature on butane conversion and selectivity to butenes for butane dehydrogenation over for Pt/Mg(In)(Al)O (In/Pt = 0.33) measured after 1 min of time on stream. Reaction conditions: catalyst mass = 5 mg, C₄H₁₀: 13%, total flow rate: 80 cm³/min, H₂/C₄H₁₀ = 2.5

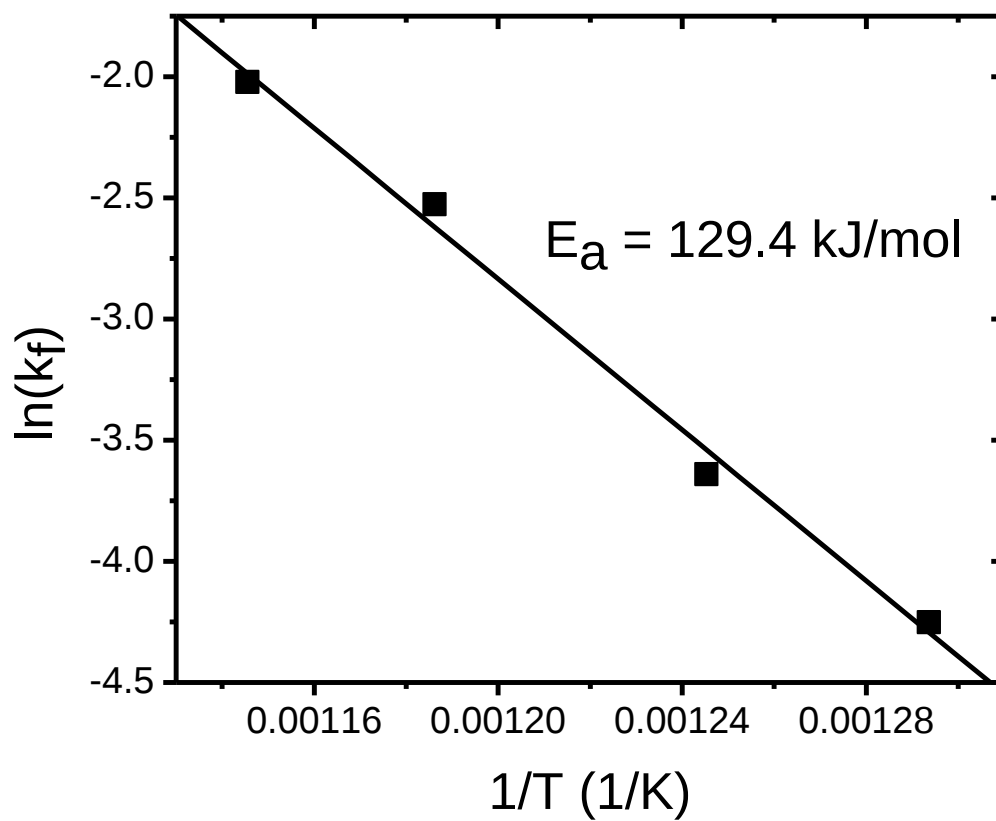


Figure 4.9. Plot of $\ln(k_f)$ versus $(1/T)$ determined from conversions and selectivities shown in Figure 2.7. Reaction conditions: catalyst mass = 5 mg, C_4H_{10} : 13%, total flow rate= 80 cm^3/min , H_2/C_4H_{10} = 2.5

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4.6. Supporting Information

4.5.1. Catalyst Characterization Methods for Pt/Mg(Al)(In)O

The BET surface area of Pt/Mg(Al)(In)O was determined by the multi-point method using an Autosorb-1 instrument (Quantachrome Corporation). Prior to measuring the adsorption isotherm, each sample was degassed at 573K for 22-24 h. The hydrotalcite-like material was characterized by X-ray powder diffraction before and after calcination, using a Siemens Diffractometer D 5000 with CuK α radiation ($\lambda = 1.5418\text{\AA}$) at 20 kV and 5 mA. The samples were scanned from 2θ values of 5° to 70° with a step size of 0.02° and a dwell time of 1.0 s. The dispersion of Pt on Pt/Mg(Al)(In)O was determined by H₂ chemisorption using a AutoChem II 2920 (Micromeritics Instrument Corporation). About 60 mg of Pt/Mg(In)(Al)O was loaded into a quartz cell and then reduced in flowing 10% H₂/Ar (50 cm³/min). The temperature of the sample was raised at 5 K/min to 873K and then maintained at this level for 2 h. The sample was then flushed in flowing Ar for 90 min and then cooled down to 313K. The uptake of chemisorbed hydrogen was then measured by determining the uptake of H₂ from pulses using a TCD detector. The pulse size was 50 cm³/g and the time between pulses was 10 min.

Electron micrographs of the support, with and without Pt, were taken using an aberration-corrected FEI Titan 80/300-kV TEM/STEM located at Oak Ridge National Laboratory. Bright-field and high angle annular dark-field (HAADF) STEM images were recorded simultaneously to get full information of the microstructure. HAADF images were acquired with a 300 kV accelerating voltage with a convergence angle of 30 mrad and a large inner collection angle of 75 mrad. The contrast of the acquired HAADF images is sensitive to atomic number. To minimize electron beam radiation on the sample, all images were acquired in regions that had not been previously illuminated, shortly after the electron beam had been aligned in a neighboring region. Electron energy loss spectra were acquired for 3 s with a convergence angle of 30 mrad and collection angle of 35 mrad. The data were processed through Digital Micrograph.

Pt L_{III}- and In K-edge XAS data were collected at the Advanced Photon Source at Argonne National Lab on beamline 10-BM with a Si(111) monochromator crystal detuned by 40%. The sample was located between two ionization chambers and a reference foil was placed after the second ionization chamber for energy calibration. Nitrogen and argon gas was used in the ionization chambers for Pt L_{III}- and In K-edges, respectively, and all samples were investigated in transmission mode. All six samples with In/Pt ratios (In/Pt = 0, 0.33, 0.48, 0.88, 1.7, 5.6) were prepared simultaneously under three different pretreatment conditions: 723 K for 1 h in 4% H₂/He at 100 cm³/min, 873 K for 1 h in 4% H₂/He at 100 cm³/min, and 873 K for 1 h in 10% O₂/N₂ after pretreatment at 873 K in hydrogen. All samples were cooled to ambient temperature in He flowing at 100 cm³/min.

Data was analyzed using Ifeffit and the GUIs Athena and Artemis. The incident photon energy was calibrated to a reference Pt foil. The edge energy was set to the first inflection point on the rising part of the absorbance edge. Data were normalized using a pre-edge line fit from -150 to -50 eV below the edge and a quadratic polynomial with a k-weight of two from 150 to 749

eV above the edge energy. A spline was fit to the data $0 < k < 15 \text{ \AA}^{-1}$ after the edge. The data for $3.5 < k < 12.1 \text{ \AA}^{-1}$ was fit from 1.8 to 3.2 $\text{\AA}$ for catalysts treated in hydrogen at 873 K and from 1.4 to 3.2 $\text{\AA}$ for the other two pretreatments using k-weights of 1, 2, and 3. For all pretreatments, the initial Pt and In paths were taken to be 2.8 $\text{\AA}$. The same mean square disorder, σ^2 , and edge energy were used for both paths, but the path lengths were allowed to vary independently. For the samples pretreated in hydrogen at 723 K, a third oxygen path was added at a distance of 2 $\text{\AA}$, and the bond length and coordination number were allowed to vary separately. The same structural disorder parameter and edge energy for the Pt and In paths was used in the oxygen path. Theoretical standards were constructed using known crystal structures of PtIn alloys [1], as well as Pt oxides [1].

4.5.2. Catalyst Characterization Results for Pt/Mg(Al)(In)O

Figure S.4.1 shows the XRD pattern of the dried, as-synthesized support (top) and the same material after calcination (bottom). Prior to calcination the XRD pattern is characteristic of the layered double hydroxide structure of hydrotalcite [2]. After calcination at 973 K the structure of the solid changes from orthorhombic to cubic, corresponding to the transformation of a two-dimensional layered structure to a three-dimensional structure, analogous to periclase MgO. The broad peaks of both materials are indicative of small crystalline particles or a partially amorphous phase. Similar changes in the XRD patterns were observed for all support materials, independent of the In/Al ratio.

Table S.4.1 lists the surface areas of the calcined mixed oxide materials. Mg(Al)O has a surface area of 176 m²/g and a pore volume of 0.6 cc/g. Neither the surface area nor pore volume of Mg(In)(Al)O changed very much upon increasing the In content from 0-5.1 wt%. Minimal change in the surface area and pore volume occurred upon the dispersion of Pt onto the support. The ratio of H atoms adsorbed to the total number of Pt atom in the catalyst is also presented in Table S.2.1. For Pt/Mg(Al)O this ratio is 0.84, which means that the dispersion of the Pt is 84%. As discussed below, the Pt particle size estimated from the dispersion, 1.3 nm, is consistent with that determined from STEM images, about 1 nm. The ratio of adsorbed H atoms to total Pt atoms measured for the Pt/Mg(Al)(In)O samples is a function of the In/Pt ratio. This ratio is 0.94 when In/Pt = 0.48 and decreases rapidly with increasing In/Pt ratio, reaching a value of 0.06 when In/Pt = 10.7. Since, as discussed below, the size of the PtIn particles remains essentially the same with increasing bulk In/Pt ratio, the observed decrease in H/Pt ratio is ascribed to increase coverage of the metal nanoparticles by In. This interpretation is consistent with previous research showing that the adsorption of H₂ on Pt alloyed with Sn and Ga is reduced by the presence of the alloying metal on the particle surface because the alloying metal does not adsorb H₂ [3, 4].

A STEM image of Pt/Mg(In)(Al)O-0.88 is shown in Figure S.4.2. After calcination, the support still exhibits a partially layered structure, similar to that seen earlier for calcined Mg(Al)O [5]. Small metallic particles about 1 nm in diameter are observed distributing evenly over the support. The similar particle size are observed for all catalysts with In/Pt ratio from 0 to 10.7. This suggests that the presence of In in the support does not change the size of the metal particles relative to that observed in the absence of In.

EXAFS spectra of Pt/Mg(Al)O and Pt/Mg(In)(Al)-0.48 reduced in H₂ at 723 K (see supplementary material) were analyzed to determine the coordination numbers for Pt-Pt, Pt-In, and Pt-O nearest neighbors. The results are presented in Table S.4.2 and Figure S.4.3 for catalysts prepared with bulk In/Pt ratio between 0 and 5.6. The data show that with increasing In/Pt ratio

the Pt-Pt coordination number decreases monotonically from 6.7 to 4.8, as the Pt-In and Pt-O coordination numbers increase from 0 to about 0.5 and 1.4. The appearance of Pt-In nearest neighbors as the bulk In/Pt ratio increases indicates that catalyst reduction at 723 K is sufficient to enable some of the In^{3+} cations present at the support surface and proximate to the Pt particles to be reduced, and resulting In atoms to form PtIn alloys with the Pt particles. This interpretation is consistent with the observation that In_2O_3 undergoes reduction in H_2 above 673 K [6]. It is notable that in the absence of In, catalyst reduction at 723 K is sufficient to remove all oxygen. However, when In is present in the support, the Pt-O coordination number rises slightly. Since the metal nanoparticles are very small (~ 1 nm), it is quite possible that the O atoms are present predominantly on the surface of the particles, rather than in the bulk.

Pt L_{III} edge XANES data acquired after catalyst reduction at 723 K is shown in Figure S.4.4. All samples show similar edge energies, but the intensity of the white line is higher for samples with In present, than for the sample without In. This might be due to the In containing samples still have O bonded to Pt, in contrast of In free samples, leading to an increase d-orbital vacancy and, hence, an increase in the white line intensity. It has generally been observed that the formation Pt alloys, such as Pt-Sn [7], Pt-Cu [8], Pt-In [9], Pt-Au [10], leads to a decrease in white line intensity of Pt L_{III} edge. The white line intensity does not show a systematic change with In/Pt bulk ratios, quite possibly because the white line intensity is affected by both In and O. There is reason to think that the oxygen effect may dominate, since the white line intensity correlates with the Pt-O coordination number.

Table S.4.3 and Figure S.4.5 show that following hydrogen reduction at 873 K, the Pt-O coordination number is zero independent of the bulk In/Pt ratio. However, as the bulk In/Pt ratio increases, the Pt-Pt coordination number decreases and the Pt-In coordination number increases. This trend indicates that the In content of the PtIn alloy particles formed upon reduction increases monotonically with increasing In/Pt ratio. Since the total coordination number (sum of $\text{CN}_{\text{Pt-Pt}}$ and $\text{CN}_{\text{Pt-In}}$) is ~ 6 for In/Pt ratios 0 to 5.6, it is concluded that the diameter of the supported alloy particles do not change significantly in increasing In content, consistent with observations by STEM.

If it is assumed that In is uniformly distributed throughout the alloy, then the fraction of In contained in the supported PtIn nanoparticles can be estimated from the relationship $\text{CN}_{\text{Pt-In}}/(\text{CN}_{\text{Pt-Pt}} + \text{CN}_{\text{Pt-In}})$ assuming isostructural, spherical particles. The atomic fraction of In in the alloy particles calculated this way is listed in Table S.2.4. It is apparent from these results that the fraction of the alloy consisting of In increases almost linearly with the bulk In/Pt ratio, in Figure S.4.6.

Tables S.4.2 and Table S.4.3 show that the Pt-Pt bond distance for Pt/Mg(Al)O reduced at both 723 K and 873 K is 2.73-2.74 Å, which is smaller than that for bulk Pt, 2.77 Å. The decrease of metallic bond distance with decreasing coordination is commonly observed [11]. This phenomenon is due to lattice relaxation of smaller particles (1-5 nm), which could result in 10% decrease in the Pt-Pt bond distance relative to that of bulk phase [12]. When In alloys with Pt, the Pt-Pt bond distance in the PtIn nanoparticles increases by no more than 0.03 Å. The calculated Pt-In bond distance exhibits more variation from sample to sample than the calculated Pt-Pt distance, but on average is 2.71 Å, which is comparable to the Pt-Pt distance.

Figure S.4.7 shows Pt L_{III} XANES spectra for Pt/Mg(In)(Al)O catalysts reduced at 873K. The intensity of the white line decreases slightly with increasing In amount but then increases at the highest In/Pt ratio. Pt L_{III} XANES characterizes dipole transitions from the $2p_{3/2}$ to the $5d_{5/2}$ orbital, since the $5d_{3/2}$ orbital is fully occupied [13, 14]. Therefore, changes in the intensity of the

white line indicate changes in the unoccupied states of the $5d_{5/2}$ orbital associated with metal oxidation and/or alloy formation. DFT calculations demonstrate that the white line density can also change with cluster size and cluster morphology because the density of states of nanometer-sized metal clusters is very different from that of the bulk phase [15, 16]. This trend is consistent with experiments showing that the white line intensity for supported metal particles decreases with decreasing metal cluster size [11, 17]. Since reduction at 873 K removes all oxygen from the supported nanoparticles and the size of the nanoparticles does not change with increasing bulk In/Pt ratio, the effects of Pt oxidation by O and changes in particle size with bulk In/Pt ratio on the intensity of the white line can be ruled out. As a result, the observed changes in the white line intensity of Pt L_{III} XANES spectra shown in Figure S.4.7 can only be attributed to the formation of a Pt-In alloy.

It is also observed that following reduction at 873 K there is an increase in the Pt L_{III} edge energy by about 1 eV with increasing bulk In/Pt ratio. This shift in edge is a further indicator of alloy formation. This trend is similar to that observed in XPS measurements when Pt is alloyed with Sn [18, 19] or In [9]. The observed increase in Pt binding energy in both cases can be attributed to charge transfer from the alloying element to Pt since the electronegativity of Pt (2.28 eV) is higher than that of Sn (1.8 eV) or In (1.7 eV). Simulation of the XANES spectrum of Pt-Au nanoparticles further supports the assignment of shifts in the white line position to charge transfer occurring between the alloying elements [10].

Table S.4.1. Catalyst surface area (BET), pore volume, average pore radius and fraction of exposed Pt sites.

