Structure Sensitivity of Alkane Hydrogenolysis on Ir/MgAl₂O₄ Catalysts

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ABSTRACT

In many catalytic systems, the catalytic performance of a metal supported catalyst would be affected by the size and shape of the metals, and this phenomena is called structure sensitivity. Generally, the structure sensitivity effect is considered being led by a combination of geometric property change and electronic property change of the surface metals. The particle size variation is an effective way to change the surface structure of the supported metal catalyst, leading to different fractions of the active sites exposing on the support that would take effect on catalyzing the reaction.

In this project, a series of Ir/MgAl$_2$O$_4$ catalysts with different particle sizes that less than 2nm were utilized for ethane and n-butane hydrogenolysis reactions to study the structure sensitivity effect as well as the potential reaction mechanism. The results show that the activity on the catalysts with nanoparticles and mostly single atoms is evidently higher than that with the subnanometer clusters in both reactions, but the selectivity to the target product of ethane is not quite dependent on the particle size in the n-butane hydrogenolysis. After the fundamental analysis, it is proposed that the reaction mechanism of alkanes hydrogenolysis on the single atom catalysts including single active sites is probably distinctive from that generally accepted on the large particles containing multiple active sites from literature. For n-butane hydrogenolysis, the parallel reaction pathway of central C-C bond cleavage is dominant at low temperature or in the low conversion range. As the temperature going up or the conversion increasing at a certain temperature, the parallel reaction pathway of terminal C-C bond cleavage becomes more and more competitive. The series reaction pathway of hydrogenolysis on propane intermediate would always take place, but the level would be drastically enhanced when the conversion keeps increasing in the very high range. The C-C bond cleavage on the ethane product would not easily happen unless the conversion is close to 100%.
Shale gas is natural gas trapped in shale rocks. Among all the countries that have abundant shale gas reserves, the US, benefited from advanced extraction technology, has the largest production of it. What’s more, the production rate will keep increasing at least for the coming 20 years, and shale gas will eventually become the largest source for natural gas. After extraction, there is a series of treatments shale gas has to go through before it can be utilized, catalytic reaction of alkanes (molecules found in most fuels) is one of these essential procedures. Although they are among the most important compositions of shale gas, different types of alkanes are difficult to separate and purify through traditional methods like condensation. To overcome this obstacle, this thesis focuses on exploring efficient catalysts to convert the n-butane (a straight chain alkane with 4 carbon atoms) to ethane (alkane with 2 carbon atoms). Two reactions are involved: n-butane hydrogenolysis and ethane hydrogenolysis.

Catalysts are some specific materials that can accelerate certain chemical reactions. The catalysts discussed in this thesis are tiny metal (iridium) particles attached to the support material (magnesium aluminate). In this study, the performance of these catalysts with different particle sizes were tested for the above mentioned hydrogenolysis reactions. The results show that changing the particle size of the catalysts considerably affects the rate of these catalytic reactions. The fundamentals of the catalytic system presented in this work can also help the researchers to rationally design the catalysts aiming at higher efficiency and lower cost in the future work.
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Attribution

Appendices A.1: Yubing Lu is currently a PhD candidate who also works with Professor Ayman Karim. He contributed on the catalyst preparation part, as well as the characterization by diffuse reflectance for infrared Fourier transform spectroscopy (DRIFT), chemisorption, and the test of extended x-ray adsorption fine structure (EXAFS).

Ayman Karim is my advisor who conducts as the principal investigator of the research group. He performed the data analysis of extended x-ray adsorption fine structure (EXAFS).

Appendices A.2: Libor Kovarik is the senior research scientist who works in EMSL Environmental Molecular Science Laboratory of Pacific Northwest National Laboratory. He conducted the STEM analysis and provided the images presenting in section A.2 of appendices.

The copyright of the synthesis and STEM characterization part in section A of appendices is reserved for the journal that the article would be published on.

# Table of Contents

Acknowledgement ........................................................................................................ iv

Attribution ..................................................................................................................... v

Table of Contents .......................................................................................................... vi

Chapter 1 Literature Review .......................................................................................... 1

1.1 Structure Sensitivity / Insensitivity ........................................................................ - 1 -
   1.1.1 Single crystal catalysts with different crystal facets ........................................ - 1 -
   1.1.2 Particle size effects in supported metal catalysts ............................................... - 4 -
   1.1.3 Particle shape effects in supported metal catalysts ........................................... - 6 -

1.2 Hydrogenolysis of Alkanes ..................................................................................... 9
   1.2.1 N-butane hydrogenolysis on metal catalysts ....................................................... - 9 -
   1.2.2 Ethane hydrogenolysis on the metal catalysts ..................................................... - 17 -

1.3 Problem Statements ............................................................................................... - 22 -

Chapter 2 Methodology ................................................................................................. 24

2.1 Catalyst Pretreatment and Characterization ........................................................... - 24 -
   2.1.1 Catalyst pretreatment ....................................................................................... - 24 -
   2.1.2 Catalyst characterization .................................................................................. - 25 -

2.2 Experimental Setup ................................................................................................ - 26 -

2.3 Gas Composition Analysis ..................................................................................... - 28 -

2.4 Activity and Selectivity Calculations ...................................................................... - 29 -
   2.4.1 Ethane hydrogenolysis ...................................................................................... - 29 -
   2.4.2 N-butane hydrogenolysis ................................................................................ - 30 -

2.5 Activity normalization ............................................................................................ - 31 -
   2.5.1 Reaction rate .................................................................................................... - 31 -
   2.5.2 Turnover frequency (TOF) with assumption 1 .................................................... - 32 -
   2.5.2 Turnover frequency (TOF) with assumption 2 .................................................... - 34 -

Chapter 3 Results of Ethane Hydrogenolysis ............................................................... 36

3.1 Particle Size Effect .............................................................................................. - 36 -
   3.1.1 Catalysts’ details ............................................................................................. - 36 -
   3.1.2 Basic experiment procedure ............................................................................. - 37 -
   3.1.3 Kinetic parameter results of ethane hydrogenolysis ......................................... - 38 -

vi
3.1.4 Reaction mechanism based on the reaction order results........................................... - 42 -
3.1.5 Ethane hydrogenolysis results correlated with n-butane hydrogenolysis ..................... - 48 -
3.2 Analysis of Transport Limitation................................................................................... - 48 -
Chapter 4 Results of N-butane Hydrogenolysis..................................................................... - 52 -
4.1 Particle Size Effect on the Product Distribution.......................................................... - 52 -
   4.1.1 Catalysts’ details ...................................................................................................... - 52 -
   4.1.2 Basic experiment procedure ................................................................................... - 53 -
   4.1.3 Comparison of product distribution trend .............................................................. - 54 -
   4.1.4 Optimal product distribution .................................................................................. - 61 -
   4.1.5 Exploration for optimal reactants ratio and concentration ..................................... - 63 -
   4.1.6 Analysis of reaction mechanism ............................................................................ - 67 -
4.2 Particle Size Effect on Activity in Kinetic Regime ......................................................... - 72 -
   4.2.1 Basic experiment procedure ................................................................................... - 72 -
   4.2.2 Comparison of activity and activation energy ......................................................... - 73 -
   4.2.3 Comparison of the selectivity and analysis on the mechanism ............................... - 81 -
Chapter 5 Summary and Conclusions................................................................................... - 87 -
Appendices......................................................................................................................... - 92 -
   A. Catalyst Preparation and Characterization ................................................................. - 92 -
   A.1 Catalyst preparation .................................................................................................. - 92 -
   A.2 TEM images ........................................................................................................... - 93 -
   B. Determination of Transport Limitation based on the Criterion[37] .............................. - 95 -
   B.1 Experiments conditions and results ......................................................................... - 96 -
   B.2 Mear’s criterion for external mass diffusion ............................................................ - 96 -
   B.3 Internal diffusion limitation by Weisz-Prater criterion .............................................. - 98 -
   B.4 Intraparticle heat transfer limitation ......................................................................... - 98 -
   B.6 Mear’s interphase heat transfer limitation .................................................................. - 99 -
   B.7 Mear’s criterion for (interparticle) heat transfer limitation ....................................... 100 -
   B.8 A summary of transport limitation criterions for ethane hydrogenolysis on all catalysts.... - 100 -
C. Derivations for the Rate Equation..................................................................................... - 101 -
Reference ......................................................................................................................... - 105 -
Chapter 1 Literature Review

1.1 Structure Sensitivity / Insensitivity

For decades, it is of great interest for the modern researchers to investigate the details of reaction mechanism on the surface of the metal catalysts and correlate the catalytic performance with the structure of different catalysts. By understanding the surface reaction mechanism, it allows the researchers to rationally design the catalysts for specific reactions and control over the reaction pathways, activity and selectivity.[1, 2] It is found that for some of the reactions, the structure of the metal catalysts has a large effect on the reactivity and product distribution. This could be explained by the different interactions of the chemical species with surface sites of the metal catalysts as the geometric properties and electronic properties change for different atom configurations. The reactions that have different catalytic performance with varying structures of the catalysts are called structure sensitive reactions, e.g., ammonia synthesis on iron [3] and ruthenium catalysts [4], and ethane hydrogenolysis over Cu-Ni alloys [5], while the reactions that are generally accepted being independent of catalyst structure change are ascribed as structure insensitive reactions, e.g., CO oxidation on Pd/Al2O3 catalysts [6], and ethylene hydrogenation on Pt/silica catalysts [7]. Recently, the ethylene hydrogenation was also reported as structure sensitive reaction on the Pt/MgO catalysts in the subnanometer regime. [8]

Basically, for metal catalysts in heterogeneous catalysis, the study of structure sensitivity / insensitivity mainly focuses on the two aspects, single crystal metal catalysts with different crystal facets and supported metal catalysts with different particle sizes and shapes.

1.1.1 Single crystal catalysts with different crystal facets

The first proposed evaluation of structure sensitivity / insensitivity is mainly based on the catalytic performance on the single crystal catalysts with different crystal facets. In general, the surface structures of the metal single crystal catalysts are distinguished as various crystal facets, depending on the arrangement
of atoms. Since the spatial environment of the surface atoms on the different facets are distinctive, their ability of adsorbing and dissociating molecules is different, leading to unique catalytic performance. Moreover, most of the surface structures of the single crystal catalysts are not ideal and contain a lot of defects in practice. As shown in the diagram below, in addition to the stable planes of terraces, there are also steps, kinks, adatoms, vacancies existing on the surface. For some of the hydrocarbon reactions on Pt metal catalysts, the kinks and steps have higher efficiency in breaking and formation of C-C bonds, resulting in the structure sensitivity of the reaction. [2]

**Figure 1.1.1** Schematic diagram of the single crystal surface with defects based on figure 5.1.4 of the open source reference [9].

One example of the structure sensitive reaction on single crystal catalysts is the ethane hydrogenolysis on Ni catalysts. Goodman did a series kinetic measurements of ethane hydrogenolysis on Ni (100) and Ni (111) surfaces and made the comparison plot in Arrhenius form as shown in figure 1.1.2. [10]
Figure 1.  A comparison of methane formation rate from ethane hydrogenolysis on (a). Ni (100) and (b). Ni (111) catalyst in the Arrhenius form at a total pressure of 100 Torr, H₂/C₂H₆=100.[10] (Reproduced with permission from Surface Science Volume 123 Issue1 (1982) Page: 7, D.Wayne Goodman, Ethane hydrogenolysis over single crystals of nickel: Direct detection of structure sensitivity. Copyright (1982), with permission from Elsevier)

From the plot, the activation barrier of ethane hydrogenolysis on Ni (100) (plot a) is obviously smaller than on Ni (111) (plot b), which is consistent with the speculation of other researchers that the (111) surface is less active than the (100) surface. [11] They also analyzed the reason for the difference in activity on these 2 crystal surfaces. One possible reason is the difference of electronic properties between the 2 crystal surfaces. If the activity is related to the back-bonding of the metal to the unfilled σ-orbital of ethane molecule, the better back-bonding ability of Ni (100) may lead to the higher activity of ethane hydrogenolysis than Ni (111). The other probability is the different atom arrangement between Ni (111) and Ni (100). As shown in the schematic diagram below, the distance between 2 four-fold hollow sites on Ni (100) is 2.5 Å, while the distance between 2 three-fold hollow sites on Ni (111) is only 1.4 Å, which is at the same level of the C-C bond length, 1.3-1.5 Å. So the C-C bonds adsorbed on the Ni (100) surface are hard to remain intact and more easily to be broken than on the Ni (111) surface, resulting in the activity difference of ethane hydrogenolysis on the 2 Ni crystal surface.[10]
1.1.2 Particle size effects in supported metal catalysts

During the recent decades, tremendous efforts have been devoted towards the improvements of catalytic performance of supported metal catalysts. It is already known that for many catalytic systems, decreasing the particle size of the supported metal catalysts is very effective in the improvement of catalytic performance. For supported metal nanoparticle catalysts, only the surface atoms could serve as active sites for reaction, while the atoms in the bulk that do not have any opportunity to get access to the reactant species are wasted and the fraction of these bulk atoms should be minimized. Besides, among all the surface atoms, those at corners and edges called under-coordinated sites might be especially active for some particular reactions because of the higher chance and better interaction with the chemical species for adsorption, comparing with the well-coordinated atoms at the terrace sites. This could be explained by the difference of electronic properties of the atoms at different positions, which means the binding strength of the metal atoms at different surface sites with the reactant species and reaction intermediates would vary, thereby leading to different product distributions.[12] As a result, when the particle size of the nanoparticles decreases, the fraction of unsaturated surface atoms in the particle would drastically increase, especially the percentage of corner and edge site atoms.
Figure 1.1.4 shows the trend of the atomic ratios of surface atoms to total atoms and the corner and edge atoms to total atoms for FCC nanoparticles with cuboctahedron shape. As we can see from the figure, when the particle size gradually decreases, the fraction of unsaturated sites greatly increases. Specifically, the increase of the fraction of corner and edge atoms is much sharper.[13]

![Graph showing atomic ratios](Image)

**Figure 1.1.4** The size dependence of atomic ratios of surface atoms to total atoms and corner and edge atoms to total atoms for FCC NPs with cuboctahedron shape.[13] (Reproduced with permission from Surface Science Reports 70.2 (2015): 135-187, Beatriz Roldan Cuenya, Farzad Behafarid, Nanocatalysis: size-and shape-dependent chemisorption and catalytic reactivity. Copyright (2015), with permission from Elsevier)

The saturation level of the surface atoms could be evaluated by the coordination number, which is the number of closest neighbored atoms that are bonded to a certain atom. In terms of the active surface atoms, usually only the first shell of coordination number of the surface atoms needs to be considered. Generally, the atoms at terrace sites have larger coordination number, while those at corner and edge sites have smaller
coordination number. The coordination number could be determined by advanced synchrotron x-ray techniques, in particular the extended X-ray adsorption fine structure (EXAFS) and X-ray adsorption near-edge structure (XANES). Nowadays, the researchers have already successfully correlated the average first-shell coordination number of the surface atoms with the particle diameter. [14]

As was mentioned above, downsizing the particle size could increase the fraction of active surface atoms with low coordination numbers, thereby changing the catalytic performance. Thus, it becomes more and more important to precisely control the particle size of the supported metal catalysts. In recent years, the discovery of the isolated metal atoms dispersed on support shed new light on heterogeneous catalysis. Theoretically, all the isolated metal atoms on the surface of the support would participate in the reactions, maximizing the efficiency of the novel metals utilization in catalysis.[15] However, the influence on the activity is uncertain. In general, the metal nanoparticles would allow multiple molecules to adsorb closely to each other, while the number of molecules adsorbed on the single atoms would be very limited. Also, the binding type between a certain reactant molecule to the nanoparticles or the single atoms might be different. In the case that the adjacent sites are required for different reactant molecules to adsorb prior to reaction, the single atom catalyst may not be the best choice to maximize the reactivity.

1.1.3 Particle shape effects in supported metal catalysts

In addition to the particle size, the shape of the catalyst particles also has an influence on the catalytic performance. Generally, it is not easy to synthesize the catalyst that have different particle shapes for comparison with the same particle size. In 2010, Mostafa, S., et al. [16] reported the shape-dependence of catalytic properties of 2-propanol oxidation over a series of Pt nanoparticles supported on γ-Al₂O₃ with different particle shapes as shown below in figure 1.1.5.
In this paper, the authors synthesized 3 catalysts with the particle size of 1 nm but with 3 different shapes, octahedron (S2), cuboctahedron (S4) and 2D structure (S3). Additionally, they also synthesized one catalyst with octahedron shape (S1) with a lower particle size of 0.8 nm comparing with S2. After the reaction, they plotted the onset temperature versus the average number of missing bonds on the nanoparticle surface in figure 1.1.5. The onset temperature could reflect the activity of 2-propanol oxidation on the catalysts. The lower the onset temperature, the higher the activity of the reaction on that catalyst. The average number of missing bonds on the nanoparticle surface could also be correlated with the average coordination number. The more missing bonds on the nanoparticle surface means the lower level of surface atom saturation, thereby resulting in the lower average coordination number. Therefore, the reactivity of 2-paropanol oxidation is correlated with the average coordination number of the Pt nanoparticles. Details of the
relationship between the reactivity and the fraction of surface atoms and corner / edge atoms could also be learned from the plots in figure 1.1.6.

**Figure 1.1.6** Onset temperature for 2-propanol oxidation over Pt NPs / γ-Al₂O₃ versus the percentage of atoms at corners / edges and faces on the NP surface. [16] (Reprinted with permission from (Mostafa, Simon, et al. "Shape-dependent catalytic properties of Pt nanoparticles." Journal of the American Chemical Society 132.44 (2010): 15714-15719.). Copyright (2010) American Chemical Society.)

The coordination number of the corner/edge atoms is 4 - 7, while those at faces is as large as 8 - 9. From the plot in figure 1.1.6, the catalyst of cuboctahedron shape (S3) with the highest percentage of corner/edge atoms and lowest percentage of face atoms is the most active for 2-propanol oxidation reaction, while the catalyst of octahedron shape (S2) with the largest fraction of face atoms but smallest fraction of corner / edge atoms is the least active. As a result, the under-coordinated atoms at the corners / edges of Pt nanoparticles are more active for 2-propanol oxidation reaction than the well-coordinated atoms. Therefore, the particle shape effect on the supported metal catalysts could be ascribed by the difference of the fraction of under-coordinated atoms on the nanoparticle surface.
1.2 Hydrogenolysis of Alkanes

The selective C-C bond cleavage on metal catalysts is a very helpful way for decreasing the chain length of n-alkanes and for the ring opening of cycloalkanes. Moreover, it would also be responsible to the yield losses during hydrocarbon reforming or isomerization. As mentioned, the hydrogenolysis of ethane and n-butane are considered as prototypical structure sensitive reactions on supported metal catalysts. [17-24] Therefore, the hydrogenolysis of alkanes reactions are very worthwhile for us to study as a model for the structure sensitivity effects in catalysis especially in the subnanometer regime that has never been reported previously, so that we can rationally design the catalysts to realize the highest activity and largest selectivity to target products during chain length decreasing reactions and hydrocarbon reforming or isomerization.

1.2.1 N-butane hydrogenolysis on metal catalysts

As we can see from the chemical formula below, the reaction of n-butane hydrogenolysis includes a combination of parallel and series reaction pathways during which the target product of ethane could also performs as an intermediate.

\[
\text{n-C}_4\text{H}_{10} + \text{H}_2 \xrightarrow{\text{①}} 2 \text{C}_2\text{H}_6 \xrightarrow{\text{④}} 2\text{CH}_4 \\
\text{n-C}_4\text{H}_{10} \xrightarrow{\text{②}} 2 \text{CH}_4 + \text{C}_2\text{H}_6 \xrightarrow{\text{⑤}} 2\text{CH}_4 \\
\text{CH}_4 + \text{C}_3\text{H}_8 \xrightarrow{\text{⑥}} \text{CH}_4 + \text{C}_2\text{H}_6 \xrightarrow{\text{⑦}} 2\text{CH}_4
\]

After adsorbing on the surface of the metal catalyst, the n-butane molecule would go through the process of central C-C bond cleavage (step ①) or terminal C-C bond cleavage (step ② and ③), producing two ethane molecules by step ①, two methane molecules and one ethane molecule by step ② or one methane molecule and one propane molecule by step ③. Then, based on the property of the metal catalysts and reaction conditions, the C-C bonds in the product of propane molecules might be further cleaved to form
one methane and one ethane (step ⑥). Meanwhile, the C-C bonds in the product of ethane molecules could also be cleaved into two methane molecules as shown in step ④, ⑤ and ⑦, which, as a consequence, further decreases the selectivity to ethane from the whole reaction. Therefore, it is of great interest to study the reaction mechanism of n-butane hydrogenolysis that would help maximize the selectivity to ethane and minimize the costs for the separation of ethane from other products.

J.R. Engstrom, D.W. Goodman and W.H. Weinberg [23] studied the hydrogenolysis of n-butane on closed-packed (111) and corrugated (110)-(1×2) surfaces of Ir metal. The reconstructed (110) surfaces displayed as (1×2) superstructure have a large fraction of edge atoms with low coordination number in this configuration, and the ratio of edge atoms to the face atoms is 1/2 per unit cell. While on the (111) surface structure, the ratio of edge atoms to the face atoms is several times smaller than that on the (110)-(1×2) surface and only a few under-coordinated atoms exist in this kind of surface structure. In addition, by assuming that the shape of the supported metal catalysts is either octahedron or square-pyramidon as shown in the figure 1.2.1, the effective particle size is about 16.6 or 8.1 nm for (111) surface, and 2.4 or 1.3 nm for (110)-(1×2) surface, respectively. Therefore, after performing the reaction on these two catalysts, it is convenient to determine whether n-butane hydrogenolysis is structure sensitive or insensitive reaction on iridium catalysts.

![Figure 1.2.1 Images of the shape of octahedron and square-pyramidon.](image)
Figure 1.2.2 Selectivity to ethane product as a function of particle size from n-butane hydrogenolysis on Ir (111) and Ir (110)-(1×2) surface (normalized by particle size), as well as the supported catalysts of Ir/Al₂O₃ and Ir/SiO₂ (data from Foger and Anderson[25]). The solid curves represent the theoretical interpolations between the two single crystal catalysts. The reaction temperature in all cases is approximately 475K. The ratio of hydrogen to n-butane is 100 with the partial pressure of 1 torr for n-butane. [23] (Reprinted with permission from (Engstrom, J. R., D. W. Goodman, and W. H. Weinberg. "Hydrogenolysis of n-butane over the (111) and (110)-(1×2) surfaces of iridium: a direct correlation between catalytic selectivity and surface structure." Journal of the American Chemical Society 108.15 (1986): 4653-4655.). Copyright (1986) American Chemical Society.)

The authors also compared their results on the iridium single crystal catalysts with those on the supported iridium catalysts published by Foger and Anderson [25] in figure 1.2.2. From the plot, there is an obvious correlation between the particle size and the selectivity to ethane which caused by the central C-C bond cleavage. And the observed improvement of the ethane selectivity with the decreased particle size could be explained by the higher fraction of under-coordinated surface atoms that participate in the reaction, as the steric hindrance for reactant adsorption on the under-coordinated atoms in the Ir (110)-(1×2) surface structure would be smaller than that on the intact Ir (111) surface. The plot shows that the selectivity to ethane is only about 30% on Ir (111) surface, but even close to 100% on Ir (110)-(1×2) surface. The major
reaction pathway might be \( n-C_4H_{10} + H_2 \rightarrow 2 CH_4 + C_2H_6 \) on the Ir (111) surface and \( n-C_4H_{10} + H_2 \rightarrow 2 C_2H_6 \) on the Ir (110)-(1×2) surface, suggesting the potentially different intermediates during the reaction.

In 1990s, D. Kalakkad et al. [22] also studied the structure sensitivity of n-butane hydrogenolysis on a series of Rh catalysts. They did the experiments of n-butane hydrogenolysis on the synthesized Rh metal supported on alumina and silica supports with different particle sizes (from < 1 to > 5 nm) by changing the metal loadings, and then compared and correlated the particle size effect as well as the pretreatment methods with single crystals to study the selectivity difference.

![Figure 1.2.3](image-url)

**Figure 1.2.3** Comparison of mole reaction of ethane of n-butane hydrogenolysis on Rh/Al\(_2\)O\(_3\) catalysts with different metal loadings by a cycle of pretreatment methods. (The ratio of hydrogen to n-butane is 20:1 with the total pressure of 630 Torr, the reaction temperature is 175°C.) [22] (Reprinted with permission from Kalakkad, D., et al. "n-Butane hydrogenolysis as a probe of surface sites in rhodium metal particles: correlation with single crystals." The Journal of Physical Chemistry 97.7 (1993): 1437-1444.). Copyright (1993) American Chemical Society.)
Figure 1.2.4 Comparison of reaction activity of n-butane hydrogenolysis on Rh/Al₂O₃ catalysts with different metal loadings by a cycle of pretreatment methods. (The ratio of hydrogen to n-butane is 20:1 with the total pressure of 630 Torr, the reaction temperature is 175°C.) [22] (Reprinted with permission from (Kalakkad, D., et al. "n-Butane hydrogenolysis as a probe of surface sites in rhodium metal particles: correlation with single crystals." The Journal of Physical Chemistry 97.7 (1993): 1437-1444.). Copyright (1993) American Chemical Society.)

As the example shown in figure 1.2.3, the selectivity to ethane from n-butane hydrogenolysis on Rh/Al₂O₃ is generally sensitive to the particle size while the activity does not vary greatly on these catalysts as shown in figure 1.2.4. When the particle size of Rh/Al₂O₃ is so small that it is even undetectable by TEM at that time (0.15% Rh/Al₂O₃), the selectivity to ethane from n-butane hydrogenolysis is about 80%, which is much higher than the selectivity of 50% on Rh (111) surface or the selectivity of 30% on Rh (100) and Rh (110) surfaces. As the metal loading and particle size increase, the selectivity to ethane keeps decreasing. In the Rh/Al₂O₃ catalyst series, when the metal loadings are 4.4% and 7.2%, while the particle sizes are 2.5 and 3.0 nm characterized by TEM, the selectivity to ethane is about 50%, which is at the same level as the Rh (111) single crystal surface, but still larger than that on the Rh (100) and Rh (110) surfaces. In general, the dependence of selectivity to ethane and reactive activity on different pretreatment methods is not very clear.
The authors also investigated the relationship between the ethane selectivity and the surface structure of the supported rhodium catalysts with different particle sizes and plotted the fraction of different types of surface atom as a function of particle diameter. The types of the surface atom in the Rh cuboctahedron are presented based on the equations developed by Van Hardeveld and Hartog. [26] The symbol $C_j$ is denoted as a surface atom with $j$ nearest neighbors. To differentiate the atoms with the same number of nearest neighbors but different arrangements, a set of superscripts is also introduced to specify the position of the atom in a particular structure, which, in this case, signifies the rhodium cuboctahedral particles.

![Figure 1.2.5](image)


From the plot in figure 1.2.5(a), as the Rh particle size decreases, the fraction of terrace atoms ($C_9^3$ and $C_8^4,5$) decreases and the fraction of edge atoms ($C_7^5$ and $C_7^9$) and corner atoms ($C_6^8$) increases, and the trends go sharper in the very small diameter range. Combining with the TEM observations, the authors concluded
that the surface structure of larger Rh particles resembles the Rh(111) surface. However, as the particle size decreases, the surface configuration with more C₇ atoms could not be simply analogized with unreconstructed Rh(110) surface. If the high selectivity on the highly dispersed metal catalyst is ascribed to the formation of metallocycle intermediates, the tightly arranged neighboring C₇ atoms in the Rh (110) structure, as shown in the red circle of the surface structure in figure 1.2.6-(a), would sterically hinder the formation of the intermediates, leading to lower selectivity to ethane comparing with the results on the catalyst with Rh (110)-(1×2) structure shown in figure 1.2.6-(b) without neighboring C₇ atoms.[22]

Similarly, it could also help explain the higher selectivity to ethane on the Ir (110)-(1×2) single crystal catalysts comparing with the Ir (111) in Engstrom, Goodman and Weinberg’s work. [23]

Figure 1. 2. 6 Schematic illustration of C₇ atoms on (a) fcc (110) surface, (b) fcc (110)-(1×2) surface, (c) edge atom in cuboctahedron. [22] (Reprinted with permission from (Kalakkad, D., et al. "n-Butane hydrogenolysis as a probe of surface sites in rhodium metal particles: correlation with single crystals." The Journal of Physical Chemistry 97.7 (1993): 1437-1444.). Copyright (1993) American Chemical Society.)
Table 1.1 A brief summary of n-butane hydrogenolysis results from literature.

<table>
<thead>
<tr>
<th>Literature Author and publish year</th>
<th>Catalyst</th>
<th>T (°C)</th>
<th>H₂ / C₄ Ratio</th>
<th>Conversion</th>
<th>Selectivity to Ethane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond and Garcia 2017 [27]</td>
<td>Ru/13X</td>
<td>134</td>
<td>10/1</td>
<td>1.3%</td>
<td>45.7%</td>
</tr>
<tr>
<td>Bond and Yide 1984 [24]</td>
<td>Pt/Silica (O873+R773)</td>
<td>335</td>
<td>20/1</td>
<td>1%</td>
<td>41.5%</td>
</tr>
<tr>
<td>Kalakkad, Anderson et al. 1993 [22]</td>
<td>0.15%Rh/Al₂O₃</td>
<td>175</td>
<td>20/1</td>
<td>0.1-10%</td>
<td>80%</td>
</tr>
<tr>
<td>Bond and Slaa 1995 [28]</td>
<td>RuEC1</td>
<td>160</td>
<td>10/1</td>
<td>-</td>
<td>65.6%</td>
</tr>
<tr>
<td>Engstrom, Goodman et al. 1986 [23]</td>
<td>Ir(110)-(1×2)</td>
<td>202</td>
<td>100/1</td>
<td>&lt;1%</td>
<td>90%</td>
</tr>
<tr>
<td>Fogar and Anderson. 1979 [25]</td>
<td>2.5% Ir/Al₂O₃</td>
<td>170-212</td>
<td>20/1</td>
<td>-</td>
<td>85.4%</td>
</tr>
<tr>
<td></td>
<td>0.9% Ir/SiO₂</td>
<td>180</td>
<td>20/1</td>
<td>7%</td>
<td>76.5%</td>
</tr>
</tbody>
</table>

Table 1.1 is a brief summary of n-butane hydrogenolysis results from literature for comparison. For kinetic study, most of them have the conversion controlled under 1%. From the table we can see that the highest selectivity to ethane, which is 90%, reported among the listed literature was realized when the reaction was performed on the single crystal catalyst Ir (110)-(1×2) at the H₂/n-butane ratio of 100/1, at 202°C. [23]

Among the metal supported catalysts, the Rh/Al₂O₃ catalyst reported by Kalakkad, Anderson et al. [22] has the selectivity as high as 80% at a lower temperature of 175°C with the H₂/n-butane ratio of 20/1. Similarly, Fogar, K., and J. R. Anderson [25] tested n-butane hydrogenolysis on Ir/Al₂O₃ and Ir/SiO₂, and the best selectivity to ethane is about 85.4% and 76.5%, respectively. However, the conversion is always less than 10% which is intentionally controlled for kinetic study in these cases, but extremely low for industry.

The plot of conversion and selectivity to methane, ethane and propane products versus the reciprocal flow rate on the oxidizing ‘decomposed’ Ru / 13X zeolite catalyst with the loading of 0.6% is shown in figure 1.2.7. From the upper plot, as the flow rate decreases, which means the increase of the reciprocal flow rate in the plot, the conversion gradually increases as expected until 45% (temperature is 160°C and constant). Nevertheless, the selectivity to the 3 products does not change at all with the changing flow rate, which is rarely seen in practice. The carbon based selectivity to ethane (defined in section 2.4.2) is about 25.8% after recalculating based on the data provided in the plot. After comparing with other results in table 1.1, the Ru catalyst with 25.8% of the selectivity to ethane at 45% conversion may not be optimal.
1.2.2 Ethane hydrogenolysis on the metal catalysts

Recall the chemical formula of n-butane hydrogenolysis mentioned above, the n-butane hydrogenolysis reaction is a combination of parallel and series reactions. To optimize the selectivity to the target product of ethane and minimize the side products of methane and propane, it is very important to minimize the parallel reaction pathway of terminal C-C bond cleavage \( \Box \) as well as the following series reactions of step \( 4, 5, 6 \) and \( 7 \). As the target product and important intermediate during the series reaction, ethane is the decisive factor for the selectivity in the hydrogenolysis environment. Therefore, the study of ethane hydrogenolysis provides important details in understanding the series reaction mechanism during n-butane
hydrogenolysis on the same series of catalysts and offers good solutions to optimize the selectivity to ethane. Ethane hydrogenolysis is an exothermic reaction as shown in the following equation,

\[
C_2H_6 + H_2 \rightarrow 2CH_4 \quad \Delta H_{298K}^o = -65.2 \text{kJ/mol}
\]

Sormojai, G.A. et al. [29] reported that ethane hydrogenolysis is structure sensitive reaction on Pt supported on SBA-15 Silica. In their work, they first synthesized a series of Pt/SBA-15 with different particle sizes by nanoparticle encapsulation method as well as Pt supported on SiO$_2$ by ion-exchange method with smaller particle sizes, then running ethane hydrogenolysis reactions on these silica supported Pt catalysts as well as Pt powder with extraordinarily large particle size of 287 nm. As a consequence, they showed that the catalytic activity and the measured apparent activation energy of ethane hydrogenolysis were highly dependent on the particle size of the catalysts as shown in figure 1.2.8. As the particle size increases, the catalytic activity of ethane hydrogenolysis, expressed as the turnover frequency of methane formation in the plot, linearly decreases by about 2 orders of magnitude over the size range of 1-3.6nm. After that, further increase in the particle size had small effect on the activity as we can see from the comparison of the Pt powder with the size of 287 nm with those supported Pt catalysts with the size lower than 10nm. Oppositely, the measured apparent activation energy sharply increases as the particle size increases to 3.6nm, after which the apparent activation energy flattens out.
Figure 1.2.8 Dependence of ethane hydrogenolysis turnover frequency and apparent activation energy on Pt particle size. The turnover frequencies were measured at 20 torr C\textsubscript{2}H\textsubscript{6}, 200 torr H\textsubscript{2}, and 658 K. (Reprinted with permission from (Song, Hyunjoon, et al. "Hydrothermal growth of mesoporous SBA-15 silica in the presence of PVP-stabilized Pt nanoparticles: synthesis, characterization, and catalytic properties." Journal of the American Chemical Society 128.9 (2006): 3027-3037.). Copyright (2006) American Chemical Society.)

The details of the catalytic activity and reaction orders of ethane hydrogenolysis on Pt nanoparticles corresponding to different particle sizes are tabulated in table 1.2. On one hand, the authors believed that the ethane molecules and C2 intermediates are very likely to bond with multiple Pt atoms of the particles, making large Pt nanoparticles with several adjacent sites necessary for the adsorption of reactant. On the other hand, the saturation level of the surface atoms is also a decisive factor for the catalytic activity in addition to large particle size. Smaller size particles resemble the crystal surfaces that are comprised of more steps, kinks, and other special sites which increase the surface roughness and lower the saturation level of surface atoms. While larger size particles resemble the flat crystal surfaces such as (111) that are mostly comprised of terrace sites with high coordination numbers. In the case of ethane hydrogenolysis, the ethane molecules are more probably bound to multiple atoms served as different sites instead of one or two atoms on the flat surface. Also, the adsorption energy of the intermediates binding with the atoms in different surface structure are different. For instance, the activation barrier of the most active C\textsubscript{2}H\textsubscript{5} species on the Pt (211) surface is much lower than that on the more flat Pt (111) surface, resulting in the different ability of C-C bond cleavage. [31, 32] These factors might be responsible for the trends that we can see from the plot in figure 1.2.8. Surface roughness of the Pt particles is a very important parameter to weigh the fraction of active sites that usually determines the reactivity.

In the most recent 5 years, David W. Flaherty, Enrique Iglesia et.al. [32] investigated the reaction mechanism of ethane hydrogenolysis by performing experiments on Ir/SiO₂ particles with the size of 7nm and by the computational study of DFT calculations using Vienna ab initio simulation package. They proposed a sequence of elementary reaction steps as potential reaction mechanisms as shown in scheme 1.1, and then confirm the intermediate that goes through the C-C bond cleavage by the combination of experimental reaction rates and reaction orders with DFT results.

\[
H_2 + 2* \rightleftharpoons 2H^* \quad (1)
\]

\[
C_2H_6 + * \rightleftharpoons C_2H_5^* \quad (2)
\]

\[
C_2H_5^* + * \rightleftharpoons C_2H_4^* + H^* \quad (3)
\]

\[
C_2H_4^* + 2* \rightleftharpoons ^*C_2H_3^* + H^* \quad (4)
\]

\[
\rightarrow
\]

\[
\rightarrow
\]

\[
\cdots
\]

\[
^*C_2H_{6-(y-1)} + * \rightleftharpoons ^*C_2H_{6-y}^* + H^* \quad (5)
\]
In the proposed sequence of elementary steps shown in scheme 1.1, the C-H bonds of ethane are gradually replaced by C-metal bonds after the ethane molecules adsorb on the metal. During this process, the C-C bonds are simultaneously weakened as the electron density of C-C bonds are transferred to the metal surface atoms. The H₂ dissociation step (1), ethane adsorption step (1.2) and the dehydrogenation of adsorbed ethane steps (3-5) are assumed as quasi-equilibrated steps based on the H/D exchange experiments during ethane hydrogenolysis process elsewhere and the calculation of activation barriers by DFT study, [34] so the C-C bond cleavage step (6) is the only rate determining step in this case. Macroscopically, the observed hydrogenolysis reaction rate should be proportional to the partial pressure of H₂ and C₂H₆ with the exponent of respective reaction order. Microscopically, the observed hydrogenolysis reaction rate should be the summation of the rates of each elementary C-C bond cleavage step for the intermediates with (6-y) H atoms, written in the equation form of \( r_{obs} = \sum_{y=0}^{\infty} (r_y) = \sum_{y=0}^{\infty} (k_{CC,y} [^*C_2H_{6-y}^*]) \). Therefore, the rate equation derived from the sequence of elementary steps with the C-C bond cleavage of intermediate (\(^*C_2H_{6-y}^*\)) as the rate determining step becomes

\[
    r_y = k_{CC,y} \cdot \left( \frac{\prod_{n=1}^{y} K_{CH,n} \cdot K_{C_2H_6} \cdot (C_2H_6)}{K_{H_2}^\lambda \cdot (H_2)\lambda} \right) \cdot [L]
\]

\( y + \gamma = 2\lambda \)
(\(\gamma\) is the number of \(H^*\)-atoms that desorb from the surface, \(y\) is the number of \(H\) atoms that lost from \(C_2H_6\) molecule to form the intermediate that being cleaved the \(C-C\) bond, \(K_{CH,n}\) is the equilibrium constant of \(H\) removal steps)

(Note: there is no index of \(\lambda\) on the rate constant of \(K_{H_2}\) highlighted in red in the denominator in the original text of reference 32. After recalculating based on the same methods and combining with other literatures published by the same author, it is considered as a mistake of the missing index, which is the same as the partial pressure of \(H_2\).)

The authors also tabulated the thermodynamic parameters for all the potential elementary steps based on the DFT calculations. The reaction enthalpy for \(C-H\) bond cleavage of intermediate \((\ast C_2H_6-y\ast)\) is always smaller than \(C-C\) bond cleavage until \(y\) equals 4. For intermediate \((\ast CHCH\ast)\), the activation barrier for \(C-H\) bond cleavage is 70 kJ·mol\(^{-1}\) higher than \(C-C\) bond cleavage. Therefore, the intermediate \((\ast CHCH\ast)\) is determined as the one that goes through the \(C-C\) bond cleavage. In this case, the number of \(H\) atoms that lost from \(C_2H_6\) molecule is 4 \((y=4)\), and the \(H^*\)atoms that desorb from the surface to makeup the methane molecule is 2 \((\gamma=2)\). Therefore, according to the relationship of \(y+\gamma=2\lambda\), the value of \(\lambda\) should be 3. The results from DFT calculations are consistent with those coming from the experiments. From experiments, they determined that the \(C_2H_6\) reaction order is 1, which is the same as the index of \(C_2H_6\) term in the numerator of the rate equation. While the \(H_2\) reaction order is -3.3, the approximation and absolute of which is exactly the same as the \(\lambda\) value of 3 coming from the rate equation derived by DFT calculations.

### 1.3 Problem Statements

In general, the conversion of \(n\)-butane hydrogenolysis would increase with temperature, but concomitantly the selectivity to the target product would also decrease. The highest selectivity to ethane reported to our knowledge is about 90% with the conversion of about 1% at 202 °C on the \(\text{Ir}(110)-(1\times2)\) surface. For industrial applications, people always expect high selectivity at high conversion range to maximize the yield of the target product. Therefore, it is demanded to design the catalyst with the lowest cost and meantime increase the efficiency of production, which would greatly benefit from the structure sensitivity
/ insensitivity study of n-butane hydrogenolysis reactions on the catalysts with different particle sizes in the subnanometer regime. The particle size effect study plays an important role on understanding the fundamentals of the adsorption and desorption of reactant molecules and the preferred surface structure for the particular reaction, hence rational design of the catalysts could help lead to target properties.

In addition to the particle size effect on the adsorption preference, another important factor that controls the selectivity much is the degree of series reaction of C-C bond cleavage in propane and ethane intermediates. The series reaction of propane hydrogenolysis could help increase the selectivity to ethane and methane simultaneously. However, the series reaction of ethane hydrogenolysis would cause less production of ethane, which is absolutely unexpected. Therefore, it is of great importance for us to figure out the reactivity of ethane on the same series of catalysts and it would be best to find ways to block the series reaction of C-C cleavage on the ethane intermediate from n-butane hydrogenolysis after fully understand the factors that controls the reaction pathways in n-butane hydrogenolysis. In this study, the result of structure sensitivity / insensitivity of n-butane hydrogenolysis and ethane hydrogenolysis reactions on the series of Ir/MgAl₂O₄ catalysts with different particle size distributions is presented. The objective is to understand the mechanism of such alkanes hydrogenolysis reactions on the supported Ir catalysts with different structures or sizes, and find out the decisive factor that controls the reaction pathways, so that the information of size distribution / structure of the catalyst and best conditions that obtained from this study could help maximize the reactivity and magnify the commercial value for industry.
Chapter 2 Methodology

2.1 Catalyst Pretreatment and Characterization

2.1.1 Catalyst pretreatment

The Ir/MgAl₂O₄ catalyst synthesis was developed by another group member, Yubing Lu. The details are presented in the appendices.

The catalyst pretreatment methods are shown in the figures below from Figure 2.1.1 to figure 2.1.4.

**Figure 2.1.1** Pretreatment procedure for 1% Ir/MgAl₂O₄ NPs. The catalyst is heated in 20% H₂ with at the heating rate of 15°C/min, stay at 800°C for 2 hours, and then cool down in H₂ atmosphere.
Figure 2.1.2 Pretreatment procedure for 0.05% Ir/MgAl₂O₄ - 200mL clusters. The catalyst is heated in 5%O₂, then flow with He only and heat to 650°C. The last step is the reduction in 20%H₂ at 700°C for 2 hours followed by cooling down in H₂ atmosphere.

Figure 2.1.3 Pretreatment procedure for 0.05% Ir/MgAl₂O₄ - 1L clusters. The catalyst is heated in 5%O₂, then cool down in He and stay at 50°C overnight. The last step is the reduction in 20%H₂ at 500°C for 2 hours followed by cooling down in H₂ atmosphere.

Figure 2.1.4 Pretreatment procedure for 0.5% Ir(CO)₂(acac)/MgAl₂O₄ NPs. The catalyst is heated in 20% H₂ with the heating rate of 10°C/min and stay at 500°C for 2 hours, then cool down in H₂ atmosphere.

2.1.2 Catalyst characterization

The quantity of CO adsorption was measured through CO chemisorption by the Micromeritics 3 Flex instrument. The characterization using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was conducted at Pacific Northwest National Laboratory.

The size distribution and quantity of CO adsorbed on each catalyst are presented in the tables below.
Table 2.1. Size distribution of 1% Ir/MgAl₂O₄ catalyst reduced at 800°C for 2 hours without calcination.

<table>
<thead>
<tr>
<th>Size range (nm)</th>
<th>Single atoms</th>
<th>0.4 - 0.7</th>
<th>0.7 - 1</th>
<th>1 - 2</th>
<th>Quantity of CO adsorbed (mmol / g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fraction</td>
<td>15.7%</td>
<td>0.2%</td>
<td>6.8%</td>
<td>77.3%</td>
<td>0.053</td>
</tr>
</tbody>
</table>

Table 2.2. Size distribution of 0.05% Ir/MgAl₂O₄-200 mL catalyst reduced at 700°C after calcination at 500 °C.

<table>
<thead>
<tr>
<th>Size range (nm)</th>
<th>Single atoms</th>
<th>0.4 - 0.7</th>
<th>0.7 - 1</th>
<th>1 - 2</th>
<th>Quantity of CO adsorbed (mmol / g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fraction</td>
<td>28.4%</td>
<td>34.7%</td>
<td>29.5%</td>
<td>7.4%</td>
<td>0.00226</td>
</tr>
</tbody>
</table>

Table 2.3. Size distribution of 0.05% Ir/MgAl₂O₄-1L catalyst reduced at 500°C after calcination at 500 °C.

<table>
<thead>
<tr>
<th>Size range (nm)</th>
<th>Single atoms</th>
<th>0.4-0.7</th>
<th>0.7-1</th>
<th>1-2</th>
<th>Quantity of CO adsorbed (mmol / g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fraction</td>
<td>69%</td>
<td>2.0%</td>
<td>15.9%</td>
<td>13.1%</td>
<td>0.00293</td>
</tr>
</tbody>
</table>

Table 2.4. Size distribution of 0.5% Ir(CO)₂(acac)/MgAl₂O₄ catalyst reduced at 500°C without calcination.