<i>Sample Name</i>	<i>Exposed Pt sites (%)</i>	<i>Surface area (m²/g)</i>	<i>Pore Volume (cc/g)</i>	<i>Average Radius (Å)</i>
Pt/Mg(Al)O	84	176	0.60	70.0
Pt/Mg(Al)(In)O-0.33	84	148	0.55	73.7
Pt/Mg(Al)(In)O-0.48	94	161	0.61	75.9
Pt/Mg(Al)(In)O-0.88	65	167	0.75	89.8
Pt/Mg(Al)(In)O-1.7	35	191	0.58	60.3
Pt/Mg(Al)(In)O-5.6	12	158	0.49	62.1
Pt/Mg(Al)(In)O-10.7	6	161	0.61	75.9

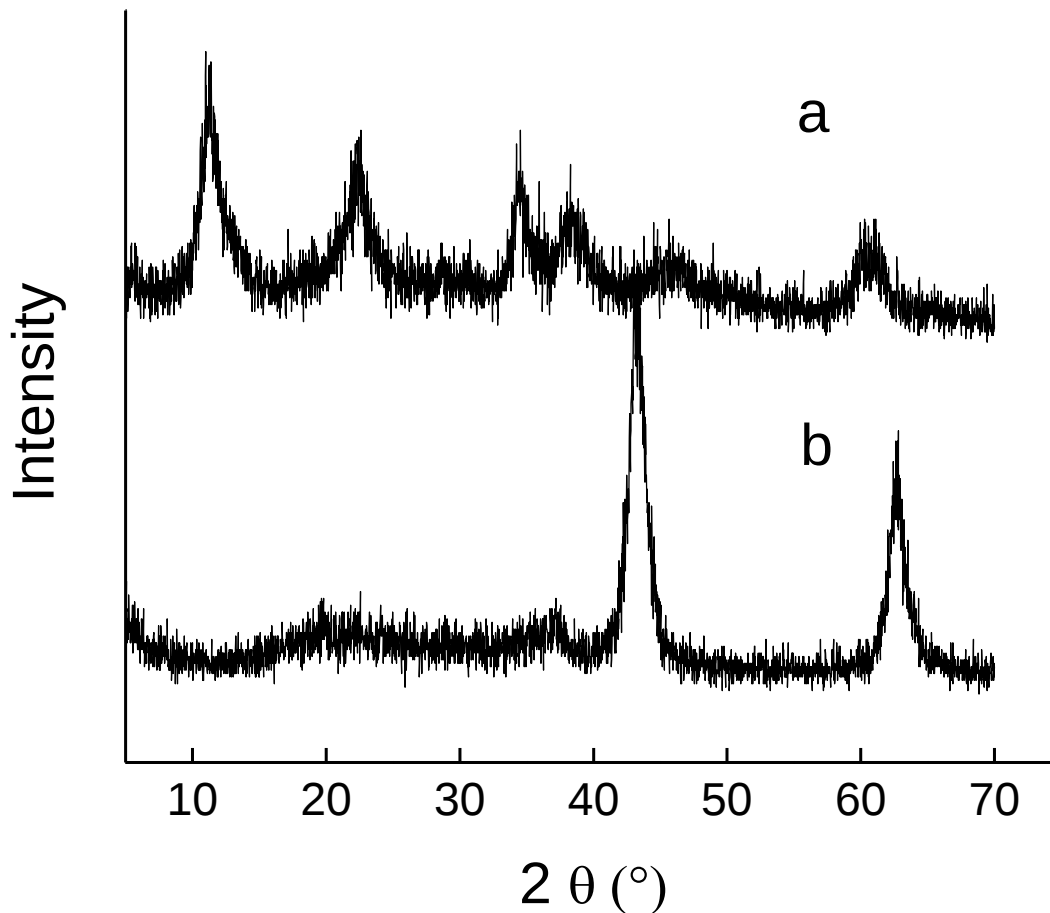


Figure S.4.1. XRD of as (a) synthesized and (b) calcined hydrotalcite.

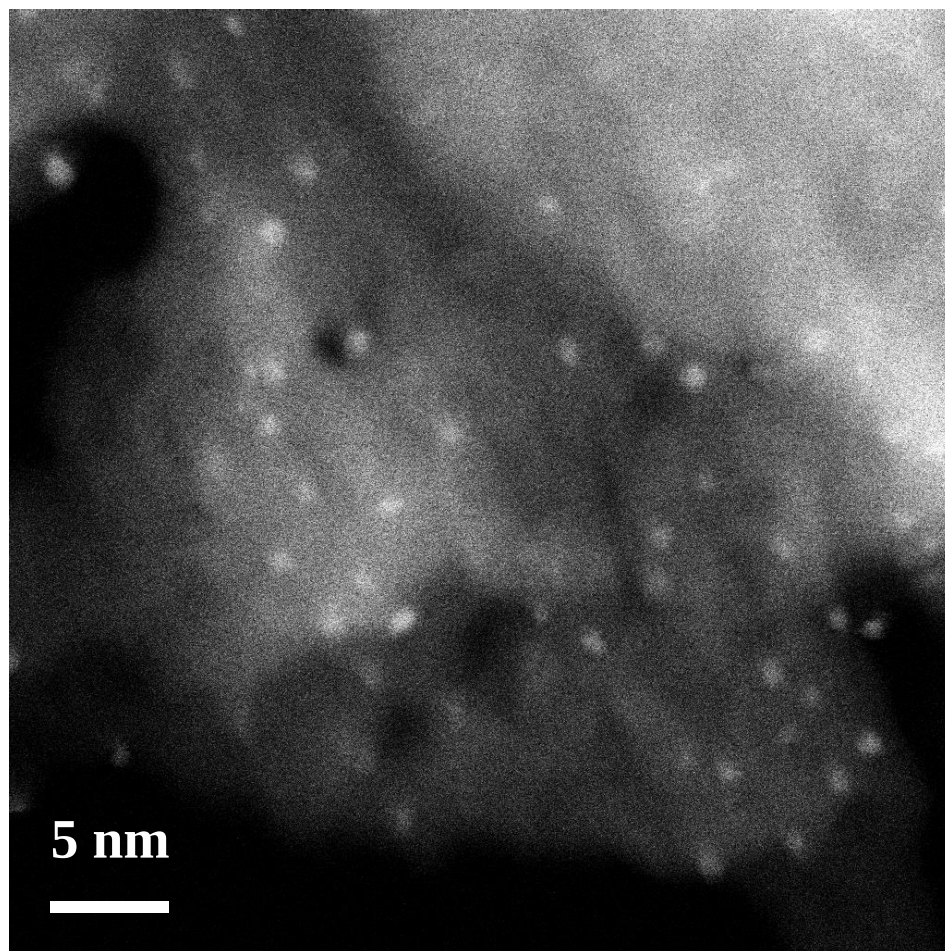


Figure S.4.2. STEM of Pt/Mg(In)(Al)O 0.88 before reaction

Table S.4.2. EXAFS fitting parameters for Pt/Mg(In)(Al)O after reaction in 4% H₂/He for 1 h at 723 K. The data ($3.5 < k < 12.1 \text{ \AA}^{-1}$) were fit ($1.4 < R < 3.2 \text{ \AA}$) with one Pt and one In backscattering path. The amplitude reduction factor, S_0^2 , was fixed to a value of 1 during the fit.

<i>Catalyst</i>	ΔE_0 (eV)	σ^2 ($\text{\AA}^2$)	CN _{Pt-In}	R _{Pt-O} ($\text{\AA}$)	CN _{Pt-In}	R _{Pt-In} ($\text{\AA}$)	CN _{Pt-Pt}	R _{Pt-Pt} ($\text{\AA}$)	<i>R-factor</i>
Pt/Mg(Al)O	5.4 ± 0.7	0.007 ± 0.001	--	--	--	--	6.7 ± 0.5	2.73 ± 0.01	0.003
Pt/Mg(Al)(In)O-0.33	4.3 ± 1.6	0.009 ± 0.001	0.5 ± 0.27	1.94 ± 0.05	--	--	6.1 ± 1.0	2.72 ± 0.01	0.020
Pt/Mg(Al)(In)O-0.48	5.9 ± 1.1	0.008 ± 0.001	0.75 ± 0.19	1.95 ± 0.03	--	--	6.5 ± 0.7	2.74 ± 0.01	0.008
Pt/Mg(Al)(In)O-0.88	5.0 ± 2.4	0.008 ± 0.002	0.61 ± 0.28	1.95 ± 0.04	0.15 ± 0.31	2.68 ± 0.18	6.1 ± 1.1	2.74 ± 0.02	0.007
Pt/Mg(Al)(In)O-1.7	7.2 ± 3.6	0.011 ± 0.002	1.42 ± 0.42	1.99 ± 0.04	0.55 ± 0.80	2.86 ± 0.08	6.5 ± 1.6	2.74 ± 0.02	0.012
Pt/Mg(Al)(In)O-5.6	2.0 ± 3.4	0.010 ± 0.003	0.79 ± 0.36	1.92 ± 0.05	0.44 ± 0.35	2.65 ± 0.10	4.8 ± 1.4	2.71 ± 0.03	0.020

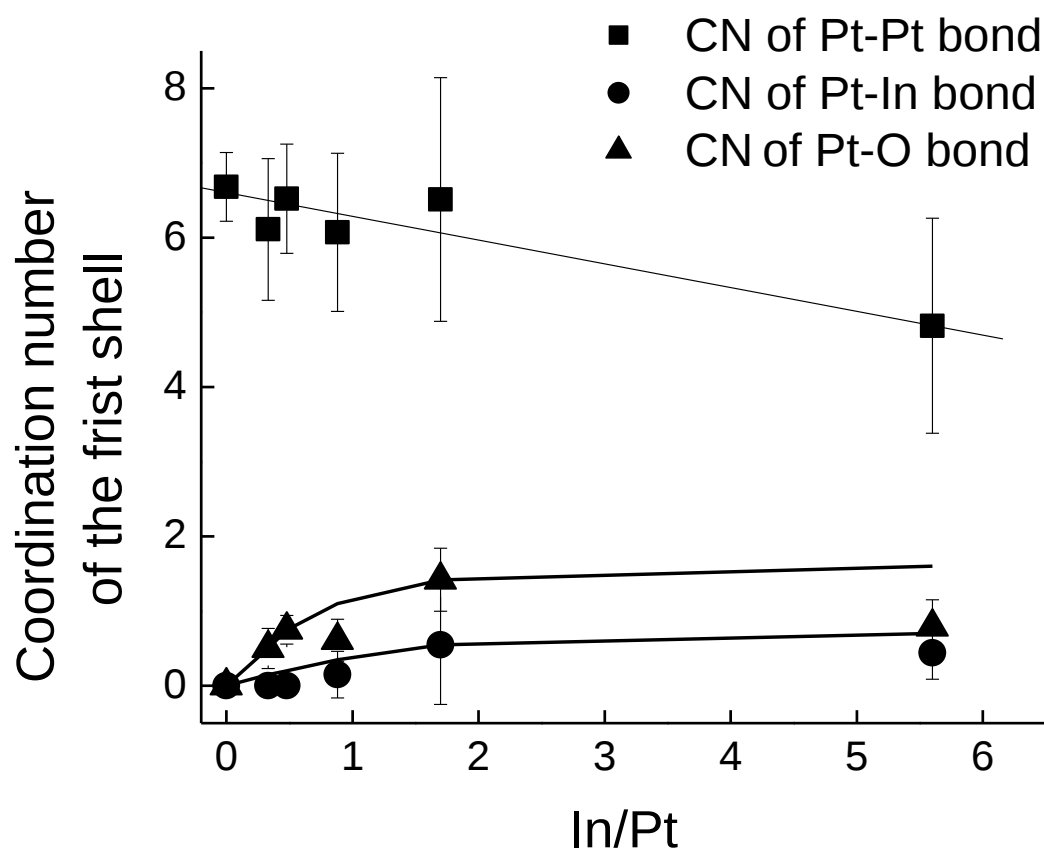


Figure S.4.3. Pt-Pt, Pt-In, Pt-O coordination numbers determined from Pt L_{III} edge. All EXAFS data were acquired after reduction in 100 cm³/min of 4% H₂/He at 723 K for 1 h. Samples were cooled to ambient temperature in 100 cm³/min of He flow before acquiring data. The error bars are the error in the coordination number were determined by the best fit for each sample

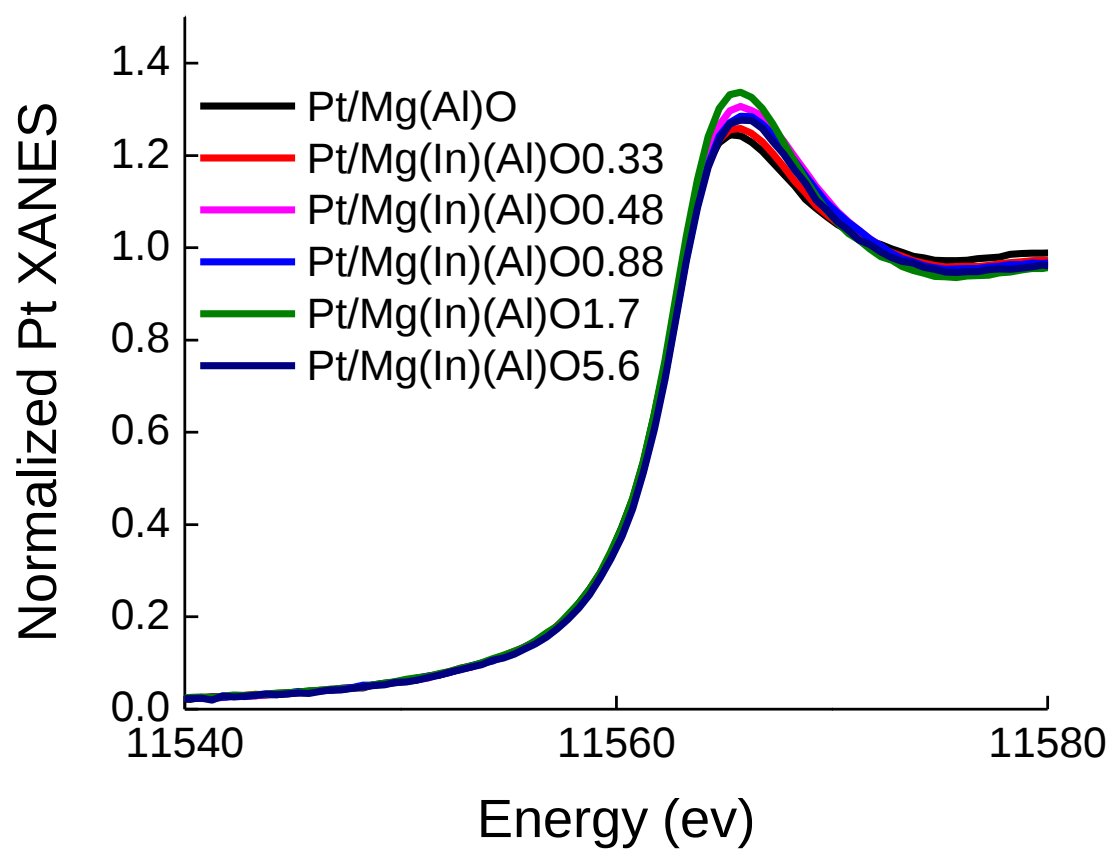


Figure S.4.4. Pt LIII XANES for Pt/Mg(Al)(In)O catalysts after treatment in 4% H₂/He for 1 h at 723 K. Samples were cooled to ambient temperature in He flow before data acquisition.

Table S.4.3. EXAFS fitting parameters of Pt/Mg(In)(Al)O after treatment in 4% H₂/He for 1 h at 873 K. The data ($3.5 < k < 12.1 \text{ \AA}^{-1}$) were fit ($1.8 < R < 3.2 \text{ \AA}$) with one Pt and one In backscattering path. The amplitude reduction factor, S_0^2 , was fixed to a value of 1 during the fit.