<table>
<thead>
<tr>
<th>Size range (nm)</th>
<th>1nm</th>
<th>Quantity of CO adsorbed (mmol / g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fraction</td>
<td>100%</td>
<td>0.0092</td>
</tr>
</tbody>
</table>

2.2 Experimental Setup

Figure 2.2.1 is the schematic illustration of the whole experimental process. The gas flow system is fully PC automated connected with LabView software system and well controlled by the mass flow controller (Brooks Instrument 5850). After the mass flow controller, the gas reactants will go into the quartz tube reactor, which was enclosed by the furnace for heating, and then connected to the gas chromatography (Agilent, 490 Micro GC System), at where the products will be sampled every 2.5 minutes and output the gas composition data to the PC. With the GC data, the conversion and selectivity of the products could be calculated based on carbon balance.
The packed bed reactor setup is shown in figure 2.2. In the study of ethane hydrogenolysis, the quartz tube applied as reactor has a smaller inner diameter of 0.4 cm to minimize the transport limitations for kinetic measurements. While in the study of n-butane hydrogenolysis, a larger inner diameter of 0.7 cm quartz tube is applied as the reactor since the more catalyst amount was loaded in the larger reactor, the higher conversion the reaction would reach.

As displayed in the reactor cross section of figure 2.2, the pelleted catalyst particles are placed in the center of the quartz tube reactor with quartz wool blocking at the two sides of the tube. The quartz wool
applied in the reactor has been confirmed as inert materials before the experiment. In addition to the
temperature monitoring system equipped with the furnace, a second K-type thermocouple is placed at the
center of the reactor bed enclosed by a spiral sheath made from a used thermocouple detector wire that
could afford very high temperature. The second thermocouple is utilized to measure the temperature of the
reactor bed center more precisely, and approximately considered as the inner temperature of the catalyst
bulk where the reaction takes place. For better insulation and temperature stabilization, quartz wool is added
at the two ends of the reactor to seal the furnace.

2.3 Gas Composition Analysis

The reactants are metered electronically by the mass flow controller (Brooks Instrument 5850) with 20%
C₂H₆/He (Airgas certified standard), 10% n-C₄H₁₀/He (Airgas certified standard), pure H₂ and He (Airgas
ultra high purity, 5.0 Grade) mixed together. The 490 Micro GC (Agilent) is calibrated with the calibration
gas (Airgas certified standard), and the calibration of the mass flow controller was conducted by the
flowmeter (Agilent ADM 2000) and the GC. The GC is equipped with a TCD detector and 3 different
columns. Channel 1 is comprised of Mol Sieve 5A PLOT (porous layer open tubular) column with the
carrier gas of Argon and initial pressure of 20 psi and the column temperature of 90°C. Channel 2 and
channel 3 are comprised of Pora PLOT U column and Al₂O₃ column with the carrier gas of Helium and
initial pressure of 22 and 25 psi, respectively. The concentration of a particular gas is calculated by the peak
area multiplying the response factor of the gas that determined from the calibration process, and the
concentration could be read directly from the software. In our study, the H₂ concentration is obtained from
channel 1, the CH₄ concentration is obtained from channel 2, the C₃H₈ and n-C₄H₁₀ concentrations are
obtained from channel 3. Both channel 2 and channel 3 could provide the concentration of C₂H₆ and the
numbers coming from the two columns are very close to each other. In this case, the C₂H₆ percentage is
chosen from channel 3. The automated peak integration by the software is not always satisfactory. At this
point, manual peak is required for obtaining the accurate peak area and better integration.
2.4 Activity and Selectivity Calculations

2.4.1 Ethane hydrogenolysis

The system of ethane hydrogenolysis reaction includes 2 reactants, ethane and hydrogen, with the balance gas of helium as discussed in section 1.2.2.

\[ C_2H_6 + H_2 \rightarrow 2CH_4 \quad \Delta H_{298K}^\circ = -65.2 \text{kJ/mol} \]

The carbon-based ethane conversion is defined as

\[
\text{Conversion} = \frac{\text{Mole of } C_2H_6 \text{ reacted}}{\text{Mole of } C_2H_6 \text{ fed}} = \frac{\text{Mole of CH}_4 \text{ produced}}{\text{Mole of CH}_4 \text{ produced} + 2 \times \text{Mole of } C_2H_6 \text{ unreacted}}
\]

The reaction rate is calculated based on the equation as follows

\[
\text{Reaction Rate} = \frac{\text{Mole flow rate of ethane (mol/s) } \times \text{Conversion}}{\text{Gram of catalyst} \times \text{Quantity of CO adsorbed (mol/g)}}
\]

\[
\text{TOF} = \frac{\text{Mole flow rate of ethane (mol/s) } \times \text{Conversion}}{\text{Gram of catalyst} \times \text{Quantity of CO adsorbed} \times \frac{1}{\text{mole of CO} \text{ total Ir}} \times \text{Dispersion}}
\]

The calculation of turnover frequency (TOF) with different assumptions would be introduced in section 2.5.

The apparent activation energy is determined by the Arrhenius plot reflecting the linear relationship with the equation

\[
\ln(\text{TOF or reaction rate}) = \ln(A) - \frac{E_a}{R \cdot T}
\]
where $R$ is the ideal gas constant with the unit of $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. The slope of the plot is exactly the activation energy in $\text{kJ} \cdot \text{mol}^{-1}$. The intercept is the natural logarithm of the pre-exponential factor, which is not very important in this study.

The reaction order of ethane and hydrogen are obtained by changing the partial pressure of ethane and hydrogen at a certain fixed partial pressure of the other reactant. The slopes of the plot “$\ln(\text{TOF})$ vs $\ln(\text{P}_{\text{C}_2\text{H}_6})$” and “$\ln(\text{TOF})$ vs $\ln(\text{P}_{\text{H}_2})$” correspond to the ethane order and hydrogen order, respectively.

### 2.4.2 N-butane hydrogenolysis

The reaction system of n-butane hydrogenolysis is a little more complicated than the ethane hydrogenolysis system. Since there is more than one product, the concept of selectivity needs to be defined.

The carbon-based n-butane conversion is defined as

$$\text{Conversion} = \frac{\text{Mole of } n-C_4H_{10} \text{ reacted}}{\text{Mole of } n-C_4H_{10} \text{ fed}}$$

$$= \frac{\text{Mole of } CH_4 + 2 \times \text{Mole of } C_2H_6 + 3 \times \text{Mole of } C_3H_8}{\text{Mole of } CH_4 + 2 \times \text{Mole of } C_2H_6 + 3 \times \text{Mole of } C_3H_8 + 4 \times n - C_4H_{10} \text{ unreacted}}$$

The reaction rate is calculated based on the equation as follows

$$\text{Reaction Rate} = \frac{\text{Mole flow rate of } n-\text{butane (mol/s)} \times \text{Conversion}}{\text{Gram of catalyst} \times \text{Quantity of CO adsorbed (mol/g)}}$$

$$\text{TOF} = \frac{\text{Mole flow rate of } n-\text{butane (mol/s)} \times \text{Conversion}}{\text{Gram of catalyst} \times \text{Quantity of CO adsorbed} \times \frac{1}{\text{mol of CO total } Ir} \times \text{Dispersion}}$$

As discussed at the beginning part of section 1.2.1, there are mainly 3 products (methane, ethane and propane) coming from the parallel reaction and series reaction without absolute stoichiometry. The selectivity to the target product of ethane is defined as
Selectivity = \frac{Carbon-based Mole of C_2H_6}{Carbon-based Mole of All C1,C2,C3 Products} \\
= \frac{2 \times Mole of C_2H_6}{Mole of CH_4 + 2 \times Mole of C_2H_6 + 3 \times Mole of C_3H_8}

The calculation method for reaction rate, turnover frequency and apparent activation energy is the same as ethane hydrogenolysis presented in section 2.4.1.

2.5 Activity normalization

One of the most important things for the structure sensitivity study on the catalyst with different weight loadings and particle size distributions is to normalize the activity to atomic level by the same standard so that the comparison would be more reasonable and accurate. Considering the coordination number of Ir-O, Ir-Al and Ir-Mg analyzed from extended X-ray adsorption fine structure (EXAFS) results, it is very probable that some of the catalysts could not be fully reduced by the respective pretreatment showing in section 2.1.1, especially the two low loading catalysts of 0.05% Ir/MgAl₂O₄ with mostly single atoms (0.05% Ir/MgAl₂O₄ -1L) and subnanometer clusters (0.05% Ir/MgAl₂O₄ -200mL). (The EXAFS results would not be analyzed in detail in this thesis.) Therefore, it is of great importance to figure out the fraction of Ir that is on the surface and function effectively.

2.5.1 Reaction rate

First of all, the activity could be normalized by the total amount of Ir surface atoms as reaction rate in the unit of mole of ethane / n-butane reacted per mole of surface Ir per second (mole C₂ or C₄ / mole Ir / s) based on the stoichiometry of “CO : Ir = 1 : 1”. The stoichiometry of “CO : Ir = 1 : 1” is the most general normalization method based on the quantity of CO adsorbed by the catalysts, and it is assumed that the ability of CO adsorption is exactly the same for the catalyst of single atoms, clusters and nanoparticles with different particle size distributions.
As presented in section 2.4.1 and 2.4.2, the following equation describes the calculation for the most general normalization as the reaction rate.

\[
\text{Reaction Rate} = \frac{\text{Mole flow rate of ethane (mol/s)} \times \text{Conversion}}{\text{Gram of catalyst} \times \text{quantity of CO adsorbed} \left( \frac{\text{mol}}{g} \right)}
\]

where the quantity of CO adsorbed is the chemisorption result and it could be read from the Micromeritics 3 Flex directly. Generally, the ability of adsorbing reactant molecules would vary with the particle size. In this case, the broad particle size distribution in the catalyst has already been confirmed by the STEM. Therefore, a more precise normalization based on the fraction of surface Ir atoms could also be derived with different assumptions.

### 2.5.2 Turnover frequency (TOF) with assumption 1

As aforementioned, some of the Ir atoms may be in the sublayer of the MgAl₂O₄ support instead of on the surface based on the EXAFS result. So the first assumption to calculate the dispersion is that the weight loading is very accurate and not all the Ir atoms are on the surface, and the single atoms are more probably being buried in the bulk rather than the clusters and nanoparticles.

Take the 0.05% Ir/MgAl₂O₄ -1L catalyst as an example. Table 2.5 listed the size distribution as well as the estimated stoichiometry of “CO : Ir” and the general accepted dispersion that corresponds to different size ranges. One iridium single atom could approximately adsorbed two CO molecules as confirmed by the Ir(CO)₂ di-carbonyl peak from diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).

**Table 2.5** Size distribution, the estimated stoichiometry of “CO : Ir” ratio and general accepted dispersion for 0.05% Ir/MgAl₂O₄ -1L catalyst.

<table>
<thead>
<tr>
<th>Size</th>
<th>Fraction</th>
<th>Stoichiometry of “CO : Ir”</th>
<th>Dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single atom</td>
<td>69%</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>0.4-0.7</td>
<td>2.0%</td>
<td>1.4</td>
<td>0.95</td>
</tr>
<tr>
<td>0.7-1</td>
<td>15.9%</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>1-2</td>
<td>13.1%</td>
<td>0.7</td>
<td>0.7</td>
</tr>
</tbody>
</table>
Theoretically, the mole of CO adsorbed per mole of total Ir could be calculated as

$$\frac{\text{mole of CO}}{\text{total Ir}} \text{(theoretically)} = 69\% \times 2 + 2\% \times 1.4 + 15.9\% \times 0.9 + 13.1\% \times 0.7 = 1.64$$

Experimentally, the mole of CO adsorbed per mole of total Ir could be obtained from the chemisorption result by

$$\frac{\text{mole of CO}}{\text{total Ir}} \text{(experimentally)} = \frac{\text{quantity of CO adsorbed} \times \text{Ir Molecular Weight}}{\text{loading}} = \frac{(0.00293/1000) \times 192}{0.05\%} = 1.125$$

After comparison it is found that the mole of CO adsorbed per mole of total Ir calculated from the experimental result is evidently lower than that calculated based on the size distribution. Therefore, when the catalyst weight loading is accurate, some of the Ir atoms must not be on the surface. The next step is to make some adjustment on the fraction of single atoms in the theoretical equation, and it is found that when the fraction of single atoms is decreased to 43%, the theoretical result of mole of CO per total Ir would be close to that result of 1.125 calculated from experimental results.

$$43\% \times 2 + 2\% \times 1.4 + 15.9\% \times 0.9 + 13.1\% \times 0.7 = 1.123$$

So the fraction of single atoms that is not in the bulk of the catalyst is 43% instead of 69% observed from HAADF-STEM images. Thereafter, a surface-based size distribution could be obtained by counting the fraction only on the surface.

<table>
<thead>
<tr>
<th>Size</th>
<th>Fraction (all)</th>
<th>Fraction (surface)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAC</td>
<td>69%</td>
<td>58.1%</td>
</tr>
<tr>
<td>0.4-0.7</td>
<td>2.0%</td>
<td>2.7%</td>
</tr>
<tr>
<td>0.7-1</td>
<td>15.9%</td>
<td>21.5%</td>
</tr>
<tr>
<td>1-2</td>
<td>13.1%</td>
<td>17.7%</td>
</tr>
</tbody>
</table>

The dispersion of the catalyst based on the newly adjusted fraction of single atoms could be also calculated as

Corrected dispersion = 43% × 1 + 2% × 0.95 + 15.9% × 0.9 + 13.1% × 0.7 = 68.4%
The turnover frequency could then be calculated by

\[
\text{TOF} = \frac{\text{Mole flow rate of } n - \text{butane (mol/s)} \times \text{Conversion}}{\text{Gram of catalyst} \times \text{Quantity of CO adsorbed} \times \frac{1}{\text{mole of CO total Ir}}(\text{experimentally}) \times \text{Corrected dispersion}}
\]

or

\[
\text{TOF} = \frac{\text{Reaction Rate}}{\frac{1}{\text{mole of CO total Ir}}(\text{experimentally}) \times \text{Corrected dispersion}}
\]

(The reaction rate here was calculated in section 2.5.1)

In the case of 0.05% Ir/MgAl₂O₄-1L catalyst,

\[
\frac{1}{\text{mole of CO total Ir}}(\text{experimentally}) \times \text{Corrected dispersion} = \frac{1}{1.125} \times 68.4\% = 0.608
\]

### 2.5.2 Turnover frequency (TOF) with assumption 2

Another assumption that all the Ir atoms are on the surface and the weight loading may not be accurate could also be made in this case. As the catalyst of 1% Ir/MgAl₂O₄ nanoparticles and 0.5% Ir/MgAl₂O₄ from Ir(CO)₂(acac) (1nm) were prepared by the incipient wetness method, it is assumed that all Ir atoms would be contained in the as-prepared sample. For the catalyst of 0.05% Ir/MgAl₂O₄-1L and subnanometer 0.05% Ir/MgAl₂O₄-200mL clusters prepared by the wet impregnation method, the filtrate contains non-detectable iridium element by inductively coupled plasma atomic emission spectrometer (ICP-AES). However, it is still possible that the actual weight loading is not as high as planned in the synthesis process. When all the Ir atoms are assumed on the surface of the support in this case, theoretically, the dispersion could be calculated based on the original size distribution and the estimated dispersion corresponding to different size range.

Original dispersion = \( \frac{\text{surface Ir}}{\text{total Ir}} \) (theretically) = 69\% \times 1 + 2\% \times 0.95 + 15.9\% \times 0.9 + 13.1\% \times 0.7 = 94.4\%
Also, since the weight loading is assumed to be inaccurate, the mole of CO adsorbed per mole of total Ir should be calculated theoretically instead of experimental-based.

\[
\frac{\text{mole of CO}}{\text{total Ir}} \text{(theoretically)} = 69\% \times 2 + 2\% \times 1.4 + 15.9\% \times 0.9 + 13.1\% \times 0.7 = 1.64
\]

The turnover frequency could then be calculated by

\[
\text{TOF} = \frac{\text{Mole flow rate of } n-\text{butane (mol/s)} \times \text{Conversion}}{\text{Gram of catalyst} \times \text{Quantity of CO adsorbed} \times \frac{1}{\frac{\text{mole of CO}}{\text{total Ir}} \text{(theoretically)}} \times \text{Original dispersion}}
\]

or

\[
\text{TOF} = \frac{\text{Reaction Rate}}{\frac{1}{\frac{\text{mole of CO}}{\text{total Ir}} \text{(theoretically)}} \times \text{Original dispersion}}
\]

(The reaction rate was calculated in section 2.5.1)

In the case of 0.05% Ir/MgAl2O4 -1L catalyst,

\[
\frac{1}{\frac{\text{mole of CO}}{\text{total Ir}} \text{(theoretically)}} \times \text{Origina dispersion} = \frac{1}{1.64} \times 94.4\% = 0.576
\]

The correction parameter for the normalization of TOF is similar based on these two assumptions in section 2.5.2 and 2.5.3. And no matter normalizing with assumption 1 or assumption 2, the activity trend on the particle size would not change.

The calculation for other catalysts is the same with the methods in section 2.5.1 – 2.5.3.
Chapter 3 Results of Ethane Hydrogenolysis

3.1 Particle Size Effect

3.1.1 Catalysts’ details

The main goal of the study on ethane hydrogenolysis is to understand the particle size effect of C-C bond cleavage in alkanes. In addition, the capability of C-C bond cleavage on ethane is also the most important determinant of the product distribution in n-butane hydrogenolysis in the following study since ethane is concurrently serving as one of the intermediates as well as the target product. In other words, the result of the reactivity of ethane hydrogenolysis would be very valuable to analyze the reaction mechanism of n-butane hydrogenolysis on the same series of Ir/MgAl₂O₄ catalysts.

Table 3.1 List of catalysts that are used for the study of ethane hydrogenolysis.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Particle Size</th>
<th>Quantity of CO Adsorbed (mmol/g)</th>
<th>Total Amount</th>
<th>Mole of Ir</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% Ir/MgAl₂O₄</td>
<td>1.3 nm</td>
<td>0.053</td>
<td>50 mg</td>
<td>1.3 E-8</td>
</tr>
<tr>
<td>0.05% Ir/MgAl₂O₄-200mL</td>
<td>0.7nm</td>
<td>0.00226</td>
<td>50 mg</td>
<td>1.3 E-7</td>
</tr>
<tr>
<td>0.05% Ir/MgAl₂O₄-1L</td>
<td>Most Single Atoms</td>
<td>0.00293</td>
<td>50 mg</td>
<td>1.3 E-7</td>
</tr>
</tbody>
</table>

(Note: The ‘200mL’ and ‘1L’ in 0.05% Ir/MgAl₂O₄-200mL and 0.05% Ir/MgAl₂O₄-1L denotes the total volume of solution for dilution during synthesis process; the mole of iridium is calculated based on the total amount in the reactor bed, the catalyst weight loading and the dilution ratio; the quantity of CO adsorbed was measured by Micromeritics 3 Flex; based on the stoichiometry of “CO:Ir=1:1”, the mole of iridium on the surface equals the quantity of CO adsorbed)

The exothermic property of the fast reaction of ethane hydrogenolysis may cause concentration and temperature gradients in the reactor bed, which would affect the accuracy of the kinetic measurement and chemical significance of the rate data. Therefore, the transport limitations need to be well recognized and avoided in all cases of kinetic study of ethane hydrogenolysis. One effective way is to dilute the supported metal catalyst with inert diluent. In this study, after several tests on the dilution ratio, no dilution was applied on the 0.05%Ir/MgAl₂O₄-1L and 0.05%Ir/MgAl₂O₄-200mL catalysts, while 200 times intraparticle dilution
with SiO$_2$ was determined for 1% Ir/MgAl$_2$O$_4$ to eliminate mass and heat transfer limitations. (The details of the dilution ratio test is presented in section 3.2 and calculations for the transport limitation criterion is presented in section B of appendices.) Also, to minimize the transport limitation, a smaller reactor with inner diameter of 0.4 cm was utilized for all the kinetic study of ethane hydrogenolysis.

For all the experiments, the catalyst was pelletized and sieved in the size range of 106-250 μm before the reaction. For all the three experiments, the total amount of 50 mg was loaded in the reactor with a short bed length of 0.6-0.7 cm without any pressure drop. The mole of iridium in the 1% Ir/MgAl$_2$O$_4$ is 1.3 E-8, which is 10 times lower than the mole of iridium in the other two catalyst of 0.05%Ir/MgAl$_2$O$_4$-1L and 0.05%Ir/MgAl$_2$O$_4$-200mL as shown in table 3.1. The average particle size of the 3 catalysts for comparison was summarized from the size distribution results obtained by HAADF-STEM in section 2.1, and as we can see that the 1% Ir/MgAl$_2$O$_4$ NPs catalyst has the largest average size of 1.3 nm, the 0.05% Ir/MgAl$_2$O$_4$-200mL catalyst mainly consists of subnanometer clusters with the average size of 0.7 nm and the 0.05% Ir/MgAl$_2$O$_4$-1L catalyst has a very large fraction of single atoms. The STEM images are provided in section A.2 of appendices.

### 3.1.2 Basic experiment procedure

The basic reaction conditions that would be considered in all experiments are:

Pressure ~ 1atm

H$_2$ / ethane ratio = 10 / 1

Total flow rate = 100 sccm

Temperature range for the activation energy measurement: 335 – 350 °C

Conditions for hydrogen order measurement: 10-19% hydrogen at 1% ethane, 335°C.

Conditions for ethane order measurement: 1-2.8% ethane at 10% hydrogen, 335°C.
After the last step of catalyst pretreatment (usually the reduction step) and the reactor system was cooled down to 60 – 70 °C in 20% H₂, sealed the furnace with quartz wool at the two ends of the reactor. Then turned on 10 sccm H₂, 5 sccm 20% ethane and 85 sccm He and increased the temperature with the heating rate of 5 °C/min, and started GC data collection at the same time. For temperature effect study, followed the real-time production results through the GC with temperature monitoring simultaneously until finding the appropriate temperature for ideal conversion. After obtaining the conversion result as a function of temperature, 335 °C was chosen as the initial temperature point for the activation energy measurement. The temperature range for activation energy measurement is 335-350 °C. For each experiment, the activation energy was measured for 2-6 times to determine the side effect of deactivation on the accuracy, which means that the activation energy result was fitted by the data of both heating process and the cooling process between 335 – 350 °C. The reaction order measurement at 335°C was followed after the cooling down step for the activation energy measurement.

Before the kinetic measurements on any of the catalysts, the blank tests with empty tube and MgAl₂O₄ support were also performed, respectively. The results show that the MgAl₂O₄ support is not active at all and the ethane reactant gas contains 2% impurity of CH₄. Therefore, the concentration of the CH₄ impurity would be excluded from the activity results during the calculation in the following.

### 3.1.3 Kinetic parameter results of ethane hydrogenolysis

Figure 3.1.1 contains the Arrhenius plots, which expressed as the logarithm of the reaction rate (mole of reacted ethane / mole of Ir on the surface / second) as a function of the inverse temperature. In this case, x-axis indicates 1000 / RT, where R is the ideal gas constant in the unit of “J / mol / K”, and temperature is in the unit of Kelvin, hence the activation energy expressed as the slope of the plot has the unit of “kJ / mol”. The “1st Ea” and “2nd Ea” showing in the figure indicate the activation energy measurements by heating and cooling down between 335 – 350 °C at the beginning of the experiment; while the “3rd Ea” and “4th Ea” signify the activation energy measurements by heating and cooling down between 335 – 350 °C at
the end of the experiment. Ethane and hydrogen orders were also tested by changing the flow rate of the reactants between the two cycles of activation energy measurements.

![Activation Energy Plot on 1% Ir/MgAl₂O₄ NPs (average size ~1.3 nm)](image)

**Figure 3.1.1** Arrhenius plot for 1% Ir/MgAl₂O₄ nanoparticles catalyst (average size ~ 1.3 nm) with 200 times intraparticle dilution with SiO₂ in the temperature range of 335-350°C. The 1st and 2nd Arrhenius plot was measured at the very beginning of the experiment by heating and cooling between the temperature of 335 – 350 °C; the 3rd and 4th Arrhenius plot was measured at the end of the experiment after the reaction order measurements.

As we can see from the plots in figure 3.1.1, the activation energy obtained by cooling down from 350 to 335 °C is a little bit higher than those obtained by heating from 335 to 350 °C because the catalyst is always deactivating during the reaction. The 1st activation energy result through heating process is 134 kJ/mol, while the last activation energy result through cooling down process is as large as 160 kJ/mol, but the difference is still no more than 20%. In this study, the 2nd activation energy data was chosen for all experiments in the comparison of the kinetic results. In general, the deactivation on each catalyst is less than 20% within 10 hours for the whole series of kinetic parameter measurement. Table 3.2 is a summary of the deactivation on the three catalysts. TOF is the reaction rate normalized by the method with
assumption 1 that the weight loading is accurate but not all the Ir atoms are on the surface as discussed in section 2.5. TOF (initial) signifies the TOF at the first condition of 1% ethane and 10% hydrogen at 335°C, while TOF (end) is that at the repeated same condition as the first one. The deactivation is calculated based on the difference of TOF (initial) and TOF (end) divided by TOF (initial).

Table 3.2 Deactivation of ethane hydrogenolysis on each catalyst. The unit of TOF is s\(^{-1}\).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Particle Size</th>
<th>Conversion</th>
<th>TOF (initial)</th>
<th>TOF (end)</th>
<th>Deactivation</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% Ir/MgAl(_2)O(_4)</td>
<td>1.3 nm</td>
<td>1.6-3%</td>
<td>1.13</td>
<td>0.91</td>
<td>19.5%</td>
<td>10.5 hours</td>
</tr>
<tr>
<td>0.05% Ir/MgAl(_2)O(_4)-200mL</td>
<td>0.7nm</td>
<td>3.4-9%</td>
<td>0.28</td>
<td>0.24</td>
<td>13.4%</td>
<td>7 hours</td>
</tr>
<tr>
<td>0.05% Ir/MgAl(_2)O(_4)-1L</td>
<td>Most Single Atoms</td>
<td>9-21%</td>
<td>0.74</td>
<td>0.70</td>
<td>5.8%</td>
<td>6.5 hours</td>
</tr>
</tbody>
</table>

As shown in figure 3.1.2, the activity on the 1% Ir/MgAl\(_2\)O\(_4\) nanoparticles is the highest among the 3 catalysts while the activation energy is the lowest, indicating that the catalyst with mostly large size particles is the most active one, and the reaction would also more easily to take place. However, it is surprising that the catalyst of 0.05% Ir/MgAl\(_2\)O\(_4\)-1L with mostly single atoms is even more active than the catalyst of 0.05% Ir/MgAl\(_2\)O\(_4\)-200mL subnanometer clusters, and the activation energy for them is 190.3 and 232.5 kJ/mol, respectively.
Figure 3. 1. 2 Comparison of the 2nd activation energy of ethane hydrogenolysis measured by cooling down from 350 to 335 °C on the catalyst of 1% Ir/MgAl$_2$O$_4$ nanoparticles (average size~1.3 nm) diluted by 200 times with SiO$_2$, the 0.05% Ir/MgAl$_2$O$_4$ - 200 mL subnanometer clusters (average size~0.7 nm), and the 0.05% Ir/MgAl$_2$O$_4$ - 1L catalyst with mostly single atoms.

Recall the size distribution presented in section 2.1.2, it seems that the most fraction of 1% Ir/MgAl$_2$O$_4$ nanoparticles in the size range of 1-2 nm contributes the most to the high activity in ethane hydrogenolysis. However, the second active catalyst of 0.05% Ir/MgAl$_2$O$_4$ – 1L only has 2.5% of particles in the same range, and the majority part is the 69% single atoms, hence the single atoms may also be very active in ethane hydrogenolysis. To estimate the activity of each part of the size range, an equation set based on the size distribution in percentage and the reaction rate (mole of ethane reacted / mole of Ir on the surface / s) at the condition of 1% ethane, 10% hydrogen at 335°C (right hand side of the equation ) is listed below,

\[
\begin{align*}
15.7\% \times x + 0.2\% \times m + 6.8\% \times y + 77.3\% \times z &= 1.13 \\
28.4\% \times x + 34.7\% \times m + 29.5\% \times y + 7.4\% \times z &= 0.28 \\
69\% \times x + 2\% \times m + 15.9\% \times y + 13.1\% \times z &= 0.74
\end{align*}
\]

where x, y, z and m represent the TOF (s$^{-1}$) at the condition of 1% ethane, 10% hydrogen at 335°C coming from the single atoms, the subnanometer clusters in the size range of 0.7 – 1 nm, the nanoparticles in the size range of 1 – 2 nm and the very small clusters in the size range of 0.4 – 0.7 nm.

The equation set could not be solved as there are 4 unknowns in the 3 equations. However, it is possible to do some estimation if the fraction of the clusters could be combined and one unknown could be removed, e.g., merging clusters in the size range of 0.4 – 0.7 nm with those of 0.7 – 1 nm. The estimation shows that the activity of the fraction of size range is always in the order that “large particles > single atoms > clusters” and the activity of the clusters is almost negligible. This estimation may not be accurate as the effect of the different conversion range on these catalysts with various particle sizes might be different on the activity.
But the main conclusion from this part is that ethane hydrogenolysis on the catalyst of nanoparticles with the size of 1-2 nm is more active than on the single atoms, and the catalyst of subnanometer clusters is the least active.

### 3.1.4 Reaction mechanism based on the reaction order results

As discussed in section 1.2.2, the reaction rate equation derived by Flaherty, David W. et al. shows first order in ethane and negative third order in hydrogen, and in that mechanism the adsorbed hydrogen is the most abundant surface species and \(*C_2H_2*\) is the intermediate that undergoes the C-C bond cleavage.[32] However, in this study, the reaction orders are quite different from their results, probably led by different reaction mechanism. Table 3.3 is the summary of all the kinetic parameters on the three catalysts with different particle sizes.

**Table 3.3** A summary of activation energy measured by cooling down from 350 to 335 °C (1% n-butane and 10% H₂ with 100 sccm total low rate) and H₂ order (1% n-butane, 10 – 19% H₂) and C₂H₆ order (10% H₂, 1 – 2.8% n-butane) at 335°C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Particle Size</th>
<th>(^{2\text{nd}}) Ea (kJ/mol) (350-335°C)</th>
<th>Conversion</th>
<th>H₂ Order</th>
<th>C₂H₆ Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% Ir/MgAl₂O₄</td>
<td>1.3 nm</td>
<td>158.5</td>
<td>0.6 – 1.5%</td>
<td>-1.2</td>
<td>0.5</td>
</tr>
<tr>
<td>0.05% Ir/MgAl₂O₄-200mL</td>
<td>0.7nm</td>
<td>232.5</td>
<td>1 – 3%</td>
<td>-0.7</td>
<td>0.05</td>
</tr>
<tr>
<td>0.05% Ir/MgAl₂O₄-1L</td>
<td>Most Single Atoms</td>
<td>190.3</td>
<td>3.5 – 9%</td>
<td>-0.3</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Since the condition of the initial H₂/C₂H₆ ratio for Ea and H₂ order measurements is 10 and similar with that in the literature, it is assumed that the dissociative adsorption of hydrogen and ethane adsorption with H removal steps are quasi-equilibrated. [31, 32] Recall the proposed sequence of the steps and intermediates during ethane hydrogenolysis on 7nm Ir/SiO₂ from Flaherty, David W., et al..

\[
H_2 + 2 * \rightleftharpoons 2 H^* \tag{1}
\]

\[
C_2H_6 + * \rightleftharpoons C_2H_5^* \tag{2}
\]

\[
C_2H_5^* + * \rightleftharpoons C_2H_4^* + H^* \tag{3}
\]
\[ C_2H_5^* + 2 \overset{\cdot}{\Rightarrow} ^*C_2H_4^* + H^* \]  \hspace{1cm} (4)

\[
\rightarrow \\
\rightarrow \\
\cdots
\]

\[ ^*C_2H_6-\langle y-1 \rangle + * \overset{\cdot}{\Rightarrow} ^*C_2H_6-\langle y \rangle + H^* \]  \hspace{1cm} (5)

\[ ^*C_2H_6-\langle y \rangle \Rightarrow CH_a^* + CH_b^* \]  \hspace{1cm} (6)

\[ CH_a^* + xH^* \Rightarrow CH_d + (x+1)^* \]  \hspace{1cm} (7)

Based on the above steps, differential equations could be listed as below.

\[
\frac{d\theta_H}{dt} = k_1^+ P_{H_2} \theta_2^2 - k_1^- \theta_H^2
\]

\[
\frac{d\theta_{C_2H_6}}{dt} = k_2^+ P_{C_2H_6} \theta_- \theta_{C_2H_6}^6 - k_2^- \theta_{C_2H_6}^5
\]

\[
\frac{d\theta_{C_2H_5}}{dt} = k_3^+ \theta_{C_2H_6} \theta_- - k_3^- \theta_{C_2H_5} \theta_H
\]

\[
\frac{d\theta_{C_2H_4}}{dt} = k_4^+ \theta_{C_2H_5} \theta_2^2 - k_4^- \theta_{C_2H_4} \theta_H
\]

\[
\frac{d\theta_{C_2H_3}}{dt} = k_5^+ \theta_{C_2H_4} \theta_- - k_5^- \theta_{C_2H_3} \theta_H
\]

\[
\frac{d\theta_{C_2H_2}}{dt} = k_6^+ \theta_{C_2H_3} \theta_- - k_6^- \theta_{C_2H_2} \theta_H
\]

\[
\cdots
\]

\[
\theta_\ast + \theta_H + \theta_{C_2H_6} + \theta_{C_2H_5} + \theta_{C_2H_4} + \theta_{C_2H_3} + \theta_{C_2H_2} + \cdots = 1
\]
As the partial pressure of hydrogen is much larger than ethane and the dissociative adsorption of hydrogen on the surface is assumed very fast, the $\theta_H$ term ($\theta_H = \sqrt{K_{H_2}P_{H_2}} \theta^*$) would be much larger than all the other terms. Therefore, $\theta^* \sim (K_{H_2}P_{H_2})^{-0.5}$.

By assuming that “*C$_2$H$_2$*”, “*C$_2$H$_3$*”, “*C$_2$H$_4$*”, “*C$_2$H$_5$” and “*C$_2$H$_6$” as the intermediate that undergoes C-C bond cleavage and all the other steps as quasi-equilibrated steps (differential equations equal zero), the derived hydrogen order would be -3, -2.5, -2, -1.5, -1, respectively, while the ethane order is always 1 for all these cases. However, the “*C$_2$H$_6$” species should not be considered as the intermediate that undergoes the C-C bond cleavage, as the adsorbed ethane species must dehydrogenate first before breaking the C-C bonds. Therefore, the “-1” hydrogen order does not make sense and should be excluded from the list. Therefore, it seems that when the C-C bond cleavage on “*C$_2$H$_5$” is considered as the rate determining step and the adsorbed hydrogen is assumed to be the most abundant surface species, the derived order of -1.5 in H$_2$ and 1 in ethane is the closest to the experimental results of the reaction orders -1.2 in H$_2$ and 0.5 in ethane.

It could also be assumed that a series of adsorbed hydrocarbon species are the most abundant surface intermediates. The derived reaction order results as well as the assumptions could be found in the table 3.4 shown below.

Table 3.4 Possibilities for H$_2$ and C$_2$H$_6$ orders with different assumptions on the most abundant surface species and the intermediates that considered for C-C bond cleavage. The rate determining step is always the C-C bond cleavage in the cases showing in this table.

<table>
<thead>
<tr>
<th>Intermediate for C-C bond cleavage</th>
<th>MASI</th>
<th>H$_2$ Order</th>
<th>C$_2$H$_6$ Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>*C$_2$H$_5$</td>
<td>*C$_2$H$_6$</td>
<td>-0.5</td>
<td>-1</td>
</tr>
<tr>
<td><em>C$_2$H$_4$</em></td>
<td>*C$_2$H$_6$</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td><em>C$_2$H$_3$</em></td>
<td>*C$_2$H$_6$</td>
<td>-1.5</td>
<td>-1</td>
</tr>
<tr>
<td><em>C$_2$H$_2$</em></td>
<td>*C$_2$H$_6$</td>
<td>-2</td>
<td>-1</td>
</tr>
<tr>
<td><em>C$_2$H$_2$</em></td>
<td><em>C$_2$H$_3$</em></td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td><em>C$_2$H$_2$</em></td>
<td>*C$_2$H$_5$</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td><em>C$_2$H$_3$</em></td>
<td>*C$_2$H$_5$</td>
<td>-0.5</td>
<td>-1</td>
</tr>
</tbody>
</table>
Form table 3.4, when the most abundant surface intermediate is assumed as *C_{2}H_{6} species, the ethane order is always -1 and the H_{2} order changes between -0.5 and -2 as the intermediate for C-C cleavage changes from *C_{2}H_{5} to *C_{2}H_{2}*'. There are also some other possibilities listed in the table as the most abundant surface intermediates are assumed as other dehydrogenated hydrocarbon species. In addition to the previous analysis when the surface hydrogen is the most abundant surface intermediate, the actual reaction mechanism is very likely shown as the combination of these two cases. In other words, the most abundant surface species might be both of the surface hydrogen and the adsorbed hydrocarbon species. For example, if the rate determine step is the C-C bond cleavage on the intermediate of *C_{2}H_{5} and both of surface hydrogen and adsorbed *C_{2}H_{6} species are assumed to be the most abundant surface intermediates, the simplified surface terms could be written as “θ_{H} + θ_{C_{2}H_{6}}~1”. And if so, the θ_{*} term has to be written as the combination of H_{2} and C_{2}H_{6} terms, and the rate equation could be written as the equation below. Details of the derivation process are shown in the appendices part C.

\[
    r = K_{C-C} \frac{K_{C_{2}H_{5}}K_{C_{2}H_{6}}P_{C_{2}H_{6}}}{(K_{H_{2}}P_{H_{2}})^{1.5} + 2 \times K_{H_{2}}P_{H_{2}} \times K_{C_{2}H_{6}}P_{C_{2}H_{6}} + \sqrt{K_{H_{2}}P_{H_{2}} \times (K_{C_{2}H_{6}}P_{C_{2}H_{6}})^2}}
\]

Besides, in the following mechanism examples, by assuming "*C_{2}H_{5}" as the intermediate that undergoes C-C bond cleavage, the derived hydrogen order could be -1.5, while the ethane order would still be 1. In fact, Cortright, R. D., et al. also proposed in their paper that *C_{2}H_{5}* is one of the two possible intermediates (the other one is “CHCH_{3}”) for C-C bond cleavage on Pt (211) and Pt (111) slabs. [31, 32]

\[
    H_{2} + 2 * \Rightarrow 2 H^{*} \quad (1)
\]

\[
    C_{2}H_{6} + * \Rightarrow C_{2}H_{6}^{*} \quad (2)
\]

\[
    C_{2}H_{6}^{*} + 2 * \Rightarrow *C_{2}H_{5}^{*} + H^{*} \quad (3)
\]

\[
    *C_{2}H_{5}^{*} \rightarrow CH_{2}^{*} + CH_{3}^{*} \quad (4)
\]

\[
    \cdots
\]
The only possibility to get the ethane order close to or less than zero is to assume the hydrogen adsorption step as the rate limiting step. When assuming the \( \text{C}_2\text{H}_6 \) as the most abundant surface species and the dissociative adsorption of \( \text{H}_2 \) is the rate determining step, the \( \text{H}_2 \) order could be 1 and the ethane order could be -2. After comparing with the experiment results, the reaction on the nanoparticles is not very likely to take place under this mechanism. As it has also been reported that the \( \text{H}_2/\text{D}_2 \) exchange under deuterium and hydrocarbon atmosphere for the nanoparticles is very fast comparing with the hydrogenolysis rate. [34] However, on the single atom catalysts or very small clusters, the dissociative hydrogen adsorption step is possibly to be the rate determining step as a consequence of the very slow \( \text{H}_2/\text{D}_2 \) exchange rate. For instance, the \( \text{H}_2/\text{D}_2 \) exchange rate on the MgO supported mononuclear Ir catalysts is very low reported by Lu, Jing, Pedro Serna, and Bruce C. Gates. [35]

In this study, the ethane reaction order measured on all the three catalysts with different particle sizes is between 0 – 0.5, comparing with that always being 1 derived from a series of reasonable reaction mechanisms in the previous analysis. Except the aforementioned very slow rate of dissociate hydrogen adsorption, there are also other more reasonable possibilities for the inconsistency. One is that the experimental results of ethane order could be a combination effect as the particle size distribution is very broad. For ethane hydrogenolysis on the large nanoparticles in the size range of 1 – 2 nm, the reaction mechanism might follow the analysis above, while for those on the single atoms, the reaction mechanism
might be quite different from those proposed for large particles in the literature. One possibility is that the binding of ethane species to the single atom requires an extra site on the support, for example, one oxygen atom of MgAl\textsubscript{2}O\textsubscript{4} support and one Ir single atom bind to the two carbon atoms simultaneously. It is also possible that the ethane species may bind only with one site and form π bond as the dehydrogenated steps happen upon adsorption, or both of the two carbon atoms in the ethane molecules could bind with one Ir single atom through di-σ bonds as the ethane molecules is dehydrogenated during the binding process, since the single atom catalyst only contain one Ir atom. And in these two cases, the intermediate that corresponds to the C-C bond cleavage could only have less than 4 hydrogen atoms. If the dehydrogenated ethane species could be adsorbed on single Ir atoms and form π bonds, the binding energy would be much weaker than that for the subnanometer clusters, which would more probably form a much stronger di-σ bond between the dehydrogenated hydrocarbon species and the neighbored Ir sites within the cluster. The adsorption of ethane molecule on the surface of nanoparticles would be also likely to form di-σ bonds, but the binding energy of the di-σ bonds should be lower than that on the surface of subnanometer clusters because of the steric effect. These possibilities might be able to explain the higher activity of ethane hydrogenolysis on the nanoparticles and single atoms than that on the subnanometer clusters.

Another possible reason for the inconsistent ethane order is the improper H\textsubscript{2}/C\textsubscript{2}H\textsubscript{6} ratio for the ethane order measurement. The hydrogen partial pressure applied in the hydrogenation / hydrogenolysis reactions is always very high and at least 10 times higher than the hydrocarbon reactant, since the hydrogen species is more favorable to cover the surface of the catalyst to prevent carbon deposition from the hydrocarbon species. Meanwhile, one of the most important prerequisite for the derivation of ethane order is that the θ\textsubscript{H} term is much larger than all the other surface coverage terms so that all the other surface coverage terms could be negligible for simplification. However, in this study, the H\textsubscript{2}/C\textsubscript{2}H\textsubscript{6} ratio decreases from 10 to 3.5 during the ethane reaction order measurement, and so the derived reaction order from the mechanism analysis could not fit the experimental result well. As discussed in the previous analysis, it is very probable that both of the surface hydrogen and the hydrocarbon species are the most abundant surface intermediates,
so that the experimental result of the ethane order is a combination of the reaction mechanisms with different intermediates as the most abundant surface species. In the future work, more catalysts would be applied in the reaction order measurement to get the ethane order at higher hydrogen partial pressure range to learn the H₂/C₂H₆ ratio effect. Moreover, the study of H₂/D₂ exchange rate on the same series Ir/MgAl₂O₄ catalysts is also a good point to determine if the dissociate hydrogen adsorption step is fast enough to be assumed as quasi-equilibrated step.

3.1.5 Ethane hydrogenolysis results correlated with n-butane hydrogenolysis

As the most important intermediate and decisive factor for the selectivity in n-butane hydrogenolysis, the reactivity of ethane hydrogenolysis would cast light on the reaction pathways of n-butane hydrogenolysis. Therefore, an extra experiment of ethane hydrogenolysis was performed on the 1% Ir/MgAl₂O₄ NPs without any dilutions at 160 °C and 200 °C that simulates the conditions in the experiment of n-butane hydrogenolysis. The result shows that with 0.88g catalyst, the conversion is only about 0.08% at 160 °C with 100 sccm total flow rate. When the total flow rate further decreases to 20 sccm, the conversion is still less than 0.2%. But at 200 °C with 50 sccm total flow rate, the conversion is as high as 10%. The influence of these results on the n-butane hydrogenolysis would be discussed in chapter 4.

3.2 Analysis of Transport Limitation

A catalytic diffusion process includes the diffusion of the reactant molecules in the gas phase to the catalyst particle surface and the transport within the pores of the catalyst particle. This is called mass transport phenomena. When the diffusion rate is much higher than the reaction rate, the catalysts are utilized in the most effective way. In addition to the mass diffusion, heat transport phenomena also needs to be considered as energy is another decisive factor that has great effect on the reactivity. For exothermic reactions, the excessive heat released during the reaction would cause the inner bed of catalyst or particle cores overheated;
for endothermic reactions, the inadequate heat diffusion might limit the energy adsorbing and the reaction rate could be lower hence. Therefore, for kinetic parameter measurements, both of heat and mass diffusion should be well controlled so that the catalytic process would be considered as “reaction-limited” and the kinetic study could be meaningful. [11] This is the reason why we need to guarantee the reaction is free of transport limitations for the intrinsic kinetic study of ethane hydrogenolysis.

The most accurate method to determine if there are transport limitations or not is to study the dilution effect in a particular catalytic system. One typical example of dilution effect study for the determination of transport limitations that would be shown in the following text is ethane hydrogenolysis on the high loading catalyst of 1% Ir/MgAl$_2$O$_4$ nanoparticles with the average size of 1.3nm.

As the details shown in table 3.4, a series of 1% Ir/MgAl$_2$O$_4$ catalysts was diluted (mass-based) with the diluent of SiO$_2$ powder before reaction. The SiO$_2$ powder was calcined in the muffle furnace at 850°C for 5 hours with a ramp rate of 5°C/min before use. The post-calcined SiO$_2$ was confirmed as inert material through the SiO$_2$ blank test of ethane hydrogenolysis reaction. After adding the post-calcined SiO$_2$ powder into 1% Ir/MgAl$_2$O$_4$ catalyst by a certain mass-based ratio, the mixture was further grinded and shock on the shaker for better mixing. Then the mixed powder was sent to the pelletizer and made the pellet with the size range of 106 – 250 μm. To minimize the heat transport limitation, the reactor applied in ethane hydrogenolysis study has the inner diameter as small as 0.4cm. With such a thin reactor tube, the catalyst bed length must not be too long in case the pressure drop would be very high and limit the throughput and conversion of the reaction. [36] Hence the total amount of catalyst utilized in these reactors was controlled between 50-100 mg (the catalyst bed length of 0.7cm - 1.5cm). For the No.1 and No.2 in table 3.5, the total amount of the diluted catalyst is 50 mg since the dilution ratio of them is in the low range, while the total amount of the diluted catalyst is 100 mg for No.3 because of the higher dilution ratio. The total mole of iridium in the reactor for comparison and the normalized activity (turnover frequency based on assumption 1 discussed in section 2.5.2) is also presented in the table.
Table 3.5 Details of 1% Ir/MgAl₂O₄ catalysts utilized for dilution effect experiments and a comparison of the activity results. The inner diameter of reactor utilized here is 0.4cm. The total flow rate is 100 sccm with 1% ethane and 10% H₂ balanced with Helium.