<i>Catalyst</i>	ΔE_0 (eV)	σ^2 ($\text{\AA}^2$)	CN _{Pt-In}	R _{Pt-In} ($\text{\AA}$)	CN _{Pt-Pt}	R _{Pt-Pt} ($\text{\AA}$)	<i>R-factor</i>
Pt/Mg(Al)O	6.4 ± 0.4	0.0065 ± 0.0004	--		6.1 ± 0.4	2.74 ± 0.01	0.002
Pt/Mg(Al)(In)O-0.33	3.3 ± 1.5	0.007 ± 0.001	0.4 ± 0.2	2.64 ± 0.05	5.7 ± 0.8	2.72 ± 0.01	0.005
Pt/Mg(Al)(In)O-0.48	3.2 ± 1.6	0.006 ± 0.001	0.7 ± 0.2	2.70 ± 0.03	5.2 ± 0.8	2.74 ± 0.01	0.004
Pt/Mg(Al)(In)O-0.88	1.6 ± 2.4	0.006 ± 0.002	1.0 ± 0.3	2.72 ± 0.04	5.6 ± 1.4	2.75 ± 0.02	0.011
Pt/Mg(Al)(In)O-1.7	1.5 ± 2.1	0.008 ± 0.002	1.5 ± 0.4	2.71 ± 0.03	5.5 ± 1.4	2.76 ± 0.02	0.013
Pt/Mg(Al)(In)O-5.6	1.2 ± 0.8	0.009 ± 0.001	3.8 ± 0.4	2.69 ± 0.01	1.9 ± 0.4	2.77 ± 0.02	0.003

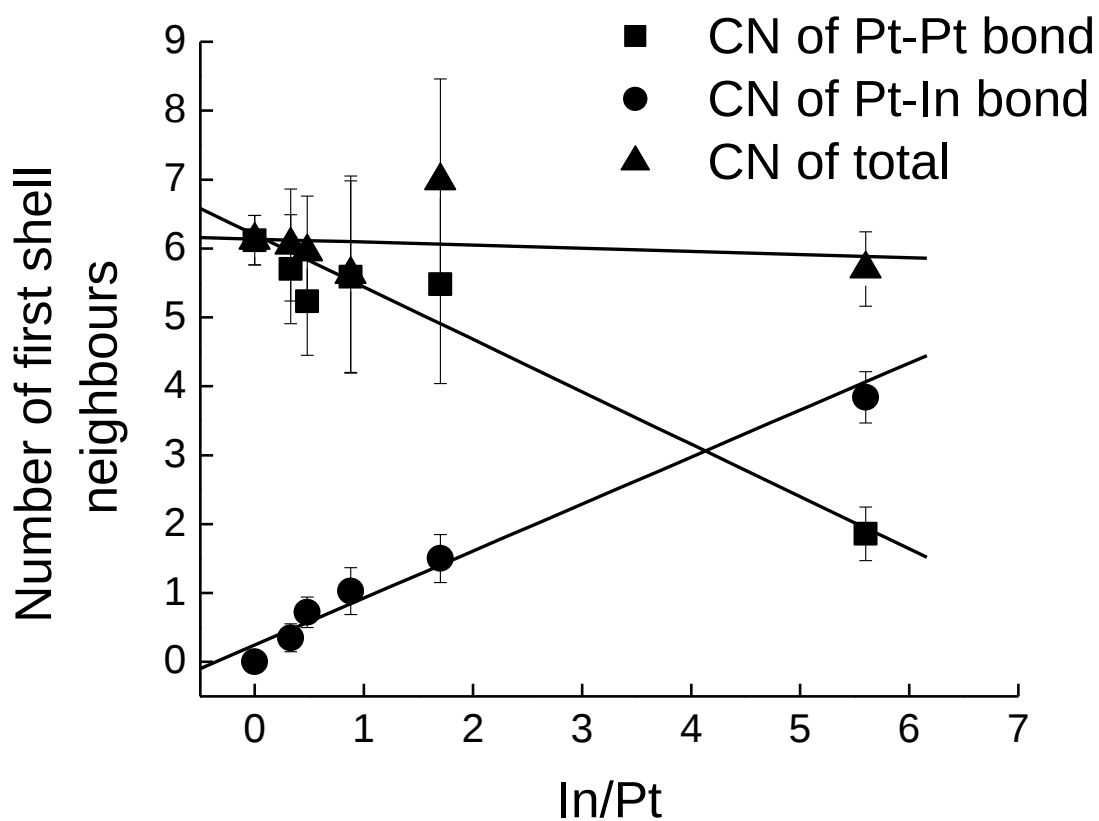


Figure S.4.5. Pt-Pt and Pt-In coordination numbers determined from Pt L_{III} edge. All EXAFS data were acquired after reduction with 100 cm³/min of 4% H₂/He at 873 K for 1 h. Samples were cooled to ambient temperature in 100 cm³/min of He flow before acquiring data. The error bars are the error in the coordination number were determined by the best fit for each sample

Table S.4.4. Estimated PtIn alloy compositions

<i>Sample Name</i>	<i>Bulk In/Pt</i>	<i>In/(Pt+In) alloy(%)</i>	<i>In in reduced state(%)</i>
Pt/Mg(Al)(In)O-0.33	0.33	6	20
Pt/Mg(Al)(In)O-0.48	0.48	12	25
Pt/Mg(Al)(In)O-0.88	0.88	16	17
Pt/Mg(Al)(In)O-1.7	1.7	21	13
Pt/Mg(Al)(In)O-5.6	5.6	67	12

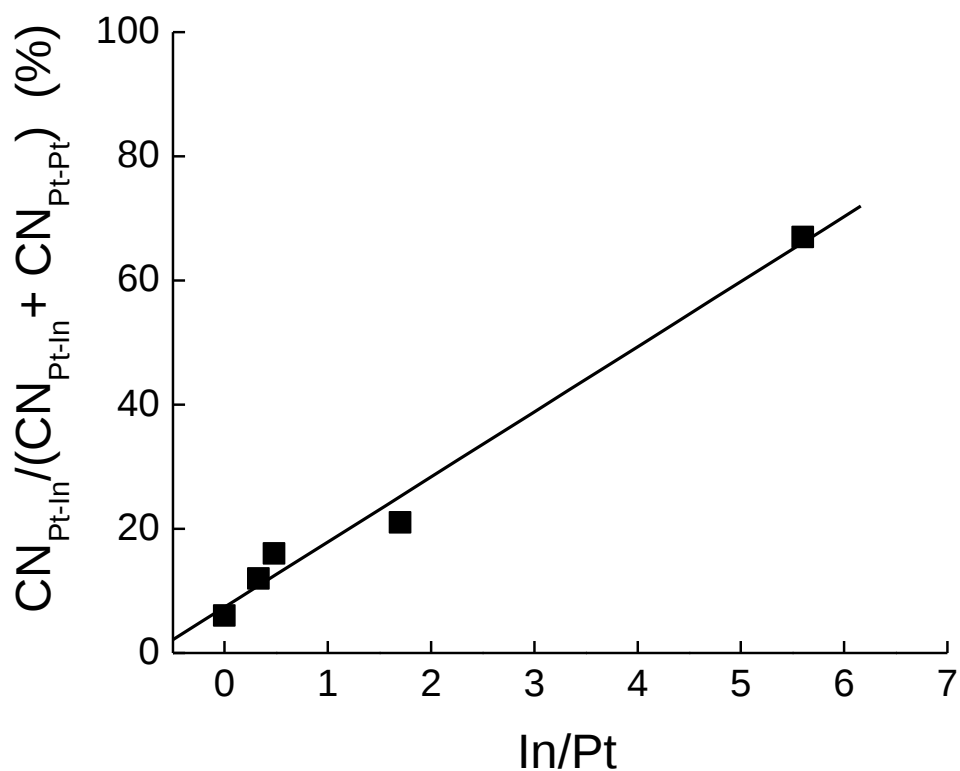


Figure S.4.6. Correlation between percent of alloy containing In with bulk In/Pt ratio

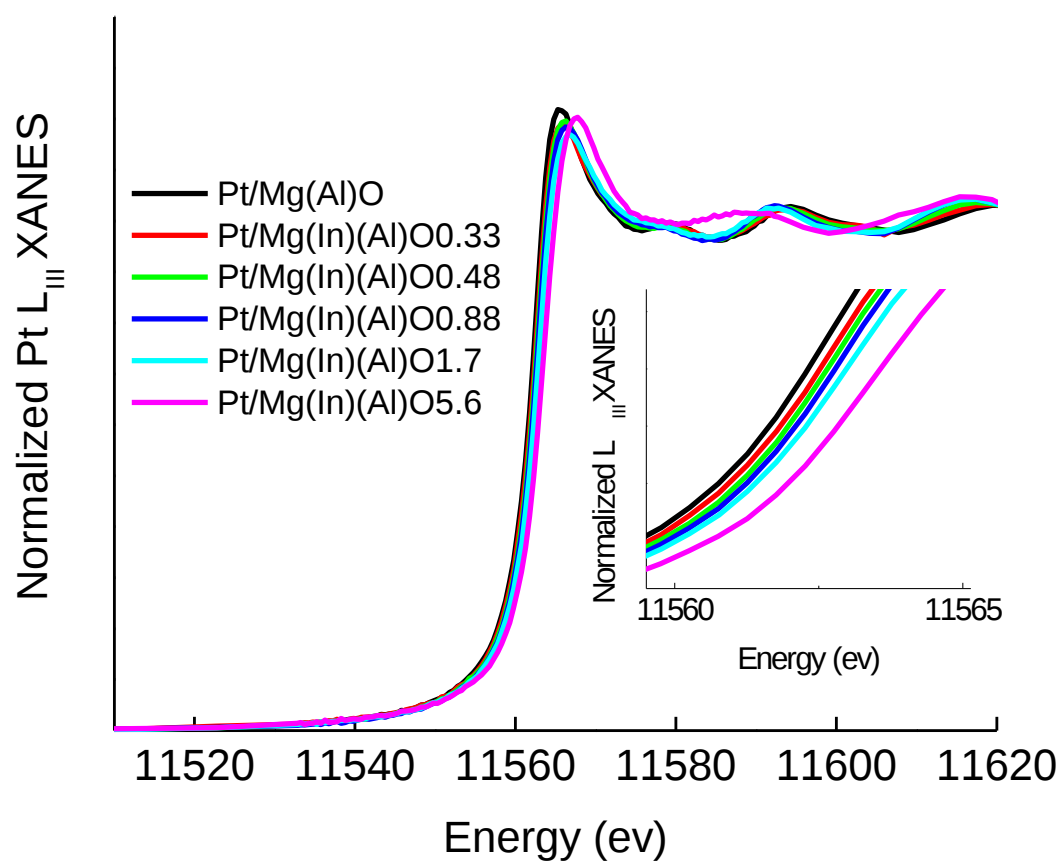


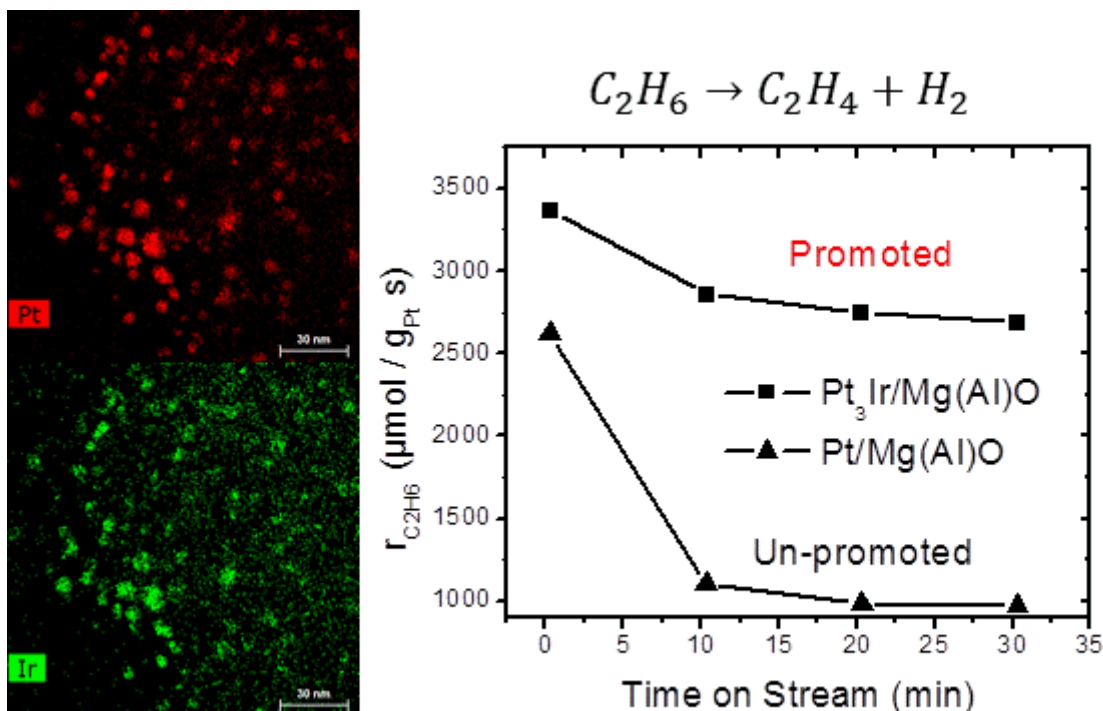
Figure S.4.7. Pt L_{III} XANES for Pt/Mg(Al)(In)O catalysts after treatment in 4% H_2 /He for 1 h at 823 K. Samples were cooled to ambient temperature in He flow before data acquisition.

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Chapter 5

Ethane and Propane Dehydrogenation over PtIr/Mg(Al)O: An experimental and theoretical study



Abstract

Increased demand for light alkenes has motivated research on the thermal dehydrogenation of the light alkanes and on understanding the role of catalyst composition on the activity, selectivity, and stability of Pt-based catalysts used for this purpose. The present study examines the structure and performance of Pt-Ir catalysts for ethane and propane dehydrogenation, and compares them with the performance of Pt and Pt-Sn catalysts. Nanoparticles of Pt, PtSn, and PtIr were prepared in a colloidal suspension and then dispersed onto calcined hydrotalcite (Mg(Al)O). After characterization to confirm formation of a bimetallic alloy, it was observed that at high conversions, Pt₃Ir/Mg(Al)O exhibit lower initial activity than Pt₃Sn/Mg(Al)O but greater stability to coke deposition. Intrinsic rate measurements at low feed residence time revealed the following trend in activity: Pt₃Sn > Pt₃Ir > Pt. DFT calculations carried out on tetrahedral clusters (Pt₄, Pt₃Ir, Pt₃Sn) show that this trend in activity can be attributed to the variation in the HOMO-LUMO gap of the cluster.

5.1. Introduction

The most active metal for alkane dehydrogenation is platinum but, in its pure form, suffers from low alkene selectivity and rapid coke deposition, leading to catalyst deactivation [1-4]. Chapters 2 and 3 explored the promoting effects of Sn and Ir, respectively. The addition of promoters such as promoters [1-11], has been found to be effective in increasing alkene selectivity and suppressing coke formation [5, 7, 12-16]. Both geometric and electronic effects of the promoters have been proposed to elucidate their roles in modifying the catalyst for the reaction [17-20]. Catalyst stability can be further enhanced by using a metal oxide support free of acid sites that can promote side reactions and additional coking [16, 21-23]. Calcined hydrotalcite, or $\text{Mg}(\text{Al})\text{O}$, has been shown to be an ideal support for this reaction. Moreover, the Al cations present at the surface of this support surface stabilize the dispersed metal nanoparticles against sintering [24].

In this final chapter, we focus on a recent computational study that has found Ir to be an effective promoter for propane dehydrogenation, and shows that Pt-Ir bimetallic particles should exhibit higher activity and greater stability than pure Pt [17]. Previous experimental studies of bimetallic Pt-Ir catalysts as reforming catalysts have shown that such catalysts are more active and less prone to coke formation compared to pure Pt [26-30]. In contrast to other promoting elements, Ir is unique in that it is capable of alkane activation [28, 31-33]. It is also noted that promotion of Ir together with Sn has been shown to significantly improve propane dehydrogenation activity while suppressing hydrogenolysis and other side reactions [34, 35]. Therefore, Pt-Ir catalysts represent an interesting system in which both metals are capable alkane activation, but in the absence of a promoter, suffer from low selectivity and stability.

The aim of the present work was to investigate the catalytic properties Pt-Ir catalysts for ethane and propane dehydrogenation, and to compare their performance with Pt and Pt-Sn catalysts. Pt-Ir nanoparticles of uniform size and composition were prepared in colloidal suspension and then supported on calcined hydrotalcite ($\text{Mg}(\text{Al})\text{O}$) using procedures described in Ref. 5. Density functional theory calculations of the energies and Gibbs free energies of ethane dehydrogenation were carried out using a Pt_3X ($\text{X} = \text{Sn}, \text{Ir}$) cluster to develop an understanding of the roles of Sn and Ir in enhancing catalyst activity for ethane dehydrogenation.