<table>
<thead>
<tr>
<th>No.</th>
<th>Dilution times (SiO₂)</th>
<th>Pellet Size</th>
<th>Mole of Ir</th>
<th>Conversion % (335°C)</th>
<th>TOF s⁻¹ (335°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>200</td>
<td>0.106-0.250 mm</td>
<td>1.3 E-8</td>
<td>1.63%</td>
<td>1.13</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>0.106-0.250 mm</td>
<td>1.3 E-7</td>
<td>4.02%</td>
<td>0.28</td>
</tr>
<tr>
<td>3</td>
<td>1000</td>
<td>0.106-0.250 mm</td>
<td>5.2 E-9</td>
<td>0.54%</td>
<td>0.94</td>
</tr>
<tr>
<td>4</td>
<td>2000</td>
<td>Fine powder</td>
<td>2.6 E-9</td>
<td>0.35%</td>
<td>1.24</td>
</tr>
</tbody>
</table>

As we can see from the table, the TOF is 1.13 when the dilution ratio is 200 times (No.1). As the dilution ratio increases 5 times (No.3), the TOF decreases by about 16%. The difference of 16% in the normalized activity could be either within experimental error or coming from the smaller heat transfer limitation as the diluents could help undertake part of the heat and prevent from overheating the catalyst bed during the reaction, as the reaction of ethane hydrogenolysis is exothermic. However, when the catalyst was diluted by 2000 times with SiO₂ (No.4) without pelletizing, the TOF is a little higher than those two with 200 and 1000 times dilution (No.1 and No.3). The overall fluctuation of TOF on the 3 catalysts with 200, 1000 and 2000 times dilution is no more than 16%, which is within the reasonable error range. These results indicate that the 200 times intraparticle dilution with SiO₂ is high enough to eliminate the heat transport limitation.

Moreover, increasing the dilution ratio could concurrently help decrease the mass transfer limitation. To make sure that 200 times dilution is not too large, a 20 times dilution was also examined. As we can see from figure 3.2.1, the TOF of the one with 20 times dilution is much smaller than the other three experiment results with 200-2000 times dilution. It is very possible that the one with only 20 times dilution has mass transfer issues. The reactant molecules could not easily travel in the porous catalyst pellets, which means many of the active sites sit on the surface of the pores inside the catalyst pellets do not take effects, leading to a much lower TOF. Therefore, 200 times intraparticle dilution ratio is optimized for ethane hydrogenolysis study on 1% Ir/MgAl₂O₄ catalyst.
Figure 3. 2. 1 Comparison of turnover frequency of ethane hydrogenolysis as a function of temperature on 1% Ir/MgAl₂O₄ catalysts with different times of intraparticle dilution with SiO₂. The pellet diameter range of catalysts with 20, 200 and 1000 times dilution was 0.106-0.250 millimeter, while the one with 2000 times dilution was applied as fine powders without pelletizing.

The heat and mass transport limitations within the catalyst bed could also be determined by the calculation of the criterion. The example of the calculation procedure on the 0.05% Ir/MgAl₂O₄ – 200mL catalyst and the summary of the results based on the criterion would be provided in the appendices B part.
Chapter 4 Results of N-butane Hydrogenolysis

4.1 Particle Size Effect on the Product Distribution

4.1.1 Catalysts’ details

The first part of the study on n-butane hydrogenolysis is to understand the particle size effect on the product distribution, which is vital for understanding the reaction pathways and rationally designing low-cost and effective catalysts for industry. The information of catalysts that applied in this study has been summarized in table 4.1.

Table 4.1 List of catalysts that are used for the structure sensitivity study on catalytic performance of n-butane hydrogenolysis.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Dilution</th>
<th>Average Particle Size</th>
<th>Quantity of CO adsorbed (mmol/g)</th>
<th>Total Amount</th>
<th>Mole of Ir</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% Ir/MgAl₂O₄</td>
<td>20 times with SiO₂</td>
<td>1.3 nm</td>
<td>0.053</td>
<td>900 mg</td>
<td>2.34 E-6</td>
</tr>
<tr>
<td>0.05% Ir/MgAl₂O₄-200mL</td>
<td>0</td>
<td>0.7nm</td>
<td>0.00226</td>
<td>900 mg</td>
<td>2.34 E-6</td>
</tr>
<tr>
<td>0.05% Ir/MgAl₂O₄-1L</td>
<td>0</td>
<td>Most Single Atoms</td>
<td>0.00293</td>
<td>900 mg</td>
<td>2.34 E-6</td>
</tr>
<tr>
<td>0.5% Ir/MgAl₂O₄ (Ir(CO)₂(acac))</td>
<td>10 times with SiO₂</td>
<td>1 nm</td>
<td>0.0092</td>
<td>900 mg</td>
<td>2.34 E-6</td>
</tr>
</tbody>
</table>

(Note: The ‘200mL’ and ‘1L’ in 0.05% Ir/MgAl₂O₄-200mL and 0.05% Ir/MgAl₂O₄-1L denotes the total volume of solution for dilution during synthesis process; the mole of iridium is calculated based on the total amount in the reactor bed, the catalyst weight loading and the dilution ratio; the quantity of CO adsorbed was measured by Micromeritics 3 Flex; based on the stoichiometry of “CO:Ir=1:1”, the mole of iridium on the surface equals the quantity of CO adsorbed)

Before the catalytic performance study of n-butane hydrogenolysis on the series of Ir/MgAl₂O₄ catalysts, blank tests were performed in an empty tube and on the MgAl₂O₄ support only, respectively, and the results show there is no impurities of methane, ethane and propane in the n-butane reactant and the support does not have any activity at all. In this project, a much larger reactor with the inner diameter of 0.7 cm was applied for n-butane hydrogenolysis reactions comparing with the smaller reactor with inner diameter of
0.4 cm applied for the ethane hydrogenolysis study. The pressure drop is negligible when the total weight of catalyst is 900 mg in the 0.7 cm reactor.

For all experiments, the catalyst was pelletized and sieved in the size range of 106-250μm before the reaction. For explicit comparison, the 900 mg catalyst was diluted by 20 times and the 0.5% Ir/MgAl₂O₄ prepared with Ir(CO)₂(acac) was diluted by 10 times with the inert diluent of SiO₂ so that the amount of iridium metal contained in the 900mg diluted catalyst could be the same as the amount of iridium in the 900mg catalyst of 0.05% Ir/MgAl₂O₄-200mL and 0.05% Ir/MgAl₂O₄-1L, which means that the total mole of iridium is 2.34×10⁻⁶ in all these 4 catalysts as shown in the last column of table 4.1. The average particle size of the 4 catalysts for comparison was summarized from the size distribution results obtained by HAADF-STEM, and as we can see that the 1% Ir/MgAl₂O₄ NPs catalyst has the largest average size of 1.3 nm, the 0.05% Ir/MgAl₂O₄-200mL catalyst mainly consists of subnanometer clusters with the average size of 0.7 nm, the 0.05% Ir/MgAl₂O₄-1L catalyst has a very large fraction of single atoms, the 0.5% Ir/MgAl₂O₄ prepared with the precursor of Ir(CO)₂(acac) has a much more uniform size distribution and the average particle size is about 1nm.

4.1.2 Basic experiment procedure

The basic reaction conditions that would be considered in all experiments are:

Pressure ~ 1atm

H₂/ n - butane ratio = 10 / 1

Total flow rate = 100 sccm

After the last step of catalyst pretreatment (usually the reduction step) and the reactor system was cooled down to 60 – 70 °C in 20% H₂, sealed the furnace with quartz wool at two ends of the reactor. Then turned on 10 sccm H₂, 10 sccm 10% n-butane and 80 sccm He and increased the temperature with the heating rate of 3 °C/min, and started GC data collection at the same time. For the temperature effect study, followed the
real-time production results through the GC with temperature monitoring simultaneously until finding the proper temperature for ideal conversion. In addition, some experiments for H₂/C₄ ratio and feed concentration was also tested to make sure the reactants partial pressure and H₂/C₄ ratio applied in the performance study are appropriate. For these study, the temperature was increased directly to target and then the reactants partial pressure was changed with the fixed H₂ and n-butane percentage or change the H₂ and n-butane fractions at the certain total flow rate of 100 sccm.

4.1.3 Comparison of product distribution trend

To begin with, it is important to measure the activity as well as the selectivity to different products as a function of temperature on a certain amount of catalysts with different particle sizes to help preliminarily determine the appropriate catalyst amount and temperature range before any intensive study. The selectivity to methane, ethane, propane and the conversion are plotted in the same chart for 900 mg 1% Ir/MgAl₂O₄ NPs with 20 times dilution with SiO₂ and 900 mg 0.05% Ir/MgAl₂O₄-1L in figure 4.1.1 and 4.1.2, respectively.

![Selectivity & Conversion vs Temperature](image)

**Figure 4.1.1** The results of conversion and selectivity to the 3 products as a function of temperature on 1% Ir/MgAl₂O₄ NPs catalyst with the average particle size of 1.3 nm with 20 times dilution by SiO₂. The selectivity to methane (yellow line), ethane (green line) and propane (purple line) correspond to the y-axis on the left, the conversion plot (blue line) corresponds to the y-axis on the right.
Figure 4.1.2 The results of conversion and selectivity to the 3 products as a function of temperature on the catalyst of 0.05% Ir/MgAl₂O₄-1L with mostly single atoms. The selectivity to methane (yellow line), ethane (green line) and propane (purple line) correspond to the y-axis on the left, the conversion plot (blue line) correspond to the y-axis on the right.

As we can see from the n-butane hydrogenolysis results on 1% Ir/MgAl₂O₄ NPs in figure 4.1.1, when the temperature is as low as 190 °C, the conversion of the reaction is only 8.8%, but the selectivity to the target product of ethane is at the highest level of 76%. As the temperature keeps increasing, the conversion quickly increases by about 8 times at 260 °C. However, the selectivity to ethane decreases from 76% to 54% within this decreased temperature range and the selectivity to propane decreases from 11.7% to 8.3%, while the methane selectivity increases by 3 times from 12% to 37%. After comparing the plots in figure 4.1.1 with those in figure 4.1.2 we can see that the selectivity and conversion trends with the increasing temperature are very similar on these two catalysts that have mostly nanoparticles and mostly single atoms, respectively. Even though the conversion on the 0.05% Ir/MgAl₂O₄-1L SAs catalyst is slightly lower than that on the 1% Ir/MgAl₂O₄ NPs at the same temperature, the selectivity to ethane is almost the same as shown in the blue plots in figure 4.1.3. The results suggest that the catalytic performance of n-butane hydrogenolysis reaction
on the larger size of nanoparticles of Ir/MgAl₂O₄ is a little better than on the catalyst with mostly single atoms, but they are still at the similar level.

To further investigate the difference of product distribution, the mole ratio of methane to propane product on the two catalysts is calculated and compared in the same plot with the dependence of temperature as shown in figure 4.1.3. The trend of the increasing mole ratio of methane to propane with the temperature shows that series reaction proceeds more at higher temperature, as the improved methane production must be coming from the C-C bond cleavage of propane intermediates. It is surprising that the selectivity to ethane plot overlaps. The mole-based methane to propane ratio on the two catalysts is slightly different, but the trend of dependence on temperature is still very similar. The comparison of the results on 1% Ir/MgAl₂O₄ with mostly nanoparticles and 0.05% Ir/MgAl₂O₄-1L with mostly single atoms illustrates that the product distribution of n-butane hydrogenolysis is independent on the particle size of Ir/MgAl₂O₄ catalysts with different loadings, in other words, the product distribution of n-butane hydrogenolysis is structure insensitive when the particle size is smaller than 2 nm.

![Product Size Distribution vs Temperature](image)

**Figure 4.1.3** The results of selectivity to ethane (green lines) as a function of temperature on the catalyst of 1% Ir/MgAl₂O₄ NPs with the average size of 1.3nm and 0.05% Ir/MgAl₂O₄-1L with mostly single atoms correspond to the left y-axis as well as the mole ratio of methane to propane products (blue lines) corresponds to the right y-axis.
The information of the catalysts that used for the catalytic performance study of n-butane hydrogenolysis was tabulated in table 4.1. As we can see clearly from the figure 4.1.4-(a), the “selectivity to ethane vs temperature” plot on the 4 catalysts with the same amount of iridium overlaps very well in the temperature range of 190-230°C. However, as shown in figure 4.1.4-(b), the conversion of n-butane hydrogenolysis on 0.05% Ir/MgAl₂O₄-200mL with mostly subnanometer clusters is evidently smaller than the other two catalysts that are mostly nanoparticles and single atoms with the same total amount of Ir. (The conversion profile for 0.5% Ir/MgAl₂O₄ prepared with Ir(CO)₂(acac) precursor is not included as the Ir amount in the catalyst was not well controlled.) Therefore, the n-butane hydrogenolysis on the Ir/MgAl₂O₄ catalyst system is structure sensitive reaction in terms of the activity, but the results show that the difference in the conversion caused by different particle sizes in such small size range does not affect the selectivity to ethane in the measured temperature range. This phenomenon is very different from that in the larger particle size range from the literature. As we discussed in section 1.2.1, the selectivity to ethane is very dependent on the particle size in the range of 2-20nm for the supported catalyst of Ir/SiO₂ and Ir/Al₂O₃ based on the work by J.R. Engstrom et al. and Foger et al.. Obviously, there is an excellent correlation between the selectivity to ethane and the mean Ir particle size in their work, as the particle size decreases from about 10-20 nm to 1-2 nm, the selectivity to ethane would be drastically increased. They also discussed that the reason of the particle size dependence should be the different fraction of corner / edge atoms that have low coordination numbers in the different catalysts, and these corner / edge atoms contribute more to the central C-C bond cleavage rather than the terminal C-C bond cleavage. In our case, the selectivity to ethane does not change much on the catalysts with different particle sizes, indicating that the fraction of the active sites for central C-C bond cleavage might be similar in all these catalysts based on their theory.
Figure 4.1.4 Comparison of the selectivity to ethane (a) and conversion (b) results of n-butane hydrogenolysis as a function of temperature on the catalyst of 1% Ir/MgAl$_2$O$_4$ NPs (with the average size of 1.3nm), 0.05% Ir/MgAl$_2$O$_4$-200mL subnanometer clusters (with the average size of 0.7nm), 0.05% Ir/MgAl$_2$O$_4$-1L SAs (with mostly single atoms) and 0.5% Ir(CO)$_2$(acac)/MgAl$_2$O$_4$ with the average size of 1nm.

Generally, for the series reaction $A \rightarrow B \rightarrow C$, when most of $A$ reacted, in other words, when the conversion is very large, the second step of series reaction $B \rightarrow C$ would be more preferable to take place and become...
more and more dominant as the conversion increases, leading to different selectivity to the products of B and C. Therefore, to figure out the reaction pathways for a combination of parallel reactions and series reactions like n-butane hydrogenolysis, it is of great interest to investigate on the selectivity change at a certain temperature with different conversions. From the plot of “conversion vs temperature” in figure 4.1.4-(b), the temperature of 250°C was chosen to study the selectivity dependence on the conversion since the conversion at this temperature is in the middle range for all of the three catalysts. As the plots presenting in figure 4.1.5, the conversion of 1% Ir/MgAl₂O₄ NPs and 0.05% Ir/MgAl₂O₄- 1L SAs is as high as about 98% at the lowest total flow rate of 20 sccm and as low as about 20% at the largest total flow rate of 200 sccm. However, by the variation in such a large conversion range, the ethane selectivity remains between 58.1-59.2% for 1% Ir/MgAl₂O₄ NPs and 52.2-56.2% for 0.05% Ir/MgAl₂O₄- 1L SAs, respectively. In addition, even though the conversion on 0.05% Ir/MgAl₂O₄-200mL subnanometer clusters is unexpectedly much lower than the nanoparticles and single atoms, the selectivity to ethane is still at the same level and the ethane selectivity change dependence on conversion also remains between 55.7-57.4%. The results indicate that at a certain temperature the selectivity to ethane is almost independent of conversion on the catalysts that have size of 1nm and smaller, and it seems that only the temperature would affect the reaction pathways, further influence the product distribution.
Figure 4. 1. 5 Comparison of the selectivity to ethane as a function of conversion on the catalyst of 1% Ir/MgAl₂O₄ NPs (average size ~ 1.3nm), 0.05% Ir/MgAl₂O₄-200mL subnanometer clusters (average size ~ 0.7nm) and 0.05% Ir/MgAl₂O₄-1L with mostly single atoms at 250 °C by changing the total flow rate.

Recall the schematic illustration of reaction pathways in section 1.2.1, the main reaction taken place based on the above experiment results might be the competition of parallel reactions of central and terminal C-C bond cleavage of n-butane. The similar selectivity to ethane on the catalysts with different particle sizes is probably because of the similar fraction of under-coordinated atoms containing active sites. From the results in figure 4.1.5, the selectivity to ethane almost remains identical when the conversion is lower than 100%. However, as we can see from the plot in figure 4.1.6 below, the selectivity to methane evidently keeps increasing on the catalyst of 1% NPs (size ~1.3nm) and 0.05%-1L with mostly single atoms as the conversion keeps increasing and being close to 100%. This means that the reaction definitely goes through the series reaction pathway, which consumes propane to produce more methane. And the fixed selectivity to ethane in the changing conversion range might be because of the complicated balance between the parallel and series reactions. As the series reaction ⑥ further going on, the parallel reaction ③ would keep moving forward and exceed the other parallel pathways, so that the extra production of ethane coming from the series reaction of propane intermediate hydrogenolysis could be balanced with the less ethane production from other parallel pathways, resulting in the observation of less propane and more methane only. These results suggest different reaction orders in n-butane for different reaction pathways that contains the central and terminal C-C bond cleavage.

In summary, the catalytic performance of n-butane hydrogenolysis on 1% Ir/MgAl₂O₄ nanoparticles (size ~1.3nm) and 0.05% -1L Ir/MgAl₂O₄ with mostly single atoms are very similar but higher than the 0.05%-200mL subnanometer clusters (size ~ 0.7nm) in terms of activity. However, the selectivity to ethane is almost the same on all the three catalysts.
Figure 4.1.6 Comparison of the selectivity to methane and propane as a function of conversion on the catalyst of 1%Ir/MgAl2O4 nanoparticles (size ~ 1.3nm), 0.05%Ir/MgAl2O4-200mL subnanometer clusters (size~0.7nm) and 0.05%Ir/MgAl2O4-1L with mostly single atoms by changing the total flow rate.

4.1.4 Optimal product distribution

Since the conclusion from section 4.1.3 is that temperature is the main factor that would affect the product distribution in n-butane hydrogenolysis, the following work is to increase the ethane selectivity at lower temperature and maintain high level activity with more amount of catalysts. Among the abovementioned 4 catalysts, the higher loading 1%Ir/MgAl2O4 NPs catalyst is the most active one even diluted by 20 times with the inert SiO2. Therefore, 0.5-0.6g catalyst of 1%Ir/MgAl2O4 NPs (106-250 μm pelletized and sieved) without any dilution was applied to explore the optimal product distribution.
Figure 4.1.7 Product distribution (left y-axis) and conversion (right y-axis) of n-butane hydrogenolysis as a function of total flow rate (sccm) at 160°C on 0.5g catalyst of 1% Ir/MgAl₂O₄ nanoparticles (size ~ 1.3nm) without any dilution.

Figure 4.1.7 is the result of conversion as well as the selectivity to methane, ethane and propane from n-butane hydrogenolysis on 0.5g 1% Ir/MgAl₂O₄ catalyst at 160°C. As expected, the conversion increases with the reducing total flow rate. At the highest total flow rate of 200 sccm, the conversion of 20.3% is the lowest. While at the lowest total flow rate of 10 sccm, the conversion is as high as 96.4%. However, the selectivity to ethane does not vary at all with the total flow rate. Surprisingly, even when the conversion is as high as 96.4%, the selectivity to ethane is still 80.6%, which is nearly the same as the selectivity to ethane of 80.25% at the lowest conversion of 20.3%. To our knowledge, the 80% of selectivity to ethane at 20 - 96% conversion should be close to the top performance, as the highest ethane selectivity reported in literature is about 90% at less than 1% conversion at 202°C obtained by Engstrom, J. R., D. W. Goodman, and W. H. Weinberg on Ir (110)-(1×2) surface, which could be normalized as either octahedral or square-pyramidal particle with effective particle size of 2.4nm and 1.3nm based on the comparison of C₇/C₉ atoms with the fraction of corner / edge atoms. Besides, the selectivity to ethane reported by Bond, Geoffrey C.,
and Juan J. Garcia also remains the same at about 26% on the catalyst of Ru / 13X zeolite with the changing conversion, but the conversion does not exceed 50% based on the plot they provided.

4.1.5 Exploration for optimal reactants ratio and concentration

A series of experiments were also performed to test the optimal ratio of H₂/C₄ and concentration of the reactants in n-butane hydrogenolysis reaction. To begin with, at 100 sccm total flow rate and fixed concentration of 1% n-butane, the H₂/C₄ ratio was changed between 10 and 80. It is found that ethane selectivity does not change much, but the conversion would drastically decrease when the H₂ / C₄ gets higher by increasing the H₂ concentration as shown by the blue plot in figure 4.1.8 (a), and the trend is consistent with the very negative H₂ order reported in literature. [25, 27] However, when the H₂/C₄ ratio is less than 10 at 1% n-butane, which means that the H₂ concentration is less than 10%, the deactivation would be very fast (about 30% in 10 minutes). Thus, the condition of H₂/C₄ ratio lower than 10 at 1% n-butane is not available for accurate measurement of activity and selectivity and the results are not included in the plot.

In contrary, still at 100 sccm total flow rate but fixed concentration of 10% H₂, when the H₂/C₄ ratio was changed between 3 and 50, the conversion shows opposite trend as shown in figure 4.1.8 (b). Therefore, it is required to consider both of the H₂/C₄ ratio effect and reactants concentration effect. As we can see from the figure, the condition at the vertical red lines in the two plots are the same, which is 10 sccm pure H₂ and 10 sccm 10% n-butane with 100 sccm total flow rate at 160°C. While at the following condition, which has higher concentration of H₂ in figure 4.1.8 (a) and lower concentration of n-butane in figure 4.1.8 (b), the conversion would decrease and increase, respectively. Meanwhile, in figure 4.1.8 (b), at lower H₂/C₄ ratio and higher concentration of n-butane with fixed 10% H₂, the conversion decreases but the deactivation is negligible comparing with the same H₂/C₄ ratio and lower H₂ concentration. But in fact, the reaction rate keeps decreasing as H₂/C₄ ratio goes up by decreasing the n-butane concentration. The reason might be the slightly positive order of n-butane as reported in the literature. [25, 27]
In summary, these results indicate that the ethane selectivity is not influenced much, but both of the H₂/C₄ ratio as well as the reactants concentration need to be considered to optimize the conversion. The H₂ concentration must be high enough (at least 10%) so that the deactivation could be minimized when the concentration of n-butane is higher than 1% (the left hand side results of the red lines in the plots (a) and (b)). Then, the higher H₂/C₄ ratio would have different effect on the conversion as the H₂ order is very negative and the n-butane order is slight positive (right hand side results of the red lines in the plots (a) and (b)). Generally, the conversion would increase when the H₂ concentration decreases and n-butane concentration increases. In this case, the H₂/C₄ ratio of 10 is chosen as optimal based on the analysis here.
Figure 4.1.8 The conversion and selectivity change as a function of H\textsubscript{2}/C\textsubscript{4} ratio at 160°C and 100 sccm total flow rate when the H\textsubscript{2} concentration is changing at fixed 1% n-butane (a), and when the n-butane concentration is changing at fixed 10% H\textsubscript{2}. The condition at the position of red lines in (a) and (b) is 1% n-butane and 10%H\textsubscript{2}, which is exactly the one chosen in the previous catalytic performance study.

Another information hidden in the product distribution results of figure 4.1.8 (a) is that at very high H\textsubscript{2} concentration, the selectivity to propane is higher than the selectivity to methane. Based on the reaction pathways as proposed, the hydrogenolysis of n-butane would happen either on the central C-C bonds or the terminal C-C bonds to produce only ethane or the same amount of methane and propane. When the series reaction taking place, the C-C bonds in the ethane and propane intermediates would be further cleaved and produce more methane. This means that the mole ratio of C\textsubscript{1}/C\textsubscript{3} must be higher than 1 or at least no less than 1 when there is no series reaction taken place. In this case, when the concentration of H\textsubscript{2} is higher than 70% (H\textsubscript{2}/C\textsubscript{4} ratio higher than 70 in the plot), the mole ratio of C\textsubscript{1}/C\textsubscript{3} is lower than 1. The reason might be ascribed to the improper analytical method by the GC. Usually, when the H\textsubscript{2} concentration is extremely high, the separation of the first peak is always terrible, as half of the methane peak shows as negative peak. Therefore, the very high concentration of H\textsubscript{2} should be avoided when choosing the optimal conditions.
Last but not least, one more experiment was performed to study the reactant concentration effect on the conversion and selectivity at the fixed H\textsubscript{2}/C\textsubscript{4} ratio of 10. In figure 4.1.10, the x-axis shows the concentration of n-butane in the range of 0.2 to 3%, which is the same as 1/10 of the H\textsubscript{2} concentration in the range of 2 to 30%. As we can learn from the plots, the lower reactants concentration would lead to higher conversion. At the condition of 0.2% n-butane and 2% H\textsubscript{2}, the conversion is even close to 100%, while the ethane selectivity almost remains identical in the whole range. Combining with the previous analysis that H\textsubscript{2} has negative order and n-butane has positive order, the decreasing conversion versus the enhancement on both of the H\textsubscript{2} and n-butane reactants means that the absolute value of the negative H\textsubscript{2} order is much higher than the absolute value of the positive n-butane order. Considering that the extremely low partial pressure of the reactants is not favored in industry, in this case, the condition of 1% n-butane and 10% H\textsubscript{2} would be the best to optimize the product distribution.

![Figure 4.1.9](image)

**Figure 4.1.9** The conversion and selectivity change as a function of the concentration of n-butane at 160°C when the H\textsubscript{2}/C\textsubscript{4} ratio is fixed at 10.
4.1.6 Analysis of reaction mechanism

As the product distribution plot shown in figure 4.1.7, the conversion change only affects the selectivity to methane and propane. When the conversion is getting close to 100%, the mole based ratio of methane to propane is 3.9, while at the highest total flow rate with the conversion of 20.3%, the mole based ratio of methane to propane is only 2.5. In other words, as the conversion increases from 20.3% to 96.4%, even though the selectivity to ethane remains almost identical, the selectivity to propane would decrease and the selectivity to methane would increase. This means that the level of series reaction pathway would increase and the parallel reaction pathway ③ becomes more competitive. The investigation on reaction mechanism could be developed on account of the phenomena of product distribution change at very high conversion.

Recall the reaction mechanism scheme shown above that proposed in section 1.2.2. After the parallel reaction pathway ①, ② and ③, there forms ethane and propane intermediates that contain one and two C-C bonds for further cleavage. However, the activity of ethane hydrogenolysis on the same catalyst at the same temperature of 160°C is extremely low (about 0.1% conversion even at the lowest total flow rate of 20 sccm), which means that the further C-C bond cleavage is unlikely to take place on the ethane intermediate during the n-butane hydrogenolysis. Therefore, in this case only the propane intermediate is considered to participate in the series reaction. After analyzing the product distribution trend with the conversion, the raw data was used to fit 4 reaction models. The first model includes the three parallel reaction pathways ①, ②, ③, and the series reaction pathway ⑥; the second model considers two parallel reaction pathways ①, ③, and the series reaction pathway ⑥; the third model contains only three parallel
reaction pathways ①, ② and ③ without consideration for any series reaction steps; the last model is the three parallel reaction pathways and a combination of series reaction pathway ⑥ and ⑦, which indicates that the two C-C bonds in the propane intermediate may be cleaved at the same time. The calculation result from MATLAB shows that the raw data in the whole conversion range only fits the second and the third model as shown below. In the second model, as the conversion increases between 20.3 - 96.4%, approximately 70-80% of reacted n-butane goes through reaction pathway ① to form ethane molecules, 20-30% goes through pathway ③ to form methane and propane, and then 40-60% of propane intermediate would participate in the series reaction to form methane and ethane. As the conversion increases, more propane intermediates would go through series reaction pathway ⑥ as the amount of propane intermediate decreases a lot comparing with that in the low conversion range. In the third model, approximately 76-79% of reacted n-butane would go through central C-C bond cleavage as shown in reaction pathway ①, 11-18% would go through reaction pathway ② and have the two terminal C-C bonds cleave at the same time and 12-16% would go through reaction pathway ③ to form methane and propane. And as the conversion increases, pathway ② is more competitive than pathway ③. However, in practice, the reaction mechanism in the third model would rarely happen, since the greatly increased conversion would provide a very high chance for the series reaction taking place especially when there is plenty of propane produced through reaction pathway ③. The reaction temperature of propane hydrogenolysis is very close to that of n-butane hydrogenolysis, the reactivity of propane hydrogenolysis should be high enough in the n-butane hydrogenolysis system at very high conversion range. Moreover, based on the computational results reported by Hibbitts, David D., David W. Flaherty, and Enrique Iglesia, 1,4-adsorption is not likely to take place because of the high activation enthalpy and Gibbs free energy derived by DFT. [33] Therefore, model 2 is more probably the correct reaction mechanism of n-butane hydrogenolysis on 1% Ir/MgAl₂O₄ nanoparticles at 160°C in the high conversion range.
Scheme 4.1 Potential reaction mechanism for n-butane hydrogenolysis on 1% Ir/MgAl₂O₄ nanoparticles (size ~ 1.3nm) at 160°C after fitting the experiment data in the reaction mechanism with different pathways without consideration for the hydrogenolysis of ethane intermediate. Model 2 is more likely to be the correct reaction mechanism.

Figure 4.10 Comparison of “selectivity to ethane vs conversion” plots on 1% Ir/MgAl₂O₄ catalyst reduced at 800°C for 2 hours and 9 hours.
To further investigate the effect of series reaction on the selectivity to ethane, another experiment was performed on the catalyst 1% Ir/MgAl$_2$O$_4$ NPs reduced at 800°C for 9 hours at 100% conversion. When the conversion reaches 100%, there is no more n-butane reactant existing at all. The only substance in the reaction system is the final product of methane and the intermediate of ethane and propane. At this point, once there would be series reaction of ethane hydrogenolysis taken place, the selectivity to ethane would be definitely decreased after consuming most of the propane intermediate. In this study, the longer reduction time for 1% Ir/MgAl$_2$O$_4$ NPs catalyst was decided to get higher fraction of larger size nanoparticles. However, the experiment results are almost the same between the two identical catalysts with different reduction time as the “selectivity to ethane vs conversion” plot presented in figure 4.1.10. The selectivity to ethane remains the same as the conversion changes between 20-97%. Therefore, it is believed that the longer reduction time does not help form larger particles comparing with the one reduced for shorter time of 2 hours. This time, the reaction temperature was raised to 200°C, at which the conversion could reach 100% for sure at the initial total flow rate of 100 sccm. Then at 100% conversion, total flow rate was further decreased to get the product distribution result.

![Selectivity to Ethane vs Total Flow Rate at 100% Conversion](image-url)
**Figure 4.1.11** Product distribution of n-butane hydrogenolysis as a function of total flow rate (sccm) when the conversion is 100% at 200°C on 0.59g catalyst of 1% Ir/MgAl2O4 NPs (reduced at 800°C for 9 hours) without any dilution.

From figure 4.1.11, at 100% conversion, further decreasing the total flow rate could change the selectivity to all the 3 products instead of propane and methane only. In general, as the total flow rate decreases to 20 sccm at this temperature, the selectivity to propane decreases from 1.3% to approximately zero and the selectivity to methane increases from 27% to 42%. Meanwhile, the selectivity to ethane evidently decreases from 72% to 58%, differing from all the aforementioned results. As the propane selectivity was extremely low in this case, the reaction rate of C-C bond cleavage on the ethane product in the n-butane hydrogenolysis system could be calculated based on the ethane selectivity change when decreasing the total flow rate from 100 sccm to 20 sccm, and the reaction rate is $4.4 \times 10^{-8}$ (unit: ethane reacted per gram of catalyst per second). Therefore, these results indicate that the C-C bond cleavage on the ethane intermediate would definitely happen when the conversion of n-butane hydrogenolysis reaches 100% and almost all the propane intermediate is consumed. Comparing with 10% conversion of ethane hydrogenolysis at 200 °C with 50 sccm total flow rate on the same catalyst in the separate experiment, the reaction rate of C-C bond cleavage on the ethane in the ethane hydrogenolysis system is about $4.2 \times 10^{-8}$ (unit: ethane reacted per gram of catalyst per second). Therefore, the level of C-C bond cleavage on the ethane intermediate in the n-butane hydrogenolysis matches well with that in the separate ethane hydrogenolysis system. These results confirm us that the C-C bond cleavage on the ethane intermediate during n-butane hydrogenolysis would not be easily take place unless the conversion reaches 100% and almost all the propane has been consumed. Therefore, the series reaction pathways ④, ⑤ and ⑦ of further hydrogenolysis on ethane intermediate is negligible.

In the case of n-butane hydrogenolysis, it is very hard to learn the reaction mechanism by exploring the exact intermediates that undergo the C-C bond cleavage in the elementary steps combining with the experimental results of the reaction orders, as the possibilities for the intermediates of C4 species would be
much more than that for the C2 species. However, we can still do some estimations. Based on Hibbitts, David D., David W. Flaherty, and Enrique Iglesia’s work, the activation barrier for the 1,4 adsorption in n-butane is much higher than that for the 1,2 adsorption or 2,3 adsorption, which correspond to the terminal C-C bond cleavage and central C-C bond cleavage during the n-butane hydrogenolysis. If the two central carbon atoms of the n-butane molecule bind to the surface of the catalyst, the hydrogen binding with the central carbon atoms would be the first to be removed before the C-H bond cleavage happen on the terminal carbon atoms. As the H removed from the central carbon atoms, the central C-C bond would be weakened progressively until the C-C bond is weaker than the C-H bond, therefore, the majority of central C-C bond cleavage on the n-butane molecules would lead to the high ethane selectivity. And the C-C bond cleavage on the intermediate such as CH₃C*C*CH₃ or CH₃CH*C*CH₃ is probably the mechanism that corresponds to the very high ethane selectivity obtained from the experiments, while the intermediates such as CH₃CH₂C*CH* is probably corresponding to the terminal C-C bond cleavage shown as reaction pathway ③ in the aforementioned discussion.

### 4.2 Particle Size Effect on Activity in Kinetic Regime

#### 4.2.1 Basic experiment procedure

The basic reaction conditions that would be considered in all experiments are:

**Pressure ~ 1 atm**

**H₂/ n-butane ratio = 10 / 1**

**Total flow rate = 100 sccm (heating process), 40, 50 or 60 sccm (activation energy measurement process)**

After the last step of catalyst pretreatment (usually the reduction step) and the reactor system was cooled down to 60 – 70 °C in 20% H₂, sealed the furnace with quartz wool at two ends of the reactor. Then turned on 10 sccm H₂, 10 sccm 10% n-butane and 80 sccm He and increased the temperature with the heating rate of 3 °C/min, and started GC data collection at the same time. For activation energy measurement, followed
the real-time production results through the GC starting from the temperature of 160 or 170°C. At 170°C, adjusted the total flow rate to make sure the conversion was between 0.3 - 0.8%. The appropriate total flow rate is usually in the range of 40-60 sccm with the certain amount of different catalyst in the reactor with the inner diameter of 0.7 cm. The details of each catalyst are listed in table 4.2. The total amount of the identical catalysts for each experiment was not controlled since the final activity results would be normalized based on the surface iridium amount (reaction rate or turnover frequency). The catalyst of 0.5% Ir/MgAl₂O₄ (prepared from the precursor of Ir(CO)₂(acac)) was tested with and without 10 times dilution with SiO₂, and the normalized reaction rate and TOF showed little difference, which means that there was no transport limitations within the reactor bed during reaction.

Table 4.2 List of catalysts that are used for the structure sensitivity study of n-butane hydrogenolysis in the kinetic regime.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Dilution</th>
<th>Average Particle Size</th>
<th>Quantity of CO adsorbed (mmol/g)</th>
<th>Total Amount</th>
<th>Mole of Ir</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% Ir/γ-Al₂O₃</td>
<td>20 times with SiO₂</td>
<td>5-8 nm</td>
<td>0.01532</td>
<td>400 mg</td>
<td>2.1 E-6</td>
</tr>
<tr>
<td>1% Ir/MgAl₂O₄</td>
<td>20 times with SiO₂</td>
<td>1.3 nm</td>
<td>0.053</td>
<td>400 mg</td>
<td>1.04 E-6</td>
</tr>
<tr>
<td>0.5% Ir/MgAl₂O₄ (Ir(CO)₂(acac))</td>
<td>0 or 10 times with SiO₂</td>
<td>1 nm</td>
<td>0.0092</td>
<td>~170 or 900 mg</td>
<td>4.42 E-6 or 2.34 E-6</td>
</tr>
<tr>
<td>0.05% Ir/MgAl₂O₄-200mL</td>
<td>0</td>
<td>0.7 nm</td>
<td>0.00226</td>
<td>900 mg</td>
<td>2.34 E-6</td>
</tr>
<tr>
<td>0.05% Ir/MgAl₂O₄-1L</td>
<td>0</td>
<td>most single atoms</td>
<td>0.00293</td>
<td>~400 mg</td>
<td>~1.044 E-6</td>
</tr>
<tr>
<td>0.0025% Ir/MgAl₂O₄</td>
<td>0</td>
<td>Single atoms</td>
<td>-</td>
<td>1000 mg</td>
<td>1.32 E-7</td>
</tr>
</tbody>
</table>

4.2.2 Comparison of activity and activation energy

Unlike the results discussed in section 4.1, the initial conversion of all the experiments at the starting temperature point of 170°C in section 4.2 were well controlled under 1%. Typically, the whole conversion range on most of the catalysts was between 0.5%-3%, except those that have very large activation energies would reach 10% conversion at high temperature (e.g., 0.05% Ir/MgAl₂O₄-200mL and 2% Ir/γ-Al₂O₃ with 20 times dilution).
The activity was compared in the form of reaction rate and turnover frequency that calculated based on different methods of normalization introduced in section 2.5. As discussed in section 2.5, the reaction rate is the activity normalized by the chemisorption result of “quantity of CO adsorbed on Ir” with the stoichiometry of “CO : Ir=1 : 1” without the consideration of the specific adsorption ability for the catalyst with different sizes. (*Note: the unit of the reaction rate “mole of n-butane reacted per mole of surface Ir per second” is denoted by “mole C4 / mole Ir / s”.*). The TOF is the activity normalized by the adsorption ability of iridium on the surface of particles with different sizes as those iridium atoms in the bulk do not have any opportunity to interact with the reactant molecules and are inactive hence. Therefore, the TOF is probably more accurate to reflect the reactivity of the catalyst. The trend of activity dependence on temperature is the same for the TOF results normalized by the two methods with different assumptions but different from the trend of activity change without consideration of different adsorption ability in the broad size distribution within the catalyst.

![Reaction Rate vs Temperature](image)

**Figure 4.2.1** Comparison of the reaction rate of n-butane hydrogenolysis as a function of temperature on the series of Ir catalysts with different particle size. The reaction rate was normalized by the Ir amount
measured by chemisorption based on the stoichiometry of “CO : Ir = 1 : 1” without the consideration of specific adsorption ability of different particle sizes in the broad size distribution within the certain catalyst. The unit of the reaction rate is the mole of n-butane reacted per mole of Ir per second.

Table 4.3 A summary of “reaction rate×100” on all the 6 catalysts at different temperatures in the unit of “mole C4 / mole Ir / s”.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Average size</th>
<th>170 °C</th>
<th>180 °C</th>
<th>190 °C</th>
<th>200 °C</th>
<th>210 °C</th>
<th>220 °C</th>
<th>Ea (kJ/mol) 170-190 °C</th>
<th>Ea (kJ/mol) 190-220 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% Ir/γ-Al2O3</td>
<td>5-8 nm</td>
<td>1.76</td>
<td>2.97</td>
<td>4.62</td>
<td>7.01</td>
<td>9.90</td>
<td>13.24</td>
<td>90.4</td>
<td>66.0</td>
</tr>
<tr>
<td>1% Ir/MgAl2O4</td>
<td>1.3 nm</td>
<td>0.10</td>
<td>0.21</td>
<td>0.40</td>
<td>0.60</td>
<td>0.87</td>
<td>1.13</td>
<td>113.1</td>
<td>65.7</td>
</tr>
<tr>
<td>0.5% Ir/MgAl2O4 (Ir(CO)2(acac))</td>
<td>1 nm</td>
<td>0.11</td>
<td>0.24</td>
<td>0.51</td>
<td>1.01</td>
<td>1.69</td>
<td>2.43</td>
<td>135.5</td>
<td>99.0</td>
</tr>
<tr>
<td>0.05% Ir/MgAl2O4-200mL</td>
<td>0.7 nm</td>
<td>0.04</td>
<td>0.09</td>
<td>0.19</td>
<td>0.38</td>
<td>0.67</td>
<td>1.03</td>
<td>137.2</td>
<td>107.9</td>
</tr>
<tr>
<td>0.05% Ir/MgAl2O4-1L</td>
<td>mostly single atoms</td>
<td>0.11</td>
<td>0.24</td>
<td>0.43</td>
<td>0.67</td>
<td>1.03</td>
<td>1.44</td>
<td>113.2</td>
<td>84.8</td>
</tr>
<tr>
<td>0.0025% Ir/MgAl2O4</td>
<td>Single atoms</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

As we can learn from figure 4.2.1, the 2% Ir/γ-Al2O3 NPs with the average particle size of 5-8 nm is extraordinarily active comparing with all the other catalysts. While the reaction rate of all the other four catalysts is at least 10 times less active. From the details in table 4.3, in the low temperature range of 170 – 190 °C, the reaction rate of n-butane hydrogenolysis on 1% Ir/MgAl2O4 NPs (1.3nm), 0.5% Ir/MgAl2O4 NPs prepared from Ir(CO)2(acac) (1nm) and 0.05% Ir/MgAl2O4 – 1L (mostly single atoms) is almost identical. While the catalyst of 0.05% Ir/MgAl2O4 – 200mL subnanometer clusters (0.7nm) has the lowest activity among all these catalysts, except that the very low loading 0.0025% Ir/MgAl2O4 single atoms with inadequate amount of Ir is actually inactive at all. However, in the higher temperature range of 200 – 220 °C, the reaction rate plots of 1% Ir/MgAl2O4 NPs (1.3nm), 0.05% Ir/MgAl2O4 – 1L (mostly single atoms) and 0.05% Ir/MgAl2O4 – 200mL subnanometer clusters (0.7nm) tend to overlap with each other, while the reaction rate of 0.5% Ir/MgAl2O4 NPs prepared from Ir(CO)2(acac) (1nm) with very uniform size distribution is almost two times higher than those three. The reason might be the very different activation energy in the low and high temperature range (170 - 190 °C and 190 – 220 °C). As shown in table 4.3, the activation energy evidently decreases on all the catalysts at higher temperature, and among those that have similar initial reaction rate, the activation energy of 0.5% Ir/MgAl2O4 NPs prepared from Ir(CO)2(acac)
(1nm) is the largest, explaining the very high activity at the temperature higher than 210 °C comparing with the other two of 1% Ir/MgAl₂O₄ NPs (1.3nm) and 0.05% Ir/MgAl₂O₄ – 1L (mostly single atoms) that have the same initial reaction rate at the temperature between 170 - 190 °C. The fitting of Arrhenius plots is very good (R²=1) on all the catalysts in the high and low temperature range.

Engstrom, J. R., D. W. Goodman, and W. H. Weinberg also observed a decreased activation energy at higher temperature range in their work. [23] In fact, this phenomenon happens in the hydrogenolysis of alkanes of C2 – C5 reactants on both Ir (111) and Ir (110)-(1×2) surface. For example, the activation energy of n-butane hydrogenolysis on Ir (111) surface in the temperature range of 152 – 227 °C is 132.2 kJ/mol, while it decreases to 105.8 kJ/mol in the temperature range of 252 – 327 °C. They pointed out the reason might be the lower hydrogen coverage at higher temperature range, since they also learned from the hydrogen order measurement that further decreasing hydrogen partial pressure would make a difference on the activity as there is an obvious rollover in the plot of reaction rate changing as a function of hydrogen partial pressure. The reason might be also applicable in this case, as a larger deactivation (~20%) were observed on all the catalysts at high temperature of 220 °C comparing with a small deactivation (~5-10%) at low temperature range (170-190 °C). When the temperature goes up and the surface is no longer saturated with hydrogen, the catalyst might be more easily coked, leading to great deactivation. Thus, the comparison of activation energy results in the low temperature range of 170 – 190 °C would be more accurate to study the structure sensitivity effect on these catalysts.

The activity normalized by the surface iridium atom based on the two assumptions mentioned in section 2.5 (called TOF) was also calculated and compared. Typically, the activity trend normalized by the two methods with different assumptions is very similar, thus, only the one with the assumption 1 that the catalyst weight loading is accurate and not all the iridium atoms are on the surface of the support is plotted in figure 4.2.2 for the trend observation, and the data is also listed in table 4.4. The activation energy does not have great difference from that fitted by the reaction rate in the previous part. However, the TOF of 0.05%
Ir/MgAl₂O₄ – 1L (mostly single atoms) suppresses all the other catalysts except the 2% Ir / γ-Al₂O₃ with very large particles in the low temperature range.

**Figure 4.2** Comparison of TOF(s⁻¹) of n-butane hydrogenolysis as a function of temperature on the series catalysts with different particle sizes. The activity was normalized by the mole of iridium atoms on the surface based on the actual stoichiometry of “CO:Ir” that calculated by combining the chemisorption result and size distribution.