5.2. Experimental

5.2.1 Synthesis of $\text{Pt}/\text{Mg}(\text{Al})\text{O}$, $\text{PtIr}/\text{Mg}(\text{Al})\text{O}$, $\text{PtSn}/\text{Mg}(\text{Al})\text{O}$

Nanoparticles were prepared ex-situ as described in a previous chapter (2.2.1). Pt-Ir nanoparticles were prepared with iridium acetylacetonate (97%, Aldrich). Details concerning the preparation of all samples are listed in Table S5.1. Synthetic hydrotalcite ($\text{Mg}_6\text{Al}_2(\text{CO}_3)_3(\text{OH})_6 \cdot 4\text{H}_2\text{O}$, 100%, Aldrich) was calcined in air at 823 K for 5 h at a rate of 5 K/min. In a typical procedure, an appropriate volume (5 mL) of the toluene suspension of Pt or Pt-X ($\text{X} = \text{Ir}, \text{Sn}$) particles dispersed in toluene was added to a suspension of 0.2 g $\text{Mg}(\text{Al})\text{O}$ in 10 mL anhydrous toluene. The mixture was stirred overnight before the resulting product was precipitated by adding three times the volume anhydrous ethanol and separated by centrifugation. The solid material was heated at 723 K for 1 h in air to remove the surface capping agents and then reduced in an atmosphere of H_2 in Ar (10 vol.%) at 873 K for 1 h.

5.2.2 Catalyst Characterization

X-ray powder diffraction (XRD) patterns were collected on a Bruker D8 Discover GADDS Powder XRD equipped with a Cu K α source (wavelength of 1.5418 Å). XRD scans were recorded digitally with a step size of 0.02 and evaluated with profile fitting methods. Transmission electron microscopy (TEM) was carried out at the Electron Microscopy Laboratory of the University of California, Berkeley using a FEI Tecnai 12 transmission electron microscope. The samples were prepared by adding ethanol (2 mL) to the colloid (1 mL), and the mixture was centrifuged to separate the particles. The black precipitate was re-suspended in 2 mL of toluene, and 0.1 mL of this solution was further diluted with 2 mL of toluene; 10 μ L of the suspension was dropped onto a lacey carbon copper grid. For the supported catalysts, 10 mg of the catalyst was grinded in 5 mL of ethanol and 20 μ L of the suspension was dropped onto a lacey carbon copper grid.

The Pt, Ir, and Sn contents of the bulk catalysts were determined by inductively coupled plasma – optical emission spectrometry (ICP-OES) by Galbraith Laboratories, Knoxville, TN. Elemental maps were recorded with a custom-modified FEI Titan electron microscope equipped with a Bruker Nano EDS detector at the National Center for Electron Microscopy. Maps were recorded at 200 kV at a beam current of 0.5 nA in the STEM mode after selecting a region of the sample by using the HAADF image. All elemental maps used a pixel dwell time of 150 ms with averaging of at least 100 frames with drift compensation. Bruker ESPRIT software package was used to quantify the maps by fitting and subtracting the Bremsstrahlung background using regions without peaks. After this step, the Pt L α emission peak at 9.439 keV and the Ir L α peak at 9.175 keV were integrated and converted to atomic compositions by using Cliff–Lorimer factors.

5.2.3 Catalyst Testing

Ethane and propane dehydrogenation was carried out in a fixed-bed, quartz reactor (7 mm internal diameter). In a standard procedure, the catalyst materials were pressed, crushed, and sieved into small pellets (250-500 μ m in diameter). Prior to testing, the pelletized catalyst was heated at 723 K overnight in air to remove possible moisture from the support. The catalyst was heated to 873 K (15 K/min) in 1 atm 20% H $_2$ (UHP Praxair) in He (UHP Praxair) using a three-zone furnace and then maintained at 873 K for 1 h to fully reduce it. A feed containing ethane, hydrogen, and helium was used to determine the activity, selectivity, and stability of all Pt/Mg(Al)O and PtX/Mg(Al)O (X = Ir, Sn) samples for ethane and propane dehydrogenation. The partial pressure of the alkane (99.95% Praxair) and the H $_2$ /alkane ratio were fixed at 0.202 bar and 1 respectively. The reaction products were analyzed on-line by a gas chromatography – mass spectrometer (GC-MS, Varian, Model 320). A flame ionization detector (FID) was used to quantify the concentrations of all organic compounds eluting from the capillary column. Rates were normalized per gram Pt in the catalyst.

5.2.4 DFT calculations (performed by Shaama Mallikarjun Sharada)

The theoretical examination of ethane dehydrogenation on Pt and its alloys was conducted along the lines of a previous computational study [20]. Tetrahedral arrangements of pure platinum, Pt $_4$, and alloys, Pt $_3$ X (X = Ir, Sn) were chosen to represent the catalyst 20. The minimum energy configurations for the Pt $_4$, Pt $_3$ Ir and Pt $_3$ Sn correspond to a spin triplet, quartet and singlet, respectively.

All calculations were performed using the Q-Chem software package [37], with the ω B97X functional [38], and the triple-zeta valence basis set of Weigend and Ahlrichs [39], from which the f-functions were removed for performance reasons. The Stuttgart/Köln effective core potential [40, 41] was used for all metals. The transition states for the rate-limiting step, the first C-H bond breaking, were calculated using the freezing string method [42, 43].

Vibrational frequency calculations were performed on all structures, in order to verify the nature of stationary points as well as to calculate thermodynamic corrections. Vibrational analysis showed several low vibrational frequencies, corresponding to hindered or rocking modes of ethane relative to the metal cluster. The most commonly employed approximation of a rigid rotor-harmonic oscillator (RRHO) can yield erroneous thermodynamic corrections for low-lying frequencies. Therefore, the quasi-harmonic interpolation approach proposed by Grimme [44, 45] was used to calculate intrinsic free energies of activation of the C-H bond. Theoretical free energies and reaction rates were then contrasted with experimental results in order to explain the differences in activity of various Pt alloys.

5.3. Results and Discussion

Figures 5.1a and 5.1b show TEM images of the as-prepared Pt₃Ir nanoparticles and the particle size distribution, respectively, with average particle size of 3.3 nm. Upon calcination of the commercially available synthetic hydrotalcite material, calcined hydrotalcite, or Mg(Al)O, is obtained as shown in Fig. 5.1c. The final Pt₃Ir/Mg(Al)O catalyst is obtained after deposition of the nanoparticles onto the support followed by calcination in order to remove the capping agents. The resulting TEM image (Fig. 5.1d) demonstrates no apparent visual change in particle size occurred upon dispersion of the nanoparticles onto the support. Table 5.1 presents a summary of the properties for the catalysts examined for ethane and propane dehydrogenation. A fair comparison of rates can be made due to the narrow range of particle sizes considered, resulting in similar dispersion values. Characterization of Pt/Mg(Al)O and Pt₃Sn/Mg(Al)O by TEM and XRD are detailed in a previous publication [5].

XRD measurements of the support and catalysts are shown in Fig. 5.2. Ex-hydrotalcite (black line) possess a brucite-like, layered, double hydroxide structure while the calcined hydrotalcite material (red line) resembles a cubic magnesium oxide (MgO) structure with interstitial Al [10, 46]. Pt/Mg(Al)O (green line) and Pt₃Ir/Mg(Al)O (blue line) were prepared with 5% metal weight loading for XRD measurements in order to amplify the signal of the supported nanoparticles. Both catalysts showed distinct (111) diffraction lines for fcc Pt or Ir metals, but due to the close proximity of the (111) peaks positions for Pt and Ir and the broad nature of the peaks, it is difficult to distinguish from XRD between a mixture of segregated Pt and Ir nanoparticles or PtIr bimetallic nanoparticles.

To confirm the microscopic composition of the individual nanoparticles, STEM-energy dispersive X-ray spectroscopy (STEM-EDS) was used to produce the elemental maps shown in Figs. 5.3a and 5.3b, which show the location of Pt and Ir, respectively. It can be seen qualitatively that there is strong overlap between the two maps, indicating that each particle contains both Pt and Ir and confirming the formation of a bimetallic Pt-Ir alloy. 10 elemental maps (~300 nanoparticles) were collected in total for statistical purposes and bimetallic formation was observed in every case, with no indication of significant segregation of pure Pt or pure Ir nanoparticles. The quantification of the acquired count maps revealed an overall elemental

composition of particles of Ir/Pt = 0.32, in good agreement with the bulk ICP analysis. The distribution of particle compositions is shown in Figure S5.2.

The rate of ethane consumption and the selectivity to ethene are shown in Fig. 5.4 for three different catalysts. Both Pt₃Ir/Mg(Al)O and Pt₃Sn/Mg(Al)O show significantly higher ethane conversion and stability compared to Pt/Mg(Al)O. Furthermore, the selectivity to ethene increases to over 95% for the bimetallic catalysts as time on stream increases. This behavior is in agreement with previous studies that have observed increased activity, selectivity, and stability for Pt catalysts promoted with Sn, In, and Ga for ethane dehydrogenation [1-9]. Pt₃Ir/Mg(Al)O represents an interesting system since Ir atoms are active for alkane dehydrogenation, as well as Pt atoms, whereas Sn is incapable of alkane activation. Therefore, it is difficult to obtain a turnover frequency for Pt-Ir catalysts since it is not known experimentally how active Pt and Ir sites are relative to each other. Fig. 5.5 shows the percent deactivation in the first 10 min as a function of M/Pt ratio (M = Ir, Sn). As more of the secondary metal is added to the catalyst, there is a significant decrease in deactivation, with Pt-Ir exhibiting slightly higher stability than Pt-Sn. Therefore, the accumulation of carbon decreases strongly with increased alloying with either Ir or Sn. This phenomenon has also been observed with other secondary metals, such as Ga and In [9, 10]. Pt-Ir catalysts have also been long heralded as very stable reforming catalysts [28], and the same conclusion can be made for ethane dehydrogenation.

The activity and selectivity of each catalyst was probed for propane dehydrogenation, and the results are shown in Fig. 5.6. Both Pt₃Ir/Mg(Al)O and Pt₃Sn/Mg(Al)O showed increased propane conversion and higher propene selectivity relative to Pt/Mg(Al)O. However, in contrast to what was observed for ethane dehydrogenation, the Sn-promoted catalyst exhibits 21% higher initial activity than the Ir-promoted catalyst. Fig. 5.7 shows the relative stability of both catalysts for propane dehydrogenation. Trends similar to those for ethane dehydrogenation (see Fig. 5.4) are observed. Therefore, we conclude that both Pt₃Ir/Mg(Al)O and Pt₃Sn/Mg(Al)O are significantly more active, selective, and stable than monometallic Pt/Mg(Al)O for both ethane and propane dehydrogenation. Pt-Sn catalysts show higher initial activity while Pt-Ir catalysts exhibit slightly higher stability.

To probe the intrinsic activity of these catalysts, the residence time was decreased in order to remove the effects of deactivation [5]. It has been observed that the initial deactivation of Pt or a promoted Pt catalyst for alkane dehydrogenation is very rapid, making it difficult to measure the true initial activity [7, 47]. We have shown from previous isotopic labeling studies that coke originates primarily from readsorption of the formed alkene; therefore by measuring rates at low conversions, or low residence times, accurate comparisons of intrinsic activity of catalysts can be made with minimal influence of deactivation [5, 7]. Figs. 5.8a and 5.8b show the rates of ethene and propene formation, respectively, at low-residence times. It is clear that both Pt-Ir and Pt-Sn catalysts are more active intrinsically for alkane dehydrogenation. From these data, we draw the conclusion that the activity for ethane and propane dehydrogenation increases in the order Pt₃Sn>Pt₃Ir>Pt.

The effect of hydrogen co-feed with ethane on ethene formation is shown in Fig. 5.9. As the H₂/C₂H₆ feed ratio increases, the rate of ethene formation goes through a maximum at H₂/C₂H₆ = 1, and then decreases. The observed effect of hydrogen has been observed previously for other Pt promoted with Ga or In [8, 10]. Theoretical studies suggest that the presence of adsorbed H atoms impedes the further dehydrogenation of adsorbed alkene molecules, a process leading to coke precursors, and facilitates alkene desorption and thereby the overall rate of alkane

dehydrogenation [20]. We have observed these effects previously for Pt-Sn systems [5] but this trend can now be extended this effect to Pt-Ir.

Figure 5.10 shows the rate and selectivity for three cycles of ethane dehydrogenation over $\text{Pt}_3\text{Ir}/\text{Mg}(\text{Al})\text{O}$. After removal of accumulated carbon by oxidation and subsequent H_2 reduction at 873 K, the original performance of the catalyst was restored close to that seen in Cycle 1. The particle size distributions in between cycles remained the same, eliminating the possibility of sintering during the oxidation and reduction steps. Because of the noble nature of Ir compared to other promoters such as Sn, In, or Ga, Pt-Ir catalysts may be a more durable catalyst in the presence of oxygen at the high temperatures needed to remove carbon species between cycles.

To gain an understanding of the cause in the observed activity with catalyst composition, a theoretical analysis of the elementary processes involved in ethane and propane dehydrogenation was carried out using tetrahedral metal clusters to represent the metal nanoparticles. The choice of this model is dictated by the fact that such clusters retain their tetrahedral architecture for all steps of the reaction sequence and have been shown previously to provide physically meaningful trends [20].

The transition states calculated for the first C-H activation step for ethane on Pt_3Ir are shown in Figure 5.11, along with the relevant bond distances. It is notable that the reaction can be catalyzed at both the Pt (Pt_3Ir) and Ir (IrPt_3) centers, unlike Pt_3Sn where dissociative adsorption of ethane does not occur on the Sn atom. The transition state geometry is similar to that previously determined for propane dehydrogenation on Pt alloy clusters (Pt_4 and Pt_3X) [20], as well as that for ethane dehydrogenation occurring on the (111) and (110) surfaces of bulk Pt [48]. Intrinsic enthalpies and free energies of activation for dissociative adsorption are reported in Table 2. Because the binding energy of ethane on Pt(111) and Ir(111) are within 0.1 kcal/mol [49], the intrinsic activation energy of the rate-determining step serves as an accurate basis for comparing the activities Pt and Pt_3Ir . The values of the activation barriers are lower than that reported for the Pt(110) surface (40 kJ/mol) [48]. However, this may be a consequence of using a very small cluster to represent the Pt_3X nanoparticles. The metals atoms are significantly under-coordinated in a 4-atom cluster, which may result in higher activity when compared to the true catalyst surface.

The trends in activation free energy predicted using theory are surprisingly close to those observed experimentally. Reaction rates and rate ratios relative to pure Pt were calculated, and reported in Table 5.2. Since the activity for Pt_3Ir varies widely depending on whether Pt or Ir is the active center, the Boltzmann averaged rates over both active sites is calculated prior to obtaining the rate ratio. As a result, the dissociative adsorption step at Pt_3Ir is determined to be 4.6 times faster than at Pt_4 . The theoretical activity trend of $\text{Pt}_3\text{Sn} > \text{Pt}_3\text{Ir} > \text{Pt}_4$ agrees qualitatively with that found experimentally. Prior work has shown that the trend in activity can be related to the HOMO-LUMO gap of the metal cluster [20]. The gap is smallest for Pt_3Sn and largest for pure Pt, which may be the cause of lower C-H activation energy at the former. A detailed analysis of factors governing activity and selectivity in Pt alloys has been presented elsewhere [25].

5.4. Conclusion

Catalysts for ethane and propane dehydrogenation were prepared by ex-situ formation of Pt, Pt-Ir, and Pt-Sn nanoparticles in solution, and subsequent deposition onto calcined ex-hydrotalcite. Characterization by XRD and STEM-EDS confirmed the presence of metallic nanoparticles with an fcc structure containing Pt and Ir in close association, indicating bimetallic alloy formation. $\text{Pt}_3\text{Ir}/\text{Mg}(\text{Al})\text{O}$ and $\text{Pt}_3\text{Sn}/\text{Mg}(\text{Al})\text{O}$ exhibited superior performance for both

ethane and propane dehydrogenation compared to Pt/Mg(Al)O, with PtIr/Mg(Al)O showing slightly higher stability than PtSn/Mg(Al)O. Low residence-time experiments revealed that PtIr catalysts are intrinsically more active than pure Pt catalyst and the trend in activity decreases in the order: $\text{Pt}_3\text{Sn} > \text{Pt}_3\text{Ir} > \text{Pt}$. The rate of ethane dehydrogenation over $\text{Pt}_3\text{Ir}/\text{Mg}(\text{Al})\text{O}$ increases with the addition of H_2 to the feed for feed ratios up to $\text{H}_2/\text{C}_2\text{H}_6 = 1$ in a manner similar to that observed previously for other promoters. Theoretical analysis of ethane dehydrogenation on Pt_4 , Pt_3Ir , and Pt_3Sn clusters yields the same trend observed experimentally, and reveals that both Pt and Ir atoms are capable of alkane activation, a characteristic not observed in the PtSn system.

5.5. Acknowledgements

This work was supported by Chevron Energy Technology Company. Work at the Molecular Foundry (Proposal #3335) was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. The author thanks Shaama Sharada and Andreas Hauser for support in theoretical computations.

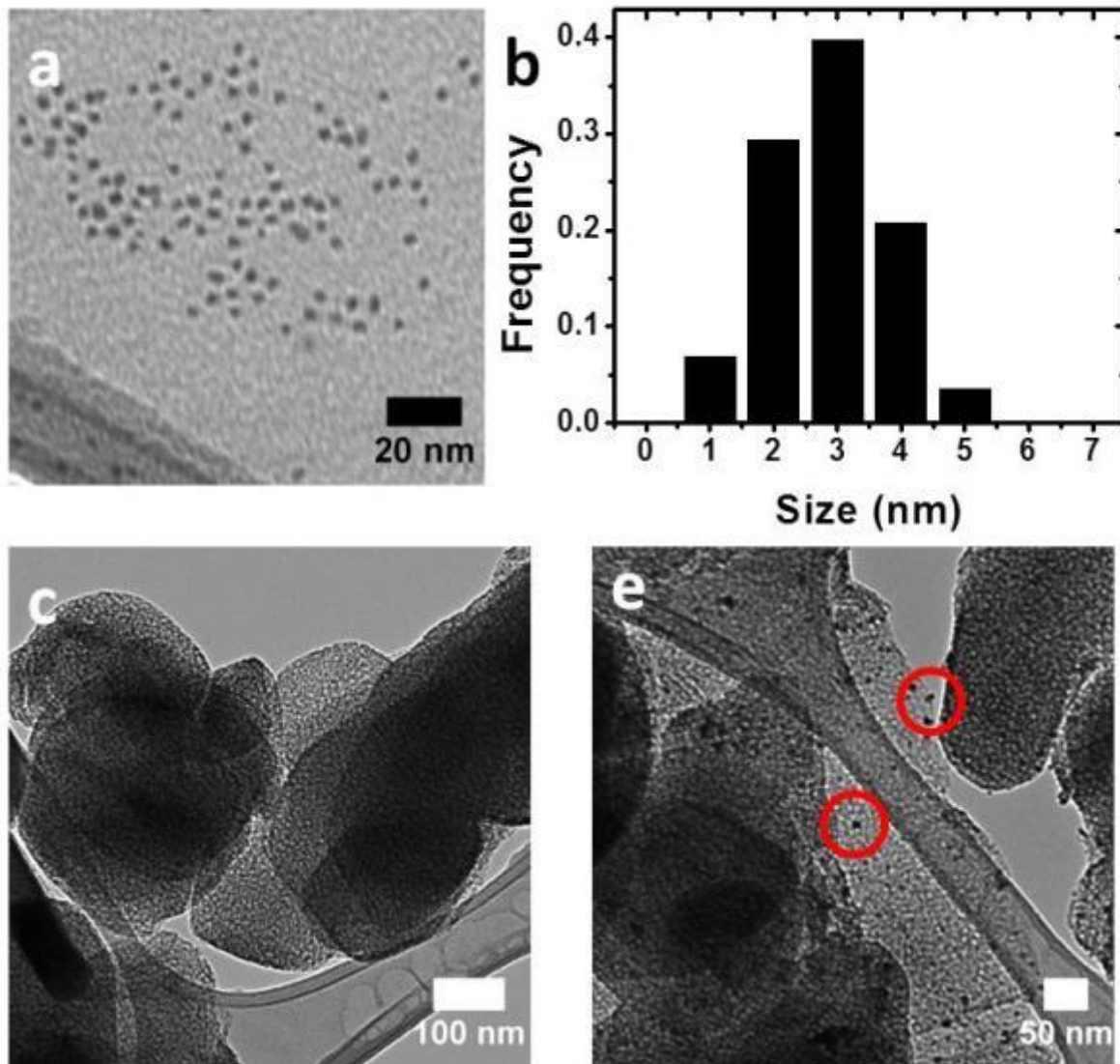


Figure. 5.1. a) Pt₃Ir nanoparticles prepared ex-situ by colloidal method, b) Particle size distribution with $\langle d \rangle = 3.3$ nm, c) Calcined hydrotalcite after calcination of synthetic hydrotalcite at 823 K for 5 h, d) Pt₃Ir/M g(Al)O catalysts after nanoparticle deposition onto calcined support.

Catalyst	Pt wt%	M wt% (M = Ir or Sn)	<d> (nm)
Pt/Mg(Al)O	1.84	0	3.8
Pt ₅ Ir/Mg(Al)O	2.00	0.47	4.2
Pt ₃ Ir/Mg(Al)O	1.91	0.68	3.3
Pt ₃ Sn/Mg(Al)O	1.63	0.42	3.5

Table 5.1. Composition and particle size distribution determined by ICP-OES and TEM, respectively.

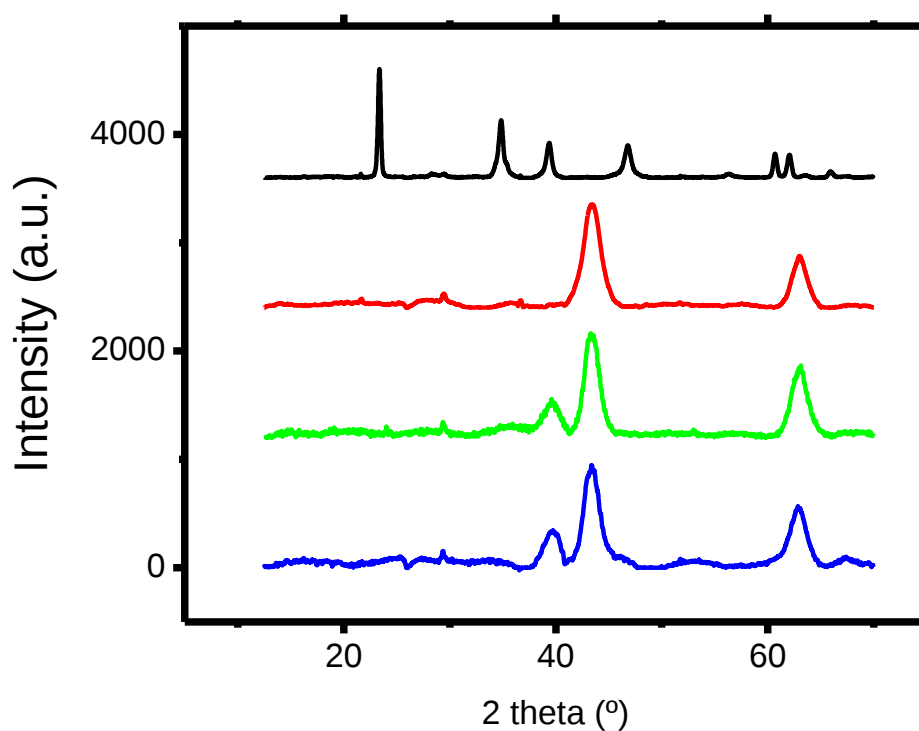


Figure. 5.2. XRD patterns for synthetic hydrotalcite (black), calcined hydrotalcite (red), Pt/Mg(Al)O (green), and Pt₃Ir/Mg(Al)O (blue).

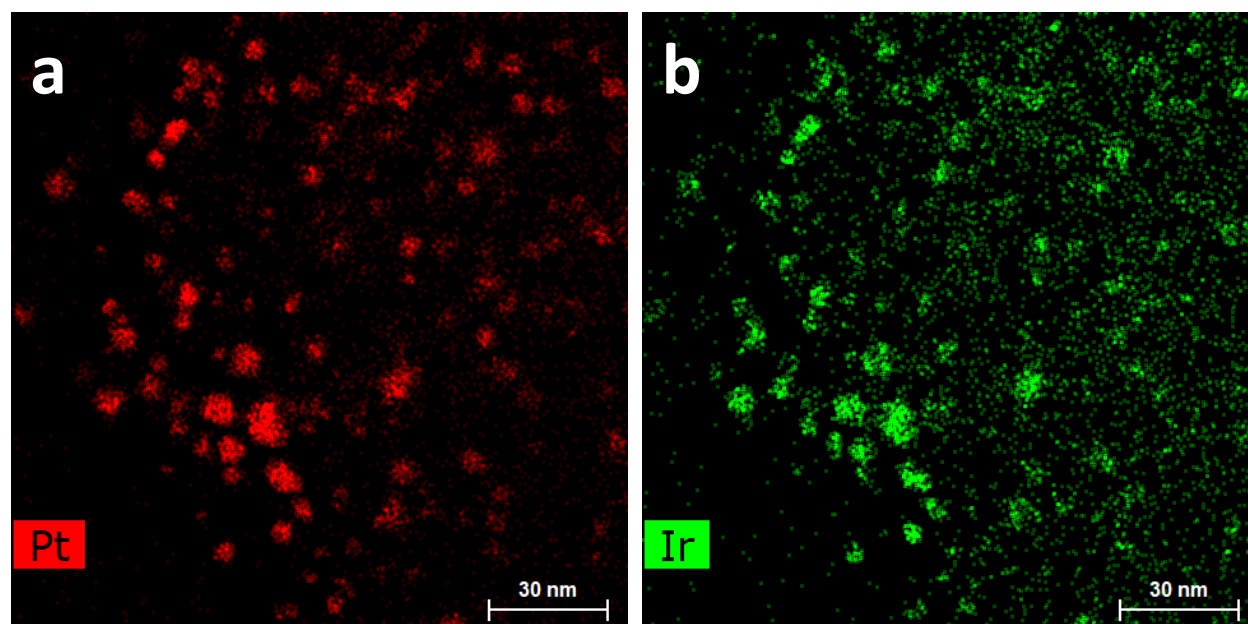


Figure. 5.3. Elemental mapping of Pt₃Ir/Mg(Al)O by STEM-EDS.

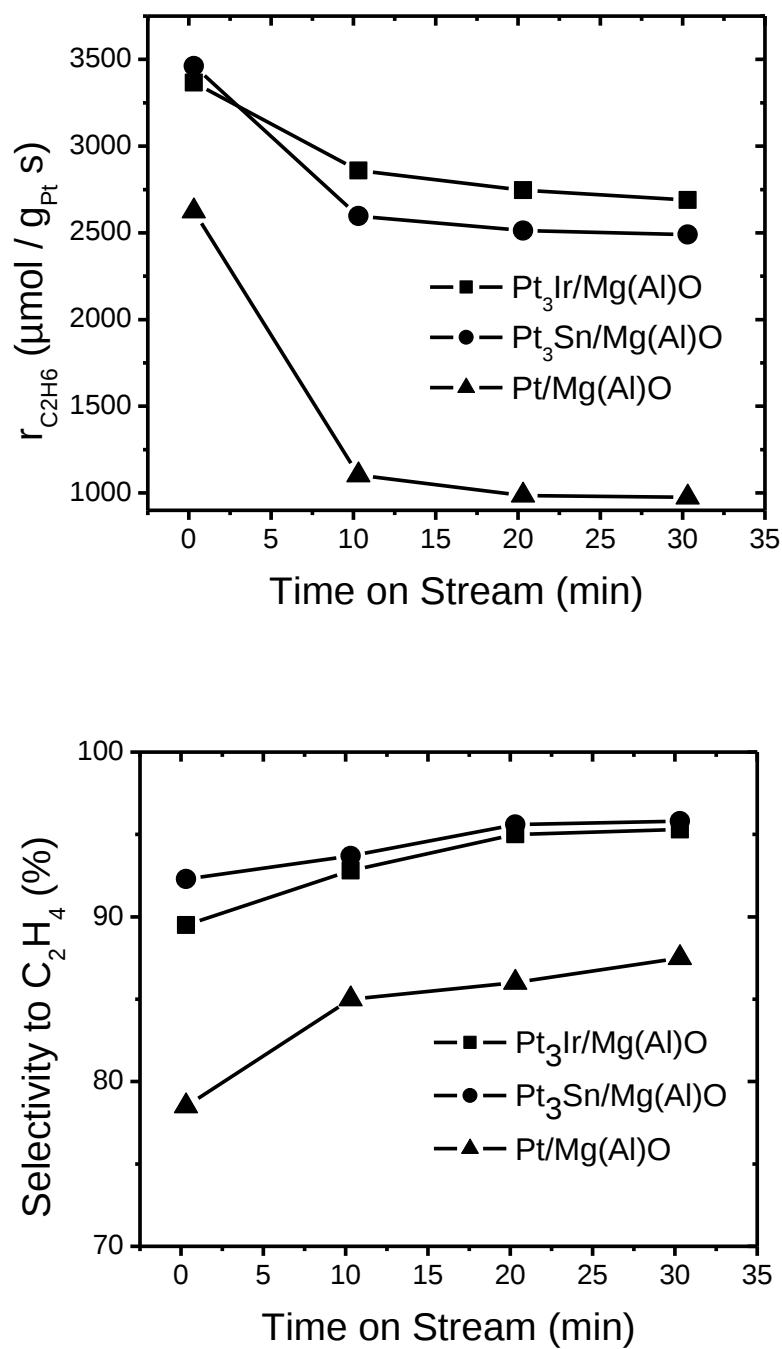


Figure. 5.4. The rate of ethane conversion and selectivity to ethene as a function of time on stream for Pt_3Ir , Pt_3Sn , and Pt catalysts supported on calcined hydrotalcite. Reaction conditions: 873 K, $m = 25$ mg, $F = 60$ mL/min, C_2H_6 : 20%, $H_2:C_2H_6 = 1$

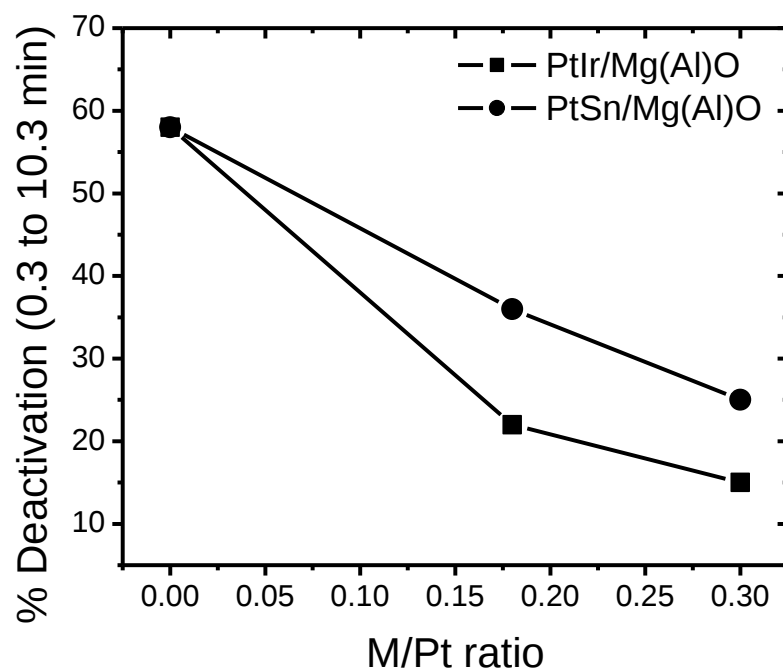


Figure. 5.5. Percent deactivation in the first 10 minutes of ethane dehydrogenation as a function of M/Pt ratio. Reaction conditions: 873 K, $m = 25$ mg, $F = 60$ mL/min, C_2H_6 : 20%, $H_2:C_2H_6 = 1$