**Table 4.4** A summary of “TOF×100” on all the 6 catalysts at different temperatures in the unit of “s⁻¹”. The TOF was normalized to surface sites based on the equation with the assumption 1 shown in section 2.5.2.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Average size</th>
<th>170 °C</th>
<th>180 °C</th>
<th>190 °C</th>
<th>200 °C</th>
<th>210 °C</th>
<th>220 °C</th>
<th>Ea (kJ/mol) 170-190 °C</th>
<th>Ea (kJ/mol) 190-220 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% Ir/γ-Al₂O₃</td>
<td>5-8 nm</td>
<td>2.51</td>
<td>4.24</td>
<td>6.60</td>
<td>10.01</td>
<td>14.14</td>
<td>18.92</td>
<td>90.4</td>
<td>66</td>
</tr>
<tr>
<td>1% Ir/MgAl₂O₄</td>
<td>1.3 nm</td>
<td>0.13</td>
<td>0.26</td>
<td>0.47</td>
<td>0.75</td>
<td>1.08</td>
<td>1.41</td>
<td>113.1</td>
<td>65.7</td>
</tr>
<tr>
<td>0.5% Ir/MgAl₂O₄ (Ir(CO)₂(acac))</td>
<td>1 nm</td>
<td>0.12</td>
<td>0.27</td>
<td>0.56</td>
<td>1.12</td>
<td>1.88</td>
<td>2.70</td>
<td>131.7</td>
<td>101.6</td>
</tr>
<tr>
<td>0.05% Ir/MgAl₂O₄-200mL</td>
<td>0.7 nm</td>
<td>0.05</td>
<td>0.11</td>
<td>0.25</td>
<td>0.49</td>
<td>0.85</td>
<td>1.31</td>
<td>137.2</td>
<td>107.9</td>
</tr>
<tr>
<td>0.05% Ir/MgAl₂O₄-1L</td>
<td>mostly single atoms</td>
<td>0.18</td>
<td>0.39</td>
<td>0.70</td>
<td>1.09</td>
<td>1.69</td>
<td>2.36</td>
<td>111.3</td>
<td>77.2</td>
</tr>
<tr>
<td>0.0025% Ir/MgAl₂O₄</td>
<td>Single atoms</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
For better observation, the reaction rate as a function of particle size is plotted in figure 4.2.3-a (Ir/MgAl$_2$O$_4$ series only) and figure 4.2.3-b (including 2% Ir/γ-Al$_2$O$_3$). In short, the activity of n-butane hydrogenolysis on the very large particles (2% Ir/γ-Al$_2$O$_3$) is extremely high and not at the same level comparing with all the other catalysts with the particle size smaller than 2 nm. And in the low temperature range, the reaction rate for 0.05% Ir/MgAl$_2$O$_4$ – 1L (mostly single atoms) is very similar with that on 1% Ir/MgAl$_2$O$_4$ NPs (size ~ 1.3nm) and 0.5% Ir/MgAl$_2$O$_4$ NPs prepared from Ir(CO)$_2$(acac) (1nm), but much higher than 0.05% Ir/MgAl$_2$O$_4$ – 200mL subnanometer clusters (size ~ 0.7nm). The only difference of the activity results normalized by different methods presented in section 2.5.1 and 2.5.2 is on the catalyst 0.05% Ir/MgAl$_2$O$_4$ – 1L (mostly single atoms). By normalizing to the TOF, the activity on the 0.05% Ir/MgAl$_2$O$_4$ – 1L (mostly single atoms) is even higher than that on the nanoparticles. But in overall, the “TOF vs particle size” trend in n-butane hydrogenolysis is very similar with that in ethane hydrogenolysis. Recall the analysis in section 3.1, the activity of ethane hydrogenolysis on the 0.05% Ir/MgAl$_2$O$_4$ – 1L with mostly single atoms is also much higher than that on the 0.05% Ir/MgAl$_2$O$_4$ – 200mL subnanometer clusters (size ~ 0.7nm). It is proposed that reaction mechanism of alkanes hydrogenolysis on the single atoms is probably very distinctive from that on the small clusters and large nanoparticles.
Figure 4. 2. 3 Comparison of reaction rate of n-butane hydrogenolysis on the Ir/MgAl\(_2\)O\(_4\) series catalysts only (a) and including the very large size particles of 2% Ir/\(\gamma\)-Al\(_2\)O\(_3\) (b) at 180 °C normalized by the surface iridium atoms based on the stoichiometry of “CO:Ir =1:1”. The average particle size of 0.05% Ir/MgAl\(_2\)O\(_4\) – 1L with mostly single atoms is denoted as 0.3 nm, which is approximately the diameter of an Ir atom. And the average particle size of 2% Ir / \(\gamma\)-Al\(_2\)O\(_3\) with very broad size distribution from 2-11nm was chosen as 6 nm presenting in the plot.

Another possibility is that the catalyst of 0.05% Ir/MgAl\(_2\)O\(_4\) – 1L with mostly single atoms might go through a structure change, e.g., the aggregation of Ir single atoms leading to the forming of clusters and nanoparticles. So after one certain reaction for the activation energy measurement, the 0.05% Ir/MgAl\(_2\)O\(_4\) – 1L was flowing in He for 30 min to remove the surface hydrocarbon species and then re-pretreated in 20% H\(_2\) at 500 °C for one hour (the initial pretreatment in 20% H\(_2\) was two hours at 500°C) before testing the activity change with temperature again by two times without taking the catalyst out of the reactor. If the single atoms in the catalyst have aggregated to form clusters and nanoparticles during the initial measurement, the activity result after the second and third time re-pretreatment should decrease and be close to that on the catalysts of 1% Ir/MgAl\(_2\)O\(_4\) NPs (size ~ 1.3nm) or 0.05% Ir/MgAl\(_2\)O\(_4\) – 200mL
subnanometer clusters (size ~ 0.7nm). However, as shown in figure 4.2.4, it is surprising that the TOF on the same batch of 0.05% Ir/MgAl₂O₄ – 1L catalyst increases by twice during the second and third time reaction test, and the “activity vs temperature” trend at the second and third time even overlaps. The result here shows it is very likely that the structure of 0.05% Ir/MgAl₂O₄ – 1L catalyst with mostly single atoms initially has been changed during the first time reaction. And the increased activity of the second and third time reaction after re-pretreatment indicates that the consequence of the re-configuration may not be the aggregation but probably the large size particles or clusters breaking apart and forming more dispersed single atoms on the surface, or the re-pretreatment helps the Ir atoms in the sublayer of the support be dragged onto the surface. As mentioned in section 2.5, the 0.05% Ir/MgAl₂O₄ – 1L catalyst may be not fully reduced after flowing 20% H₂ for two hours at 500°C based on the very high coordination number of Ir-O, Ir-Al and Ir-Mg from EXAFS. A postreaction surface characterization by HAADF-STEM as well as the chemisorption would be helpful and necessary to confirm if and how the surface structure of isolated iridium atoms changes after the n-butane hydrogenolysis reaction.

Figure 4.2.4 Comparison of TOF(s⁻¹) as a function of temperature on 0.05% Ir/MgAl₂O₄ – 1L with mostly single atoms initially and re-pretreated and test by two more cycles.
One more interesting point is the role that the coverage of hydrogen plays. From literature, it is generally accepted that there would be carbonaceous forming on the surface of the catalysts during hydrogenation or hydrogenolysis reactions, especially when the ratio of hydrogen / hydrocarbon is not high enough. Engstrom, J. R., D. W. Goodman, and W. H. Weinberg reported that the only product from the titration of carbonaceous residue after the reaction is methane. However, in this case on all the 5 catalysts, there is no product coming out by titrating with 10 – 30% \( \text{H}_2 \) after the turning off the n-butane even after one hour at about 200 °C, and the only hydrocarbon species detected by GC is the leftovers of n-butane reactants. Once the hydrogen was turned off and only helium was flowing, there would be a lot of C1 and C2 coming out. These results indicate that the hydrogen on the surface may play the role on the dehydrogenation of the hydrocarbon intermediates, and only after the \( \text{H}_2 \) is off, the C-C bonds in the highly-dehydrogenated hydrocarbon intermediates could be cleaved and then the short chain hydrocarbon products would come out.

4.2.3. Comparison of the selectivity and analysis on the mechanism

As discussed in section 4.1, the product distribution contains much information on the reaction mechanism. From plots of the selectivity to methane, ethane and propane as a function of temperature in figure 4.2.5, we could learn that the product distribution dependence on temperature on the catalysts with particle size smaller than 2 nm in the low conversion range is quite different from that in the high conversion range. As shown in figure 4.1.1 and 4.1.2, the selectivity to methane keeps increasing while the selectivity to ethane and propane is decreasing as a function of temperature. Therefore, the series reaction of C-C bond cleavage on the propane intermediate must happen when the conversion is in the high range starting from 8%. However, in the low conversion range starting from about 0.5%, the selectivity to the propane slightly increases on the series of Ir / MgAl\(_2\)O\(_4\) catalysts with the particle size smaller than 2 nm. The trend of product distribution clearly indicates that during the heating process, the parallel reaction pathway \( 3 \) that has the terminal C-C bond cleavage producing one methane and one propane becomes more competitive than the reaction pathway \( 1 \) that has the central C-C bond cleavage producing two ethane molecules. And
the mole increase of C1 is higher than the mole increase of C3 at any temperature, showing that the series reaction pathway ⑥ that contains further C-C bond cleavage on the propane intermediate may also take place. Take the catalyst of 1% Ir/MgAl2O4 NPs (size ~ 1.3nm) as an example, the level of each reaction pathway in the model 2 could be obtained by fitting the raw data of mole of C1, C2 and C3 and conversion from different experiments that performed in the high and low conversion range at the same temperature using MATLAB.

![Model 2](image)

**Table 4. 5** Comparison of the calculation results on the level of different reaction pathways on the 1% Ir/MgAl2O4 NPs (size ~ 1.3nm) catalyst in high and low conversion range denoting as “exp A” and “exp B”, respectively. “x%, y% and z%” represent the percentage of the level corresponding to the parallel reaction pathway ①, ③ and the series reaction pathway ⑥. The sum of x% and y% should be approximately 100%.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Conversion</th>
<th>x%</th>
<th>y%</th>
<th>z%</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>8.8%</td>
<td>0.57%</td>
<td>68.7%</td>
<td>71.0%</td>
</tr>
<tr>
<td>200</td>
<td>13.4%</td>
<td>0.84%</td>
<td>64.6%</td>
<td>66.8%</td>
</tr>
<tr>
<td>210</td>
<td>18.7%</td>
<td>1.2%</td>
<td>59.7%</td>
<td>62.4%</td>
</tr>
<tr>
<td>220</td>
<td>25.9%</td>
<td>1.57%</td>
<td>54.1%</td>
<td>58.4%</td>
</tr>
</tbody>
</table>
As shown from the data in table 4.5, in the low conversion range (exp B), the parallel reaction pathway is indeed less competitive than that in the high conversion range (exp A). And as expected, the series reaction level is also about two times higher in the high conversion range than in the low conversion range. Therefore, as the product distribution results are similar, the reaction mechanism is basically the same on the series of Ir/MgAl_2O_4 catalysts with the particle size smaller than 2 nm, and only the level of the parallel and series reaction pathways is different after doing the same analysis.
Figure 4.2.5 Comparison of the selectivity to C1 (a), C2 (b), C3 (c) products as a function of temperature on the whole series of Ir/MgAl$_2$O$_4$ catalysts and the 2% Ir / γ-Al$_2$O$_3$ with very large particles.

However, it is very obvious that the product distribution on the 2% Ir/γ-Al$_2$O$_3$ NPs is quite distinctive from the others based on the plots in figure 4.2.5 (a), (b) and (c). The selectivity to ethane slightly increases until 210 °C and then quickly decreases. This rollover trend has never been seen on any of the other Ir/MgAl$_2$O$_4$ catalysts, and it clearly illustrates that the C-C bond on the ethane product start being further cleaved and forming more methane molecules even when the propane intermediate is still existing (at 220°C, the selectivity to propane is about 6%), so the reaction mechanism would be more complicated and quite different from the previous analysis in this case.
Figure 4.2.6 Comparison of the selectivity to methane, ethane and propane on the catalysts with different average particle sizes at 180°C. The average particle size of 0.05% Ir/MgAl\textsubscript{2}O\textsubscript{4} – 1L with mostly single atoms is denoted at 0.3 nm, which is approximately the diameter of an Ir atom. And the average particle size of 2% Ir / γ-Al\textsubscript{2}O\textsubscript{3} with very broad size distribution from 2-11nm was chosen as 6 nm in the plot.

Figure 4.2.3 and figure 4.2.6 include the overall comparison of TOF and selectivity dependence on the particle size of Ir/MgAl\textsubscript{2}O\textsubscript{4} catalysts and the extra 2% Ir / γ-Al\textsubscript{2}O\textsubscript{3} with very broad size distribution from 2-11nm (chosen as 6 nm) at 180 °C. The product distribution fluctuates a little for the catalysts with the particle size smaller than 2 nm and the slight fluctuation is negligible combining with the selectivity data at other temperatures (recall the overlapped plots of “selectivity to ethane vs temperature”). The exceptional low ethane selectivity on the 2% Ir / γ-Al\textsubscript{2}O\textsubscript{3} might be because of the much larger particle size, which is inconsistent with the close to 90% ethane selectivity on the same series of Ir / γ-Al\textsubscript{2}O\textsubscript{3} catalyst with the particle size about 1-2 nm reported by Fogler, K., and J. R. Anderson. [25] But the decreasing ethane selectivity with enhanced particle size in their work is accordant in this case. However, it is also very possible that the different support plays a role, as proposed in the previous analysis on the higher activity of 0.05% Ir/MgAl\textsubscript{2}O\textsubscript{4} -1L catalyst with mostly single atoms that the support of MgAl\textsubscript{2}O\textsubscript{4} may provide extra sites for the adsorption of n-butane, or the acid sites on the γ-Al\textsubscript{2}O\textsubscript{3} support may affect the interaction
between the reactant molecules and the Ir metal. Further study on the support effect is still required to understand the fundamentals on the 2% Ir / γ-Al₂O₃ NPs in the case here. One good way is to synthesize one more Ir/MgAl₂O₄ catalyst with much larger particle size to complete the structure sensitivity study of alkanes hydrogenolysis on the same series of Ir/MgAl₂O₄ catalysts, and then add up the experiments on the Ir/γ-Al₂O₃ catalysts in the small particle size range, so that the particle size effect or the support effect would be clear after the complete study.
Chapter 5 Summary and Conclusions

In summary, the ethane hydrogenolysis on the series of Ir/MgAl₂O₄ catalysts is structure sensitive as the activity and kinetic results are very dependent on the particle size. Table 5.1 includes the reaction rate, TOF (calculated by the method in section 2.5.2 with assumption 1), activation energy and reaction orders of ethane hydrogenolysis on the three catalyst of 1% Ir/MgAl₂O₄ NPs, 0.05% Ir/MgAl₂O₄ – 200mL subnanometer clusters and 0.05% Ir/MgAl₂O₄ – 1L with mostly single atoms.

Table 5.1 Comparison of the activity, activation energy and reaction orders of ethane hydrogenolysis on the 3 catalysts with different particle sizes. The activation energy was measured under 1% C₂H₆, 10%H₂ between 335 – 350°C; the H₂ order was measured under 1%C₂H₆ at 335°C between 10 – 19%H₂; the C₂H₆ order was measured under 10%H₂ at 335°C between 1 – 2.8%C₂H₆.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Particle Size</th>
<th>Reaction Rate (mole C₂/mole Ir/s)</th>
<th>TOF(s⁻¹) 335 °C</th>
<th>Ea (kJ/mol)</th>
<th>H₂ Order</th>
<th>C₂H₆ Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% Ir/MgAl₂O₄</td>
<td>1.3 nm</td>
<td>0.91</td>
<td>1.13</td>
<td>158.5</td>
<td>-1.2</td>
<td>0.5</td>
</tr>
<tr>
<td>0.05% Ir/MgAl₂O₄-200mL</td>
<td>0.7nm</td>
<td>0.22</td>
<td>0.28</td>
<td>232.5</td>
<td>-0.7</td>
<td>0.05</td>
</tr>
<tr>
<td>0.05% Ir/MgAl₂O₄-1L</td>
<td>Most Single Atoms</td>
<td>0.45</td>
<td>0.74</td>
<td>190.3</td>
<td>-0.3</td>
<td>0.1</td>
</tr>
</tbody>
</table>

The 1% Ir/MgAl₂O₄ NPs catalyst is the most active, while the catalyst of 0.05% Ir/MgAl₂O₄ – 200mL subnanometer clusters is the least active one in the ethane hydrogenolysis reaction based on the reaction rate and TOF data. Also, after the analysis by combining the activity and the size distribution data, it is found that the reactivity of the catalyst with different sizes is in the order of “nanoparticles > single atoms > clusters”. The reaction orders on the 1% Ir/MgAl₂O₄ NPs is not very consistent with the reaction mechanism reported in the literature that the dissociative hydrogen adsorption step as well as the hydrogen removal steps from the hydrocarbon intermediates are quasi-equilibrated. It is possible that both off the surface hydrogen and the adsorbed *C₂H₆ species are the most abundant surface intermediates. However, the
reaction mechanism on the small clusters and single atoms is probably very different from the particles based on the reaction order results from experiments. The alkanes molecules might be dehydrogenated and form $\pi$ bonds with the Ir metal upon adsorption on the single atom catalysts, while the alkanes molecules might dehydrogenate and form di-$\sigma$ bonds upon adsorption on the subnanometer clusters. The stronger $\sigma$ bonds than the $\pi$ bonds could help explain the higher activity on the single atoms than the subnanometer clusters in both of the ethane hydrogenolysis and n-butane hydrogenolysis cases. Also, the hydrogen dissociate adsorption step might not be quasi-equilibrated on the small size clusters based on the work published by Lu, Jing, Pedro Serna, and Bruce C. Gates [35]. Therefore, further study is required on the $H_2$ / $D_2$ exchange on the same series of catalyst with smaller size, especially the single atoms, which could help confirm if the adsorption of hydrogen step is fast enough, thereafter leading to the conclusion if the reaction mechanism should be unique on the single atoms or small clusters.

Besides, the n-butane hydrogenolysis on the same series of Ir/MgAl$_2$O$_4$ catalysts is also structure sensitive in terms of the activity. The activity on 1% Ir/MgAl$_2$O$_4$ NPs and 0.05% Ir/MgAl$_2$O$_4$ – 1L is evidently much higher than that on 0.05% Ir/MgAl$_2$O$_4$ – 200mL. However, it is surprising that the ethane selectivity is not sensitive to the catalyst structure. In the catalytic performance study, the plots of “ethane selectivity vs temperature” on different catalysts are almost overlapped, meaning the invariant product distribution with the particle size.

As shown in the scheme above, the reaction pathways of n-butane hydrogenolysis in the high conversion range for the performance study basically include the parallel pathways of central C-C bond cleavage and terminal C-C bond cleavage on the n-butane and the series reaction pathway of one C-C bond cleavage on
the propane intermediate. During the temperature increasing process, the selectivity to both of methane and propane products would increase, but the selectivity to ethane would drop. The results clearly show that the parallel reaction of terminal C-C bond cleavage becomes more and more competitive during the heating process. In another study, as the conversion changes at a certain temperature by varying the total flow rate, the ethane selectivity does not change, but the selectivity to propane begins to decrease at higher conversion. The results mean that as the reaction further going on, the terminal C-C bond cleavage would definitely increases, and the series reaction also moves more and more forward. Only when the conversion is close to 100% and almost all the propane has been consumed, the ethane product would start to react, leading to an obvious lower selectivity to ethane.

The H₂/C₄ ratio effect was also studied, and it is found that when the H₂/C₄ ratio is lower than 10 by decreasing H₂ concentration to less than 10%, there would be nonnegligible deactivation; when the H₂/C₄ ratio is lower than 10 by increasing n-butane concentration at 10%H₂, the deactivation is not huge. The H₂/C₄ ratio change has opposite effect by increasing the H₂ concentration at fixed 1% n-butane and decreasing the n-butane concentration at fixed 10% H₂, and the effect could tell a negative order in H₂ and a positive order in n-butane. When the reactant concentration keeps increasing at a fixed H₂/C₄ ratio, the conversion evidently drops, indicating a larger absolute value of the negative H₂ order than the positive n-butane order. After analyzing on the details of conversion change with H₂ concentration and H₂/C₄ ratio, it shows that the extremely high H₂ concentration might lead to bad GC peak separation and increase the error. Therefore, the very high H₂ concentration should be avoided.

A comparison of the activity, ethane selectivity and activation energy in the kinetic regime is also summarized in table 5.2. As we can see from the table, the selectivity to ethane on the series of Ir/MgAl₂O₄ are almost the same (~76%) except the catalyst of 0.05% Ir/MgAl₂O₄ – 200mL clusters that has a slightly higher selectivity of 79%. Moreover, the activity of the 0.05% Ir/MgAl₂O₄ – 200mL clusters is also the lowest among all the catalysts, and the activity on the three catalysts with the average size of 1.3 nm and 1nm as well as the one with mostly single atoms is almost identical. Similarly with the ethane
hydrogenolysis, further study is required to figure out if the n-butane hydrogenolysis would go through a unique reaction mechanism on the single atoms, or a structure change would happen on the single atoms during the reaction, leading to the similar performance with the nanoparticles. The postreaction analysis by HAADF-STEM and chemisorption would help confirm if there is structure change during the reaction or not.

Table 5.2 Comparison of the activity, activation energy and reaction orders of n-butane hydrogenolysis on the 3 catalysts with different particle sizes. The activation energy was measured under 1% n-C₄H₁₀, 10%H₂ between 170 – 190°C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Average size</th>
<th>Reaction Rate (mole C₄/mole Ir/s) (180 °C)</th>
<th>TOF (s⁻¹) (180 °C)</th>
<th>Ethane Selectivity (180 °C)</th>
<th>Ea (kJ/mol) 170-190 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% Ir/γ-Al₂O₃</td>
<td>5-8 nm</td>
<td>0.030</td>
<td>0.042</td>
<td>58.2%</td>
<td>90.4</td>
</tr>
<tr>
<td>1% Ir/MgAl₂O₄</td>
<td>1.3 nm</td>
<td>0.002</td>
<td>0.003</td>
<td>75.6%</td>
<td>113.1</td>
</tr>
<tr>
<td>0.5% Ir/MgAl₂O₄ (Ir(CO)₂(acac))</td>
<td>1 nm</td>
<td>0.002</td>
<td>0.003</td>
<td>76.9%</td>
<td>135.5</td>
</tr>
<tr>
<td>0.05% Ir/MgAl₂O₄-200mL</td>
<td>0.7 nm</td>
<td>0.0009</td>
<td>0.001</td>
<td>79.2%</td>
<td>137.2</td>
</tr>
<tr>
<td>0.05% Ir/MgAl₂O₄-1L</td>
<td>mostly single atoms</td>
<td>0.002</td>
<td>0.004</td>
<td>76.5%</td>
<td>113.2</td>
</tr>
<tr>
<td>0.0025% Ir/MgAl₂O₄</td>
<td>Single atoms</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

The reaction mechanism on the series of Ir/MgAl₂O₄ catalysts in the kinetic regime is similar with those for the catalytic performance study in the high conversion range. But the level of the series reaction is much lower when the reaction was running in the kinetic regime.