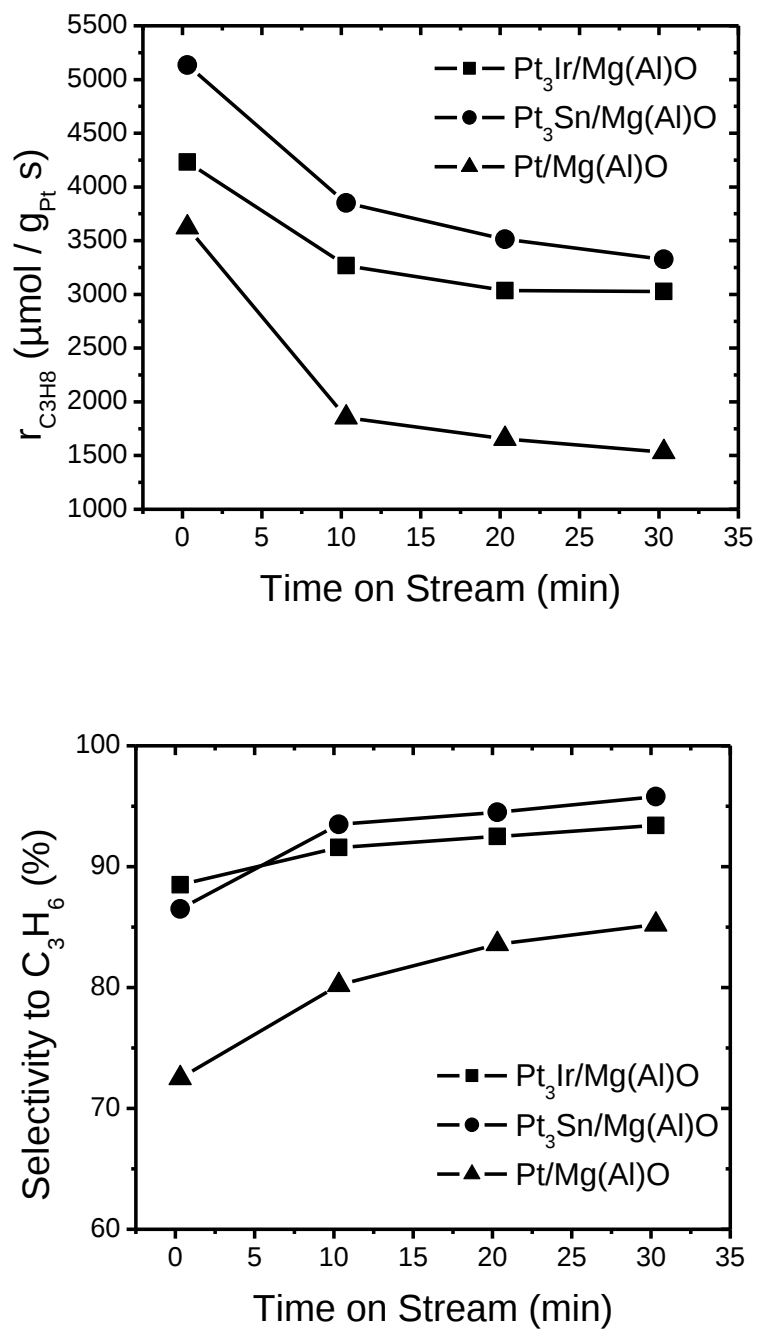


Figure. 5.6. The rate of propane conversion and selectivity to propene as a function of time on stream for Pt_3Ir , Pt_3Sn , and Pt catalysts supported on calcined hydrotalcite. Reaction conditions: 873 K, $m = 25$ mg, $F = 60$ mL/min, C_3H_8 : 20%, $\text{H}_2:\text{C}_2\text{H}_6 = 1$

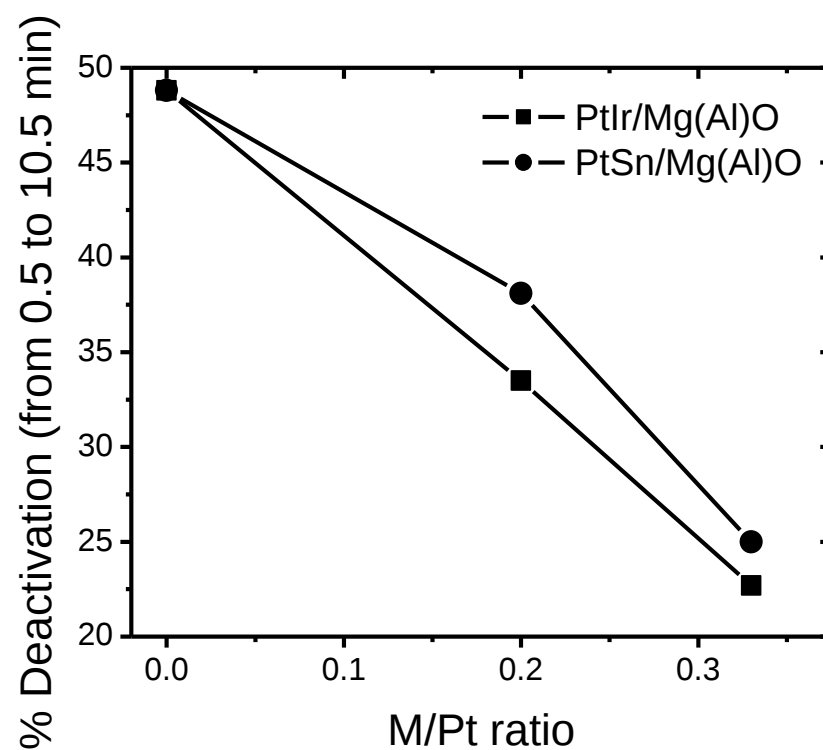


Figure. 5.7. Percent deactivation in the first 10 minutes of propane dehydrogenation as a function of M/Pt ratio. Reaction conditions: 873 K, $m = 25$ mg, $F = 60$ mL/min, C_3H_8 : 20%, $H_2:C_3H_8 = 1$

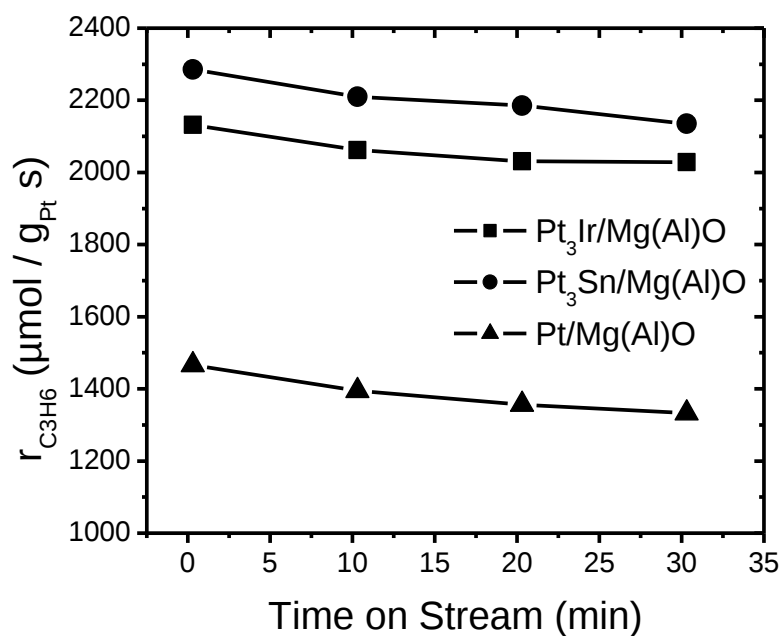
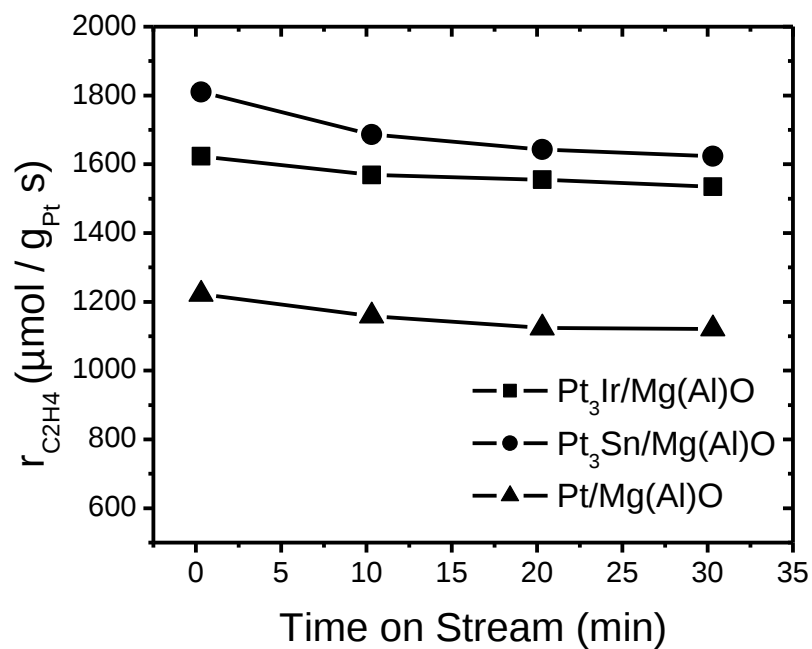


Figure. 5.8. Rate of ethene and propene production as a function of time on stream at low-residence time. Reaction conditions: 873 K, $m = 5$ mg, $F = 80$ mL/min, C_2H_6 or C_3H_8 : 20%, $H_2:(C_2H_6 \text{ or } C_3H_8) = 1$

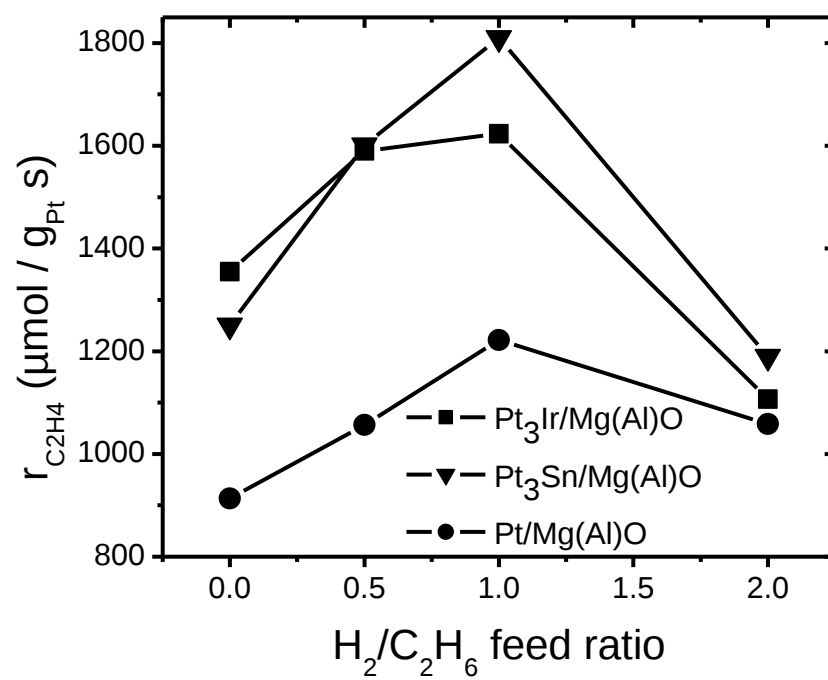


Figure. 5.9. Rate of ethene production as a function of hydrogen to ethane feed ratio. Reaction conditions: 873 K, $m = 25$ mg, $F = 60$ mL/min, C₂H₆: 20%

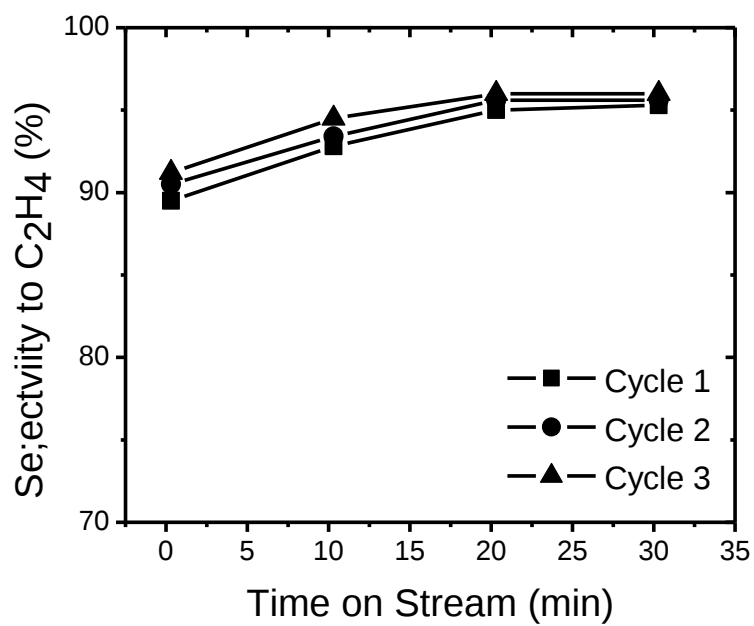
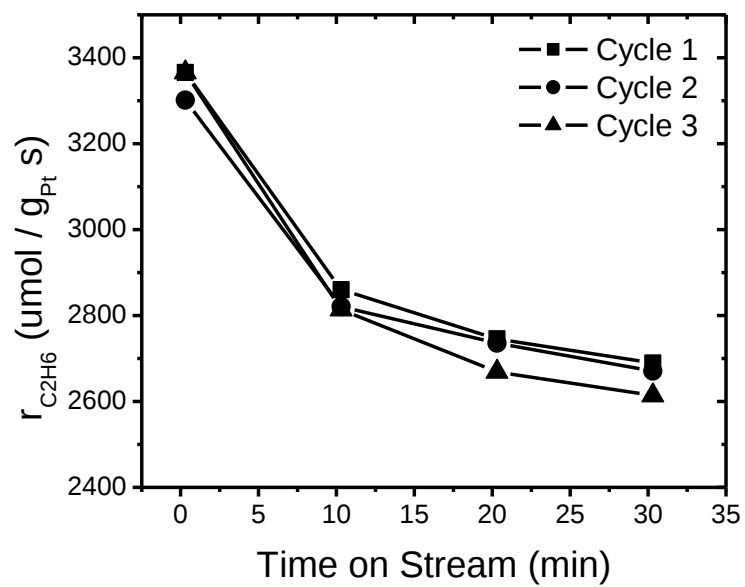


Figure. 5.10. Regeneration of $Pt_3Ir/Mg(Al)O$ catalyst. In between each cycle, catalyst is treated at 873 K , 0.2 bar O_2 , followed by 873 K, 0.2 bar H_2 .

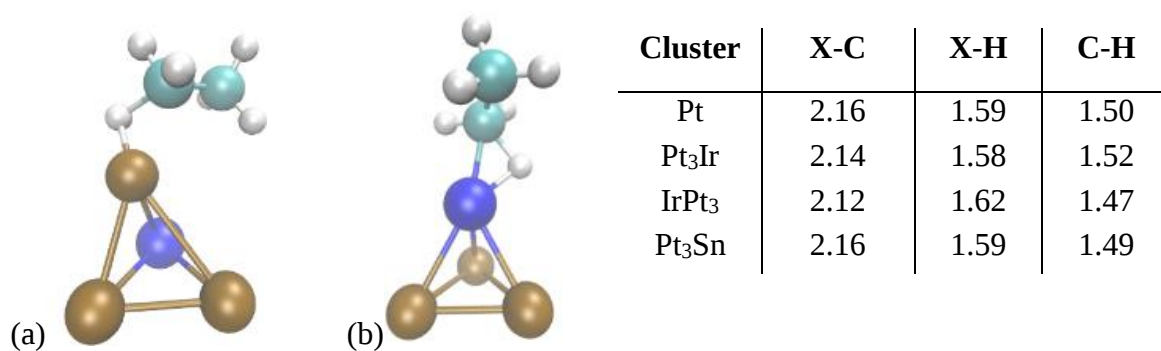


Figure. 5.11. Transition state for dissociative adsorption of ethane on Pt₃Ir cluster with active center as (a) Pt (Pt₃Ir) and (b) Ir (IrPt₃). The structure of the transition state and distances between the C, H and active metal atoms are similar for all the metal clusters examined, as shown in the table (all distances in Å).

Cluster	ΔH_{int}	ΔG_{int}	$k_{\text{Pt3X}}/k_{\text{Pt4}}$
Pt	23	30	1
Pt ₃ Ir	20	28	1.2
IrPt ₃	11	15	14.9
Pt ₃ Sn	20	17	9.2

Table 5.2. Intrinsic enthalpic and free energy activation barriers (kJ/mol) for the dissociative adsorption of ethane on 4-atom clusters. Ratio of reaction rate coefficients for each alloy with respect to pure Pt is shown in the last column.

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5.6. Supporting Information

Table S5.1. Synthetic parameters for making $\text{Pt}_x\text{Sn}_{100-x}$ nanoparticles and the compositions in the final products based on EDX

Sample #	$\text{Pt}(\text{acac})_2$ (μmol)	$\text{Sn}(\text{acac})_2$ or $\text{Ir}(\text{acac})_3$	OAm (mL)	OA (mL)	Ramp Rate ($^{\circ}\text{C}/\text{min}$)	Rxn T ($^{\circ}\text{C}$)
3.8 nm Pt	125	0	0.1	0.1	2	290
3.5 nm $\text{Pt}_{72}\text{Sn}_{28}$	125	42	0.5	0.5	5	290
3.3 nm $\text{Pt}_{75}\text{Sn}_{25}$	125	42	0.8	0.8	2	290

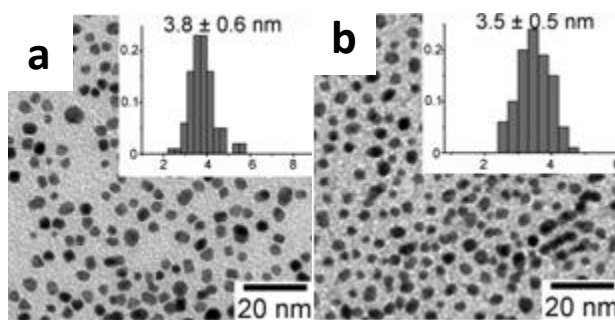


Figure S5.1. TEM images and particle size distribution of a) Pt and b) Pt_3Sn nanoparticles.

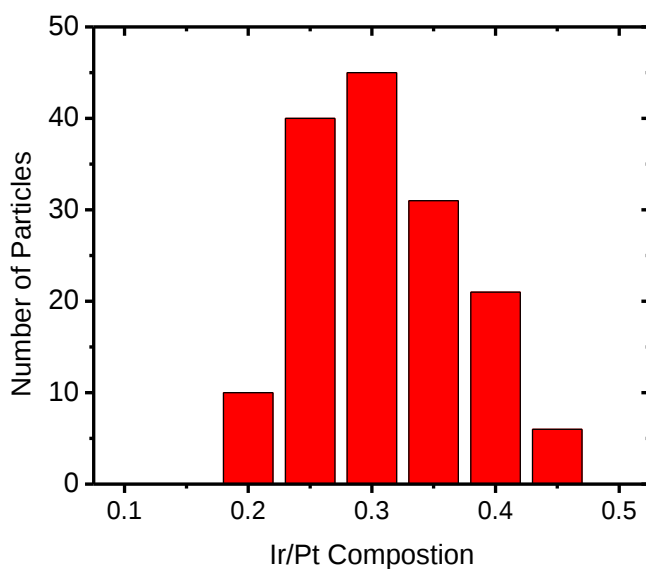
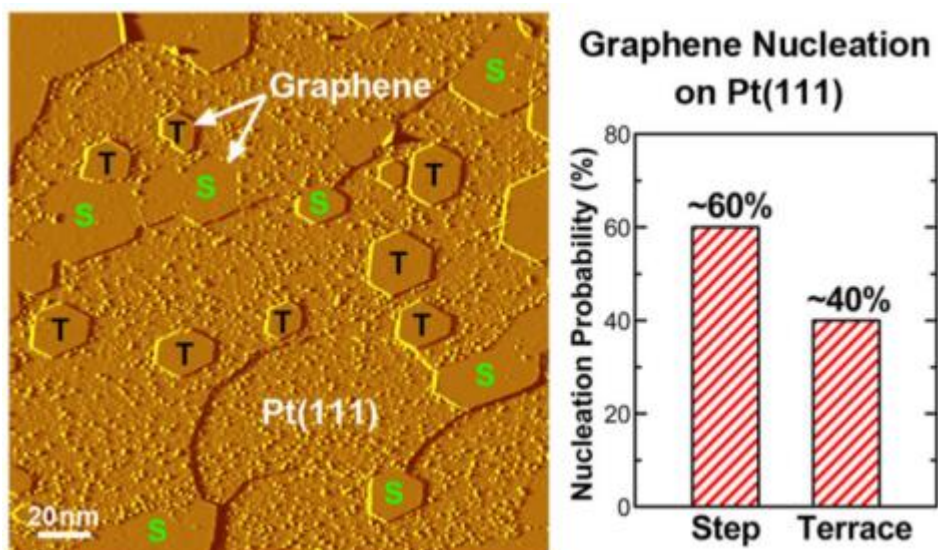


Figure S5.2. Ir/Pt composition per particle distribution of $\text{Pt}_3\text{Ir}/\text{Mg}(\text{Al})\text{O}$ catalyst as determined by STEM-EDS.

Appendix A

An Atomic-Scale View of the Nucleation and Growth of Graphene Islands on Pt Surfaces



Abstract

We study the nucleation and growth of epitaxial graphene on Pt(111) surfaces at the atomic level using scanning tunneling microscopy (STM). Graphene nucleation occurs both near Pt step edges and on Pt terraces, producing hexagonally shaped islands with atomically sharp zig-zag edges. Graphene interacts strongly with Pt substrate during growth, by etching and replacement of Pt atoms from step edges, which result in the re-faceting of Pt steps. The favorable lattice orientations of graphene islands are found to be parallel to those of the Pt substrate, but other orientations are still possible. Grain boundaries are formed when two graphene islands merge with different lattice orientations. Improved growth conditions such as smaller nucleation density and higher growth rate, can produce high-quality graphene film with larger grain sizes.

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A.1. Introduction

Graphene, a single layer of graphite, has recently attracted extensive attention due to its extraordinary physical and chemical properties, making it a promising material for numerous applications [1]. Currently, the major bottleneck for graphene applications lies in the controlled synthesis of large-area, high-quality graphene films. Epitaxial graphene on metal substrates (e.g., Ru, Cu, Ni, and Pt) has been demonstrated to be a promising route [2-6]. Thus, numerous efforts have been made to understand the growth mechanism of graphene on metal substrates [7-17]. For example, the nucleation of graphene islands has been explored by Gao et al. using density functional theory (DFT) calculations [8], indicating that nucleation near a metal step edge is more likely than on a terrace. Using low-energy electron microscopy (LEEM), Loginova *et al.* measured the growth rate of graphene islands on Ru(0001) and suggested that graphene grows by adding carbon clusters of about five atoms [10]. Growth intermediates prior to graphene formation, such as carbon dimers, carbon rectangles and carbon chains, have been identified by using scanning tunneling microscopy (STM) [12]. The strong interaction of graphene with metal substrate during graphene growth, such as metal etching effect, has also been revealed by LEEM and STM [13].

From a catalysis point of view, the formation of graphene film on catalyst metal surfaces is undesired, because the graphene layers coat the catalyst, which prevents the adsorption of reactant species and leads to catalyst deactivation [18]. For example, Pt nanoparticles are active catalysts for alkane dehydrogenation, but they exhibit a high tendency for coke formation and deactivation [19]. Transmission electron microscopy (TEM) observation suggested that graphene formation initiates at low-coordination number sites located at steps on the surface of Pt nanoparticles [20]. Interestingly, the addition of Sn or In atoms to Pt can reduce coke formation, as they might inhibit the formation of carbon films on Pt surfaces [19, 21]. In order to better understand how promoters help achieve a more stable catalyst, a more thorough understanding of carbon growth on the monometallic Pt catalyst is needed. At the same time, the decomposition and conversion of ethene to carbon clusters and graphene films on Pt substrates has been studied by STM [22-26], to obtain a better understanding of carbon-producing surface reactions on metal surfaces, with the goal of controlling coke formation in heterogeneous catalysis.

The present study aims at extending the existing knowledge on graphene nucleation and growth on metal surfaces and providing details on the atomic-level interactions between graphene and metals using STM. The nucleation and growth of graphene on Pt(111) was prepared by the adsorption of a monolayer ethene followed by annealing to 1223 K, producing hexagonal graphene nanoislands. A quantitative statistics of the graphene nucleation sites (step vs terrace) was acquired. The graphene growth resulted in the reshaping of Pt steps, indicating a strong graphene-metal interaction during growth. The formation of grain boundaries in graphene films was also discussed. The results contribute to a deeper understanding of graphene nucleation and controlled growth on metal surfaces.

A.2. Experimental

The experiments were performed using a homebuilt, low-temperature ultrahigh vacuum (UHV) STM operated at a base pressure below 5×10^{-11} Torr [27]. Two Pt samples were used in this study: one is a flat Pt(111) single crystal from MaTeck with broad terraces (>100 nm), and the other is a stepped Pt(111) single crystal from Metal Crystals & Oxides Ltd. with narrow terraces (~ 3 nm). Both samples were cleaned through cycles of degassing at 1323 K, annealing in oxygen,

and Ar ion sputtering at 1 keV. The long-term stability and cleanness of the samples was confirmed by both STM and Auger electron spectroscopy. After Ar ion sputtering the samples were annealed to 1173 K in vacuum before graphene growth. Two methods were used to prepare graphene on Pt. Growth method 1: expose the Pt sample to ethene (2×10^{-7} Torr) at room temperature to saturate the surface with hydrocarbons, and subsequently anneal it to 1223 K in vacuum for 10 min to form graphene. This method was developed to capture the initial nucleation stage of graphene. Graphene growth at lower annealing temperature (1073~1173 K) was also tried, which resulted in graphene islands with similar structures but lower crystallinity. Growth method 2: directly expose the Pt sample to ethene (2×10^{-7} Torr) at 1223 K for 2 min to produce large-area graphene films. The sample was then transferred to the STM station in a connected UHV chamber. All STM images presented in this paper were acquired at 77 K.

A.3. Results and Discussion

Figure A.1a shows an STM image of the flat Pt(111) surface with atomically resolved lattice in the inset. The Pt surface exhibits broad terraces (>100 nm) with relatively smooth step edges. After the adsorption of ethene at room temperature followed by annealing to 1223 K, distinct islands with hexagonal boundaries (forming 120°) were found near the steps (Figure A.1b). Atomically resolved images are shown in the inset revealing the honeycomb lattice of graphene in the islands. The rest of the Pt surface was covered by clusters, likely due to carbon species arising from hydrocarbon decomposition not yet incorporated into crystalline graphene islands [12]. These clusters are typically 1~3 nm in diameter, similar to the clusters formed after ethene dehydrogenation shown in previous reports [24, 26]. The contrast between graphene islands and Pt surfaces covered by carbon clusters is more apparent in the derivative STM image, as demonstrated in Figure A.1c. While most area of the Pt substrate ($\sim 70\%$) was covered by clusters, only a certain fraction of the carbonaceous species nucleated to form graphene islands, either near a step edge or on a terrace.

The locations of the graphene islands were examined to identify the preferred nucleation sites of graphene. For example, Figure A.2a shows a typical STM image of the graphene islands with the contrast enhanced in the derivative image (Figure A.2b). The graphene islands are marked with either ‘S’ or ‘T’, corresponding to their location (near a step edge or on a terrace). Thus, a statistical distribution of the graphene nucleation sites has been acquired over 300 graphene islands, as illustrated in Figure A.2c, which indicates that about 60% of nucleation events occurred near a step edge and 40% on a terrace. This result implies that step edges are slightly preferred for graphene nucleation in this case. This agrees with previous studies suggesting that graphene nucleation is more favorable near a metal step edge than on a terrace [8], as step edges can lower the energy barrier for graphene formation [28]. At high carbon concentrations, however, graphene nucleation occurs both near step edges and on terraces [10], as observed here.

The nucleated graphene islands are mainly hexagonally shaped, with $\sim 120^\circ$ corners, regardless of their locations near a step edge or on a terrace, as shown in Figure A.2. Therefore, the edges are all parallel to a specific crystallographic direction, due to the 6-fold rotational symmetry of graphene lattice. Figure A.3a shows another example of nucleated graphene islands, with an expanded view of an edge of a graphene island in Figure A.3b, where the atomically resolved image indicates the atomically sharp zig-zag structure as the preferred edge direction [29-31]. Similarly, the hexagonal graphene islands on the terraces mainly consists of zig-zag edges, also supporting the notion that C-zig-zag edges are the dominating edge type of graphene formed

on Pt, Cu and Co surfaces [29-31]. Theoretical calculations indeed confirm that zig-zag edges have the lowest formation energy [31], while the interaction with metal substrates may also play a key role in stabilizing the edge structures.

The interaction between graphene and Pt substrate plays a certain role in determining the structure and orientation of nucleated graphene islands. For example, the binding energy and charge transfer between graphene and metal substrate depend on the relative orientation between them [32]. Here we examined the relative lattice orientation between graphene islands and the Pt substrate to understand their interaction. Figure A.3c shows the boundary area between a Pt terrace and a graphene island sitting on a lower terrace. The derivative STM image in Figure A.3d enhances the resolution and helps resolve the atomic lattice structures for both the Pt substrate and graphene islands. It shows that the lattice orientations on the Pt substrate and on the graphene are parallel, as schematically illustrated by the crossing lines (blue for Pt substrate and red for graphene). More precisely, the rotational angle of graphene lattice relative to the Pt lattice is measured to be less than 1° . This alignment may give rise to a higher binding energy and is thus energetically favorable during graphene growth [32]. Nevertheless, rotated graphene domains are still possible due to thermal fluctuations, kinetic limitations, and heterogeneity of the metal substrate. This will result in graphene grains with different Moiré patterns [9, 16] and the formation of grain boundaries that we discuss later.

In addition, the image in Figure A.3d shows a contrast change near the graphene-Pt interface, as pointed out by arrows, which could indicate that the graphene lattice near the Pt boundary is strained and suggest a strong interaction between the growth frontier of the graphene island and adjacent Pt step [33]. Previous thermodynamic models suggest that the nucleation and growth of graphene islands on metal substrates involves an energetic cost due to the lattice mismatch between the metal step edges and graphene [34]. This strain energy could play an important role in graphene synthesis or coking processes.

The graphene-metal interaction is also manifested by the etching and re-faceting of metal steps during graphene growth. Figure A.4a shows an STM image of graphene islands nucleated near step edges. The images reveal that graphene islands can grow by partially embedding into the upper Pt terrace, which implies that Pt atoms were etched away by the growing graphene. An expanded view of a graphene island is shown in Figure A.4b with the atomic lattice structure revealed in the inset. A height profile along the red line and schematic illustration in Figure A.4c show the step etching process by growing graphene. The graphene layer on Pt substrate shows an apparent height of around 1.2 Å, which is much smaller than the geometric spacing measured by LEED (3.7 Å) [22]. This is due to an electronic effect [35], that is, the density of states near Fermi level in graphene is much lower than that in Pt substrate, which forces the tip of the STM to be closer to the surface over the graphene areas. Metal etching during graphene growth on Ru and Au surfaces has been reported in previous studies [13, 36, 37], and here, we also observe that metal etching facets Pt steps, suggesting that graphene prefers particular binding configurations at Pt steps. The hexagonal shapes of embedded graphene islands indicate that the graphene edges facing the Pt steps exhibit the zig-zag termination, indicating that such configuration probably gives rise to a stronger binding between C and Pt steps [38-40]. This is manifested by a graphene film growth mode where Pt steps atoms are etched away, rather than growing over the top of Pt steps. This observation should have important implications in the coking of hydrocarbon reforming catalysts.

The etching or faceting of Pt steps during graphene growth was also examined on a highly stepped Pt surface. Figure A.4d shows an STM image of a clean surface with an average terrace width ~ 3 nm. Such a dense step configuration is probably a better model for the surfaces of

practical Pt catalysts in the form of small nanoparticles. After ethene adsorption at room temperature followed by annealing to 1223 K, the surface reconstructed producing a certain broader terraces, as shown in Figure A.4e. The image in Figure A.4f, in derivative mode, confirms the formation of graphene islands that can be distinguished by the Moiré patterns. The distribution of Pt terraces has changed: some are narrowed, while others are broadened and covered by graphene films. The reconstruction of Pt terraces was also caused by the etching of Pt steps during graphene growth. Compared to the relatively uniform orientation of graphene islands on the large terraces (Figure A.1), the different Moiré patterns indicated a larger fraction of rotated graphene domains. This suggests that the orientation of graphene domains depends on the graphene edge-metal interactions [33]. From the results of graphene growth on stepped Pt surface, it is reasonable to conclude that for practical materials such as Pt nanoparticles used in alkane dehydrogenation, coking processes likely will cause restructuring of the nanoparticles, with important implications for catalytic activity.

Epitaxial graphene films grown on metals are typically polycrystalline, consisting of single-crystalline grains connected by grain boundaries [41-43]. Grain boundaries may affect the properties of graphene film, such as weakening its mechanical strength, and enhancing its chemical reactivity [44-46]. Understanding the formation of grain boundaries is helpful for controlled synthesis and applications of graphene. Generally grain boundaries are formed when two graphene grains merge with different lattice orientations [41]. Figure A.5a shows one example of a grain boundary, where two graphene islands (marked with ‘Gr-1’ and ‘Gr-2’) joint to form a continuous layer. An expanded view in Figure A.5b shows the atomic structure of the grain boundary, where the lattice orientations of the two grains are rotated with each other ($\sim 27^\circ$ in this case). The connectivity between the two graphene grains varies along the boundary line, which might degrade the quality of the graphene sheet [41].

Compared to the growth strategy followed above to prepare the graphene films and study the nucleation, a second growth method was used consisting of directly exposing the Pt sample to ethene at 1223 K for 2 min. Figure A.5c shows a typical image of the produced graphene film using this mode. The atomic lattice structure in the inset indicates the high quality of the graphene film. In this preparation mode, graphene could grow across the steps forming a contiguous layer in contrast with the metal-etching mode where ethene is adsorbed on a room temperature surface and dissociates and diffuses progressively as the temperature increases, a process that more likely corresponds to that of catalytic reactions.

The “hot” growth mode, leading to graphene carpeting over steps, has also been studied using low energy electron microscopy (LEEM) [2]. The key feature of the second method is that ethene adsorbs on a hot surface well above the dissociation temperature, so that the diffusing entities are completely dehydrogenated C clusters. This leads to fewer nucleation centers (smaller nucleation density) and higher growth rate. The nucleation and growth process can therefore be controlled by modifying the heating ramp rate [47].

A.4. Conclusions

To summarize, we have presented a study on the growth mechanism of graphene on Pt surfaces using STM. We have shown that graphene growth by heating pre-adsorbed ethene is very sensitive to graphene-Pt interaction. We have seen that nucleation occurs both near Pt step edges and on Pt terraces, producing hexagonal islands with atomically sharp zig-zag edges. The atomic lattice orientations of the graphene islands are found to be parallel to those of the Pt substrate. We

found that the interaction of graphene with the Pt substrate during growth from pre-adsorbed molecules leads to etching or faceting of the Pt steps. However, when graphene is grown by directly exposing Pt to ethene at high temperature it forms a contiguous film, smoothly carpeting the metal surface over the atomic steps. These results contribute to a better understanding of the nucleation and growth of graphene on metal surfaces and has important implications on the structure and coking of Pt catalysts used in hydrocarbon reactions.

A.5 Acknowledgements

This work was supported by the Office of Basic Energy Sciences, Division of Materials Sciences and Engineering of the U.S. DOE, under Contract No. DE-AC02-05CH11231.

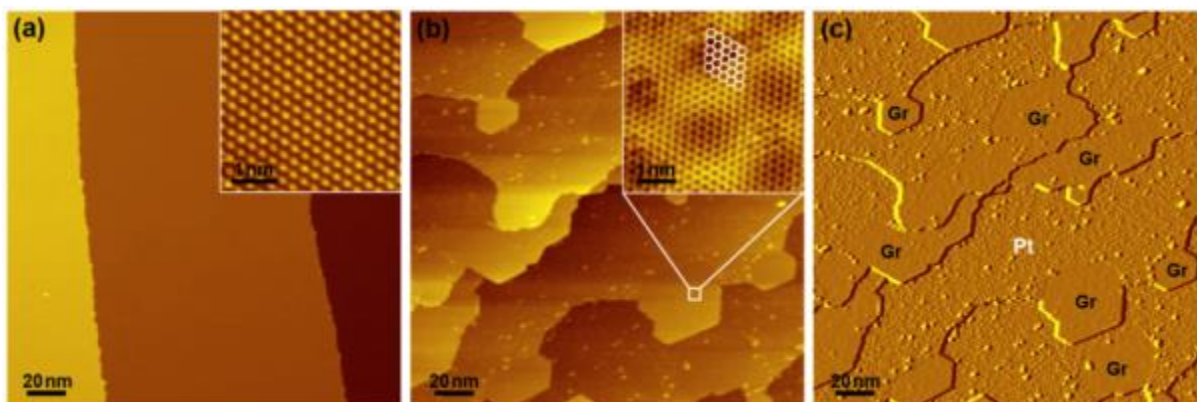


Figure A.1. STM images showing graphene nucleation on flat Pt(111) surface. (a) An STM image of clean Pt(111) surface with atomic structure resolved in the inset. (b) STM topography and (c) derivative image of the Pt surface after graphene nucleation at 950 °C. Graphene islands (smooth areas) are found and can be distinguished easily in the derivative image (c). The atomic structure of the graphene islands is shown in the inset of (b). Imaging parameters: (a) sample bias voltage $V_s = 200$ mV, tunneling current $I_t = 15$ pA; (inset) $V_s = 27$ mV, $I_t = 200$ pA; (b) $V_s = 300$ mV, $I_t = 14$ pA; (inset) $V_s = 20$ mV, $I_t = 400$ pA.

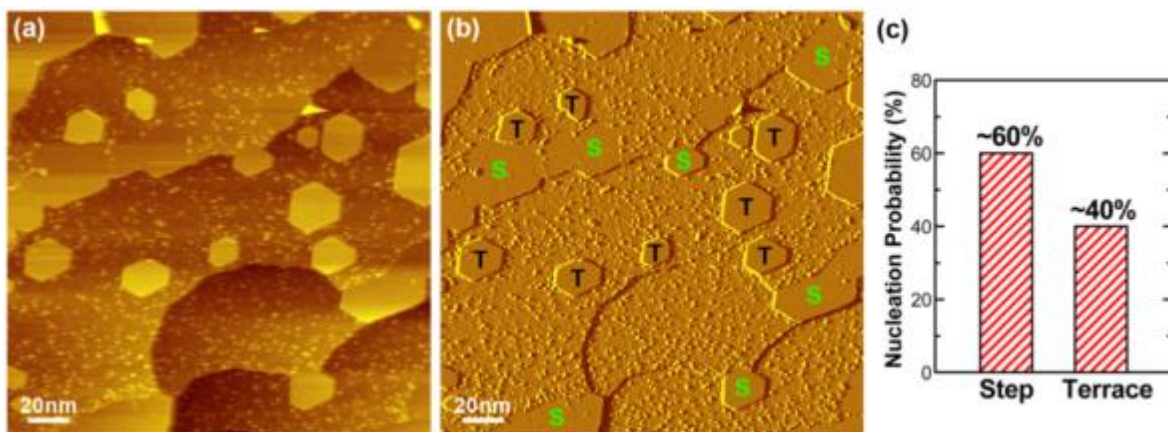


Figure A.2. STM topography (a) and derivative (b) images showing the nucleation of graphene islands on Pt(111) surface. The hexagonal graphene islands are clearly visible in (b), which are marked with 'S' or 'T' according to their locations (near a step edge or on a terrace). Imaging parameters: $V_s = 300$ mV, $I_t = 14$ pA. (c) Statistical data over 300 graphene islands indicate that about 60% of them are located near a step and 40% are on top of a terrace.

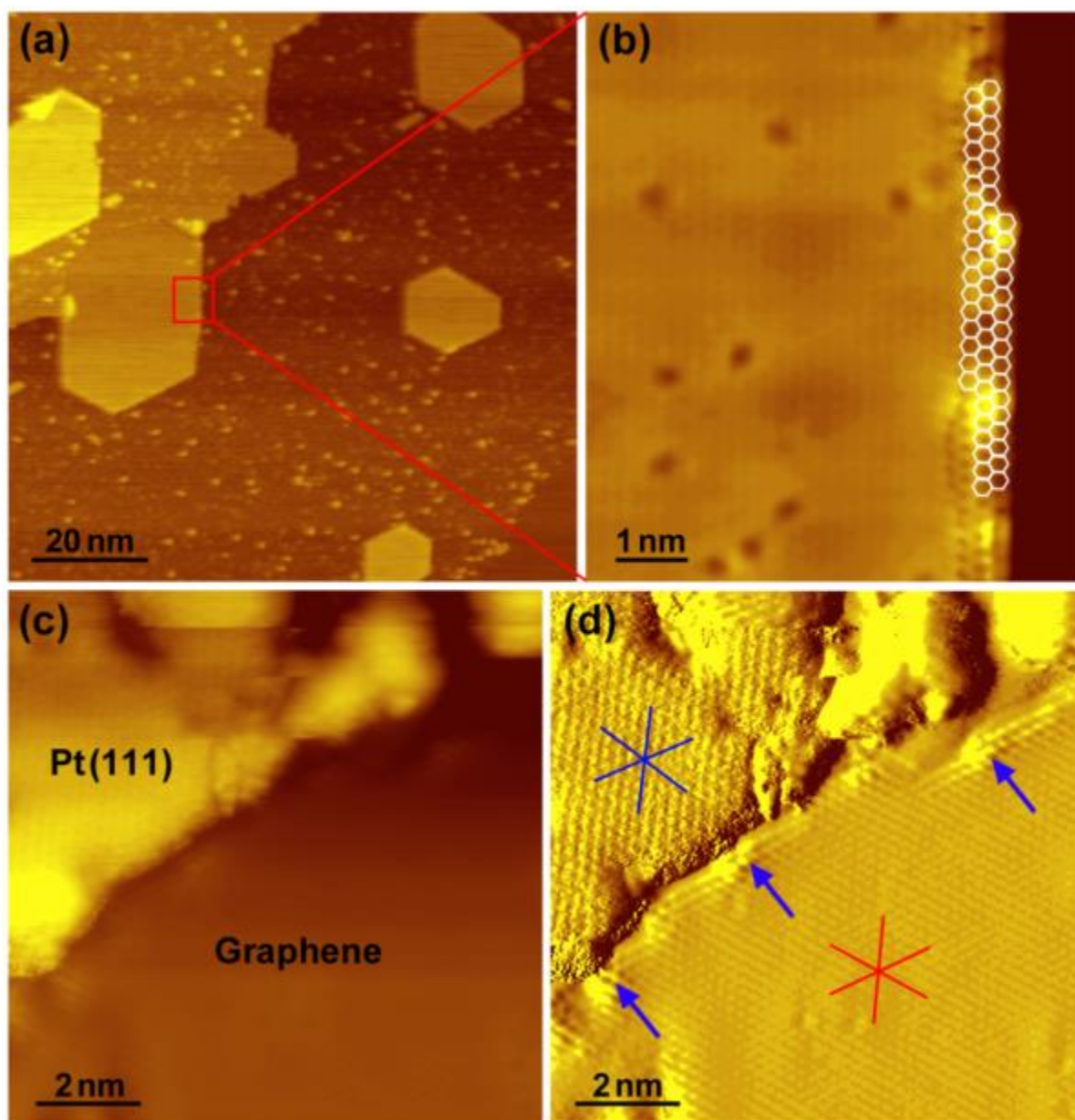


Figure A.3. Edge structure and atomic lattice orientation of graphene islands on Pt(111). (a) STM image showing graphene islands on Pt surface. (b) Expanded view of the zigzag edge structure enclosed by red square in (a). (c) STM topography of the Pt-graphene boundary. (d) Derivative image of (c), showing the atomic lattice of graphene and Pt substrate. The lattice directions of the graphene islands are found to be parallel to those of the Pt substrate. The blue arrows indicate the strained graphene area near the border. Imaging parameters: (a) $V_s = 300$ mV, $I_t = 14$ pA; (b,c) $V_s = 20$ mV, $I_t = 400$ pA.

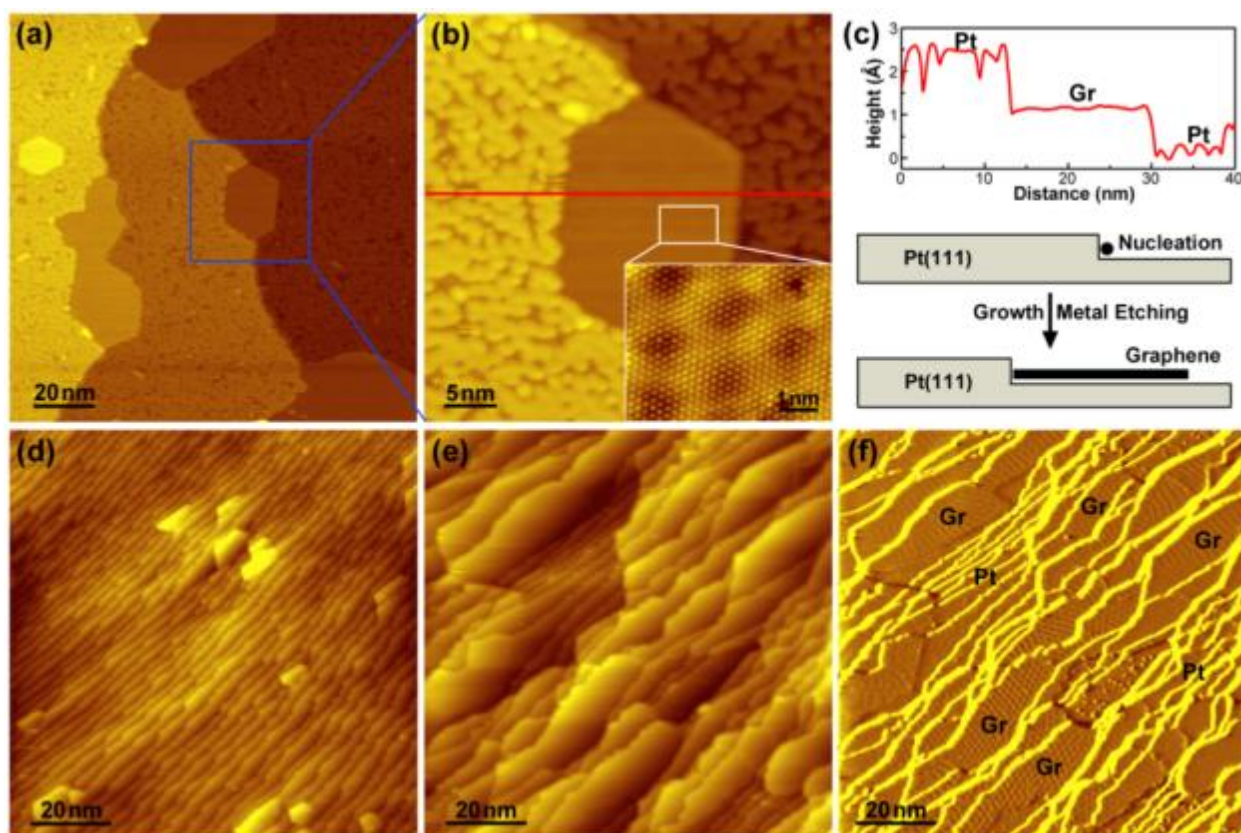


Figure A.4. The interaction between graphene and Pt substrate during graphene growth. (a,b) STM image showing a graphene island that partially etched into the Pt terrace. (c) Height profile along the red line in (b), and schematic illustration of the metal etching during graphene growth. (d) STM image of a stepped Pt(111) surface with a terrace width of about 3 nm. (e) After graphene growth, some of the Pt terraces became broader. (f) Derivative image of (e), which shows the Moiré pattern of graphene domains on the broad terraces. Imaging parameters: (a,b) $V_s = 200$ mV, $I_t = 13$ pA; inset in (b) $V_s = 16$ mV, $I_t = 400$ pA; (d,e) $V_s = 500$ mV, $I_t = 14$ pA.

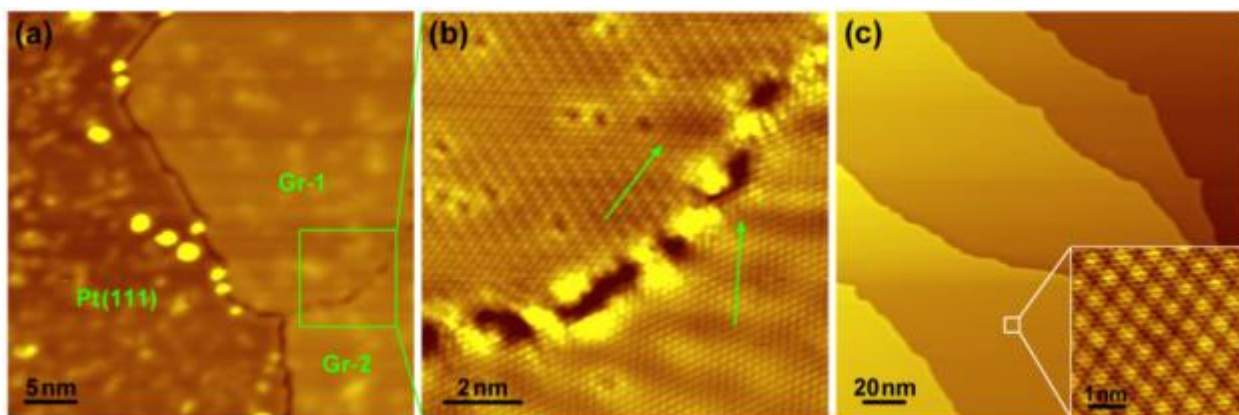


Figure A.5. (a) Two graphene domains merge with different lattice orientations, forming a grain boundary. (b) Expanded view of the atomic structure over the boundary, showing different lattice orientations. (c) The fast growth mode produced continuous high-quality graphene film over the Pt terraces, with atomic structure shown in the inset. Imaging parameters: (a,c) $V_s = 200$ mV, $I_t = 14$ pA; (b) $V_s = 18$ mV, $I_t = 400$ pA; inset in (c): $V_s = 16$ mV, $I_t = 200$ pA.

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