In the kinetic study, the activity and product distribution result on the 2% Ir/γ-Al₂O₃ NPs is distinctive from all the others. The obvious drop of the propane selectivity with temperature clearly shows that the series reaction on propane hydrogenolysis moves much more forward than that on the other catalysts. More exceptional, the C-C bond in the ethane product could be further cleaved in the case of 2% Ir/γ-Al₂O₃ NPs when the temperature is higher than 220 °C, corresponding to the obvious decreasing in the ethane selectivity plot in that temperature range. But it is still unclear if the reason for the unique activity and product distribution on the 2% Ir/γ-Al₂O₃ NPs is the extraordinarily large particle size comparing with the
Ir/MgAl\textsubscript{2}O\textsubscript{4} series, or the special role of the \textgamma-Al\textsubscript{2}O\textsubscript{3} support in this case. The investigation could be realized by performing the reaction at the same conditions on the larger size of Ir/MgA\textsubscript{2}O\textsubscript{4} catalyst, or on a series of Ir/\textgamma-Al\textsubscript{2}O\textsubscript{3} catalyst in the small size range in the future work.
Appendices

A. Catalyst Preparation and Characterization

A.1 Catalyst preparation

The 1% Ir/MgAl_2O_4 catalyst was synthesized by incipient wetness method. 2 gram of MgAl_2O_4 (Puralox MG30, Sasol, calcined 500 °C before use) was weighed and poured into a 250 mL Pyrex bottle. Ir nitrate (8.7 wt. % Ir, Furuya Metal CO. Ltd.) was diluted in deionized water based on the 1% weight loading with 2 gram of MgAl_2O_4 support. The diluted Ir nitrate solution was added to the support dropwise with a 20 μL autopipette, then left for 1 day before reduction at 800°C in 50% H_2 in the tube furnace. The pretreatment method was described in section 2.1.1 (figure 2.1.1).

The catalyst of 0.5% Ir/MgAl_2O_4 was also synthesized by wet impregnation method from Ir(CO)_2(acac) precursor with the toluene solvent. A pre-weighed, clean, empty vial was sent into the glove box for getting some of the Ir(CO)_2(acac) precursor and the top of the vial was sealed before moving out of the glove box. Then weighed the vial and the mass of the Ir(CO)_2(acac) precursor could be obtained by the differential method (total mass of the vial and precursor minus the mass of the empty vial). Based on the amount of solid precursor, injected the toluene solvent to dissolve the precursor. After that, quickly added a certain amount of MgAl_2O_4 support (Puralox MG28, Sasol, calcined 500 °C before use) calculated based on the 0.5% weight loading into the vial and simultaneously start the nitrogen flow to avoid the exposure to air. The catalyst was flowing in N_2 for a whole day before use and there was no calcination step for this catalyst. The pretreatment method was described in section 2.1.1 (figure 2.1.4).

The catalyst of 0.05% Ir/MgAl_2O_4 -200mL subnanometer clusters was synthesized by wet impregnation method. 200 mL deionized water was added into the 250 mL Pyrex bottle for dilution before adding the diluted Ir nitrate precursor based on the 0.05% weight loading with 5 gram of MgAl_2O_4 support (Puralox MG30, Sasol, calcined 500 °C before use). After 2 hours stirring, the solid catalyst was separated by
filtration, and then sent for calcination at 500°C for 4 hours. The pretreatment method was described in section 2.1.1 (figure 2.1.2).

The catalyst of 0.05% Ir/MgAl₂O₄ – 1L with mostly single atoms was synthesized by the same method with the previous “200mL” sample, except that the volume of deionized water was 1L for dilution in a 1L Pyrex bottle. The pretreatment method was described in section 2.1.1 (figure 2.1.3).

In terms of the calcination step, the catalysts were first calcined at 80 °C for 12 hours with a heating rate of 0.5 °C/min, and then 100 °C for 4 hours with a heating rate of 1 °C/min, and finally calcined at 500 °C for 4 hours with a heating rate of 5 °C/min.

**A.2 TEM images**

The TEM image of all the samples utilized in this study are presented in the following text.

![HAADF-STEM image and size distribution for 1% Ir/MgAl₂O₄ NPs catalyst with the average size of 1.3nm. The 1% Ir/MgAl₂O₄ NPs sample was reduced at 800 °C.](image)

*Figure A. 2. 1* HAADF-STEM image and size distribution for 1% Ir/MgAl₂O₄ NPs catalyst with the average size of 1.3nm. The 1% Ir/MgAl₂O₄ NPs sample was reduced at 800 °C.
Figure A. 2 HAADF-STEM image and size distribution for 0.05% Ir/MgAl$_2$O$_4$ -1L with mostly single atoms. The 0.05% Ir/MgAl$_2$O$_4$ -1L sample was calcined at 500 °C and reduced at 500 °C.
Figure A. 2.3 HAADF-STEM image and size distribution for 0.05% Ir/MgAl₂O₄ -200mL clusters with the average particle size of 0.7nm. The 0.05% Ir/MgAl₂O₄ -200mL sample was calcined at 500 °C and reduced at 700 °C.

Figure A. 2.4 HAADF-STEM image and size distribution for 0.5% Ir/MgAl₂O₄ prepared with Ir(CO)₂(acac) with very uniform size distribution and the particle size is about 1nm. The 0.5% Ir/MgAl₂O₄ sample was reduced at 500 °C.

B. Determination of Transport Limitation based on the Criterion[37]

In addition to the analysis based on experimental results of dilution effect, another fast way to determine if there is existing transport limitation or not is on the basis of the criterion. In the following, one example of 0.05% Ir/MgAl₂O₄-200mL would be utilized to display the procedures of calculation to determine the existence of transport limitation based on the criterion, and the calculation results of other experiments would also be summarized in a table.
B.1 Experiments conditions and results.

Catalyst amount: \( m = 50 \text{ mg} = 5 \times 10^{-5} \text{ kg} \)

Particle size: 106-250 μm
- Average particle diameter \( d_p = 1.78 \times 10^{-4} \text{ m} \).
- Average particle radius \( R_p = 8.9 \times 10^{-5} \text{ m} \).

Total flow rate = 100 sccm, the percentage of ethane = 1%

Mole flow rate of \( \text{C}_2\text{H}_6 \) = \( \frac{(100 \text{ sccm} \times 1\%) \times (101325 \text{ Pa}) \times (10^{-6} \text{ m}^3)}{(60 \text{ s}) \times (8.314 \text{ J/K}^{-1} \cdot \text{mol}^{-1}) \times (273 \text{ K})} = 7.44 \times 10^{-7} \text{ mol} \cdot \text{s}^{-1} \)

(Note: at lab conditions, mass flow rate \( \approx \) volumetric flow rate)

Activity Results.
- At 335°C (608K)
  - Conversion = 3.38%  TOF=0.28 s\(^{-1}\)
  - Reaction rate = \( 5.02 \times 10^{-7} \text{ mol} / (\text{g of cat} \cdot \text{s}) \)
- At 350°C (623K)
  - Conversion = 8.82%  TOF = 0.59 s\(^{-1}\)
  - Reaction rate = \( 1.32 \times 10^{-6} \text{ mol} / (\text{g of cat} \cdot \text{s}) \)

Reaction rate in the unit of \( \text{m}^3 / (\text{kg} \cdot \text{s}) \):

\[
r = \frac{100 \times 1\% / 10^6}{60} \text{ (m}^3/\text{s}) \times \text{conversion} / \text{catalyst amount in 'kg'}
\]

At 335°C, plug in the conversion and catalyst amount:

\[
r = \frac{10^{-6} \text{ (m}^3/\text{s}) \times 3.38\% / (5 \times 10^{-5})\text{kg}}{60} = 1.13 \times 10^{-5} \text{ m}^3/\text{kg} \cdot \text{s}
\]

B.2 Mear’s criterion for external mass diffusion

In the ethane hydrogenolysis reaction system, there are \( \text{C}_2\text{H}_6 \) and \( \text{H}_2 \) served as reactants balanced with helium and also \( \text{CH}_4 \) as the only product. As we could learn from the CRC handbook of chemistry and physics [38], the smallest binary diffusion coefficient in the reaction system is the diffusion coefficient between methane and helium. \( D_{\text{CH}_4-\text{He}}(673.15\text{K}) = 2.784 \text{ cm}^2/\text{s} \).
Based on the temperature and pressure dependence equation for diffusion relationships for gases[36],

\[ D_{AB}(T_2, P_2) = D_{AB}(T_1, P_1) \times \frac{P_1}{P_2} \times \left( \frac{T_2}{T_1} \right)^{1.75} \]

In this case, at 335°C (608K),

\[ D_{CH_4-He(608K)} = D_{CH_4-He(673.15K)} \times \left( \frac{608.15K}{673.15K} \right)^{1.75} = 2.331 \text{ cm}^2/\text{s} = 2.331 \times 10^{-4} \text{ m}^2/\text{s}. \]

Bulk density:

\[ \rho_b = \frac{\text{Total catalys amount in the reactor}}{\pi \times (\text{inner radius of the reactor}) \times \text{bed length}} = \frac{5 \times 10^{-5} \text{ kg}}{\pi \times (0.2 \times 10^{-2} \text{ m})^2 \times (0.7 \times 10^{-2} \text{ m})} = 568.4 \text{ kg/m}^3 \]

Granule density:

\[ \rho_c = \frac{\rho_b}{1 - \phi} = \frac{568.4 \text{ kg}}{1 - 0.4} = 947.35 \text{ kg/m}^3, \]

where the pellet porosity \( \phi = 0.4 \)

Mass transfer coefficient:

\[ k_c = \frac{2 \cdot D_{CH_4-He}}{d_p} = \frac{2 \times (2.331 \times 10^{-4} \text{ m}^2/\text{s})}{1.78 \times 10^{-4} \text{ m}} = 2.62 \text{ m/s} \]

\( k'_1 \) is defined as the product of reaction rate in the unit of \( \text{m}^3 / (\text{kg} \cdot \text{s}) \) multiply the granule density:

\[ k'_1 = 1.127 \times 10^{-5} \text{ m}^3/(\text{kg} \cdot \text{s}) \times 947.35 \text{ kg/m}^3 = 0.0107 \text{ s}^{-1} \]

**Mear’s Criterion for External mass diffusion:** \( \frac{k'_1 \cdot R_p}{k_c} < 0.15 \)

In this case,

\[ \frac{k'_1 \cdot R_p}{k_c} = \frac{0.0107 \text{ s}^{-1} \cdot (8.9 \times 10^{-5} \text{ m})}{2.62 \text{ m/s}} = 3.63 \times 10^{-7} \ll 0.15 \]
Therefore, there is no external concentration gradients between the reactants fluid bulk and the surface of the catalyst pellet.

**B.3 Internal diffusion limitation by Weisz-Prater criterion**

Effective diffusivity in the catalyst pellet:

\[
De = \frac{D_{AB} \phi_\sigma}{\tilde{t}} = \frac{D_{CH_4 - He} \phi_\sigma}{\tilde{t}} = \frac{2.331 \times 10^{-4} m^2/s \times 0.4 \times 0.8}{3},
\]

where the constriction factor \(\sigma = 0.8\);

the tortuosity \(\tilde{t} = \frac{\text{Actual distance a molecule travels between 2 points}}{\text{Shortest distance between the 2 points}} \approx 3\).

Therefore, \(De = \frac{2.331 \times 10^{-4} m^2/s \times 0.4 \times 0.8}{3} = 2.5 \times 10^{-5} m^2/s\)

**Weisz-Prater Criteria:** \(\frac{k_1 \rho_C R_P^2}{De} < 0.6\)

In this case, \(\frac{k_1 \rho_C R_P^2}{De} = \frac{(1.127 \times 10^{-5} m^3/(kg \cdot s) \times (947.35 kg/m^3) \times (8.9 \times 10^{-5} m)^2}{(2.5 \times 10^{-5} m^2/s)} = 3.38 \times 10^{-6} \ll 0.6\)

Therefore, there is no existing internal concentration gradients in the catalytic system.

**B.4 Intraparticle heat transfer limitation**

Heat of ethane hydrogenolysis reaction: \(\Delta H_R = 65000 J/mol\)

Thermal conductivity of \(\text{MgAl}_2\text{O}_4\): \(\lambda_{\text{MgAl}_2\text{O}_4} = 0.1 W/(cm \cdot K) = 10 W/(m \cdot K)\)

\((\text{Particle thermal conductivity of the catalyst } \lambda_i \text{ is estimated by the thermal conductivity of } \text{MgAl}_2\text{O}_4 \text{ support, since the catalyst is mainly composed of the support at such a low loading iridium of 0.05%.)}\)

Concentration of ethane: \(\frac{P_{C_2H_6}}{RT} = \frac{1% \times 101325 Pa}{8.314 J/(K \cdot mol) \times 608 K} = 0.2 mol/m^3\)

Measured reaction rate per unit particle volume:
\[ R = \frac{k_1 \rho \text{c}_{\text{C}_2\text{H}_6}}{1 - \phi} = \left( \frac{1.127 \times 10^{-5} m^3/(kg \cdot s)}{56 \times 10^3 k \cdot m^3/(mol \cdot s)} \right) \times (0.2 \text{mol} / m^3) = 2.134 \times 10^{-3} \text{mol} / (m^3 \cdot s) \]

The criterion for intraparticle heat transfer limitation: \[ \frac{|\Delta H_R| R^2 \rho^2 \lambda}{R_g R_p^2} = 0.75, \]

where \( R_g \) is the ideal gas constant in the unit of J/(mol·K); \( T_0 \) is the temperature at the surface of the particle, which, in our case, is the approximately the same as reaction temperature that measured by the additional thermocouple attached at the center of the catalyst bed; \( E_a \) is the activation energy in the unit of J/mol.

In this case,

\[
\frac{|\Delta H_R| R^2 \rho^2 \lambda}{R_g R_p^2} = \frac{(65000 J/mol) \times (2.134 \times 10^{-3} \text{mol} / (m^3 \cdot s) \times (89 \times 10^{-6})^2 (230.4 \times 10^3 J/mol)}{(10 W/(m \cdot K)) \times 8.314 J/(mol \cdot K) \times (608 K)^2} = 8.2 \times 10^{-9} \ll 0.75
\]

Therefore, there is no intraparticle heat transfer limitation in the catalytic system.

### B.6 Mear’s interphase heat transfer limitation

Gas-solid heat transfer coefficient: \( h = \frac{2 \lambda_g}{d_p} \), where \( \lambda_g = y_{\text{He}} \lambda_{\text{He}} + y_{\text{H}_2} \lambda_{\text{H}_2} + y_{\text{C}_2\text{H}_6} \lambda_{\text{C}_2\text{H}_6} \).

\[ \lambda_{\text{H}_2} = 317.6 \text{ mW} / (m \cdot K) \text{ at } 600K, 0.1\text{MPa}; \]
\[ \lambda_{\text{He}} = 252.4 \text{ mW} / (m \cdot K) \text{ at } 600K, 0.1\text{MPa}; \]
\[ \lambda_{\text{C}_2\text{H}_6} = 73.338 \text{ mW} / (m \cdot K) \text{ at } 600K, 0.1\text{MPa}. \]

(The condition of 600K, 0.1MPa is very close to our condition of 608K, 1atm, therefore, the thermal conductivity of the reaction components at the condition of 600K, 0.1MPa could be calculated by 89% × 0.2524 W/(m·K) + 10% × 0.3176 W/(m·K) + 1% × 0.073338 W/(m·K) = 0.257 W/(m·K))

From above, \( h = \frac{2 \lambda_g}{d_p} = \frac{2 \times 0.257 W/(m \cdot K)}{178 \times 10^{-6} m} = 2887.64 \text{ W} / (m^2 \cdot K) \).

Mear’s criterion for interphase heat transfer limitation: \[ \frac{|\Delta H_R| R^2 \rho^2 \lambda}{R_g R_p^2} < 0.15 \]

In this case,
\[
\frac{\Delta H_R}{R_g \Delta T_0} = \frac{(65000 J/mol) \times (2.314 \times 10^{-3} mol/(m^3 \cdot s)) \times (89 \times 10^{-6} m) \times (202 \times 10^3 J/mol)}{8.314 J/(mol \cdot K) \times (2887.64 W/(m^2 \cdot K)) \times (608K)^2} = 3.0 \times 10^{-7} \ll 0.15
\]

Therefore, there is no interphase heat transfer limitation in the catalytic system.

**B.7 Mear’s criterion for (interparticle) heat transfer limitation**

The effective thermal conductivity of the bed:

\[
\lambda_{eff} = \lambda_g \cdot \beta \left( \frac{1-\phi}{\lambda_g + \psi} \right), \text{ where } \beta=1, \ \psi=0.04 \text{ when } \Phi=0.4, \ \lambda_s \approx \lambda_{MgAl_2O_4} = 10 W/(m \cdot K)
\]

Thus, \[
\lambda_{eff} = 0.257 W/(m \cdot K) \times \frac{1-0.4}{0.257 W/(m \cdot K) + 0.04} = 2.35 \frac{W}{m \cdot K}
\]

Wall heat transfer coefficient:
\[
h_w = \frac{1.2 \lambda_g}{d_p} = \frac{1.2 \times 0.257 W/(m \cdot K)}{1.78 \times 10^{-4} m} = 1732.6 W/m^2 \cdot K
\]

Reactor radius: \( R_t = 0.2 \text{ cm} = (2 \times 10^{-3}) \text{ m} \)

**Mear’s criterion for radial heat transfer limitation:**
\[
\frac{|\Delta H_R| R_t^2}{\lambda_{eff} \Delta T_0 R_g} \left( 1 + \frac{4\lambda_{eff}}{R_t h_w} \right) < 0.4
\]

In this case,
\[
\frac{|\Delta H_R| R_t^2}{\lambda_{eff} \Delta T_0 R_g} \left( 1 + \frac{4\lambda_{eff}}{R_t h_w} \right) = \frac{(65000 J/mol) \times (2.134 \times 10^{-3} mol/m^3 \cdot s)}{2.35 W/m \cdot K \times 608K^2 \times 8.314} \times (2 \times 10^{-3} m)^2
\]
\[
\times \frac{4 \times 2.35 W}{(2 \times 10^{-3} m) \times 1732.6 W/(m^2 \cdot K)} = 6.58 \times 10^{-5} \ll 0.4
\]

Therefore, there is no interparticle heat transfer limitation in the catalytic system.

**B.8 A summary of transport limitation criterions for ethane hydrogenolysis on all catalysts**
The results of ethane hydrogenolysis on other catalysts with or without dilution were also used to do the calculation for the transport limitation criterions. From the calculation results in the table shown below, we could learn that theoretically there is no existing transport limitation in these catalytic systems as the calculated numbers are all much smaller than the criterion. The criterion results are important reference for researchers to determine if there is transport limitation or the activity results are reliable or not.

**Table B.** A summary of the calculation results for transport limitation criterion of ethane hydrogenolysis on all catalysts with or without dilution.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>External Mass Diffusion</th>
<th>Internal Mass Diffusion</th>
<th>Intraparticle Heat Transfer</th>
<th>Interphase Heat Transfer</th>
<th>Interparticle Heat Transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% Ir/MgAl2O4 (D=200 SiO2)</td>
<td>$k_1' \cdot \frac{R_p}{k_c} &lt; 0.15$</td>
<td>$k_1' \cdot \frac{\rho \cdot R_p^2}{D_e} &lt; 0.6$</td>
<td>$</td>
<td>\Delta H_R</td>
<td>\frac{R^2 E_a}{\lambda_p R_0^2} &lt; 0.75$</td>
</tr>
<tr>
<td>0.05% Ir/MgAl2O4-1L (no dilution)</td>
<td>9.5 E-7</td>
<td>8.9 E-6</td>
<td>1.8 E-8</td>
<td>6.9 E-7</td>
<td>1.4 E-4</td>
</tr>
<tr>
<td>0.05% Ir/MgAl2O4-200mL (no dilution)</td>
<td>3.6 E-7</td>
<td>3.4 E-6</td>
<td>8.3 E-9</td>
<td>3.2 E-7</td>
<td>6.6 E-5</td>
</tr>
</tbody>
</table>

**C. Derivations for the Rate Equation**

The process of the derivations for the rate equation of ethane hydrogenolysis shown in section 3.1.4 would be presented in the following text.

Recall the proposed sequence of the steps and intermediates during ethane hydrogenolysis on 7nm Ir/SiO2 from Flaherty, David W., et al..[32]

\[
H_2 + 2 \cdot \Leftrightarrow 2 \cdot H^* \tag{1}
\]

\[
C_2H_6 + \cdot \Leftrightarrow C_2H_5^* \tag{2}
\]

\[
C_2H_5^* + \cdot \Leftrightarrow C_2H_4^* + H^* \tag{3}
\]

\[
C_2H_4^* + 2 \cdot \Leftrightarrow C_2H_3^* + H^* \tag{4}
\]

\[
*C_2H_4^* + \cdot \Leftrightarrow *C_2H_3^* + H^* \tag{5}
\]
The experimental results of the reaction orders in this study are unlikely to follow the same mechanism with the literature. Based on the analysis in section 3.1.4, if \( \text{C}_2\text{H}_5 \) is the intermediate that undergoes the C-C bond cleavage, and the C-C bond cleavage step is exactly the rate determining step.

The elementary steps could be presented as below.

\[ \text{H}_2 + 2 * \rightleftharpoons 2 \text{H}^* \]  
Quasi-equilibrium (1)

\[ \text{C}_2\text{H}_6 + * \rightleftharpoons \text{C}_2\text{H}_5^* \]  
Quasi-equilibrium (2)

\[ \text{C}_2\text{H}_5^* + * \rightleftharpoons \text{C}_2\text{H}_5^* + \text{H}^* \]  
Quasi-equilibrium (3)

\[ \text{C}_2\text{H}_5^* + * \rightleftharpoons \text{CH}_2^* + \text{CH}_3^* \]  
Rate determining step (6)

\[ \text{CH}_2^* + 2\text{H}^* \rightleftharpoons \text{CH}_4 + 3^* \]  
Quasi-equilibrium (7-1)

\[ \text{CH}_3^* + \text{H}^* \rightleftharpoons \text{CH}_4 + 2^* \]  
Quasi-equilibrium (7-2)

The rate equation for each of the elementary step before C-C bond cleavage could also be listed below.

\[ \frac{d\theta_H}{dt} = k_1^+ P_{H_2} \theta_H^2 - k_1^- \theta_H^2 \]

\[ \frac{d\theta_{\text{C}_2\text{H}_6}}{dt} = k_2^+ P_{\text{C}_2\text{H}_6} \theta_{\text{C}_2\text{H}_6} - k_2^- \theta_{\text{C}_2\text{H}_6} \]

\[ \frac{d\theta_{\text{C}_2\text{H}_5}}{dt} = k_3^+ \theta_{\text{C}_2\text{H}_5} \theta_{\text{H}} - k_3^- \theta_{\text{C}_2\text{H}_5} \theta_{\text{H}} \]

As these steps are quasi-equilibrated, the terms of \( \frac{d\theta_H}{dt} \), \( \frac{d\theta_{\text{C}_2\text{H}_6}}{dt} \), and \( \frac{d\theta_{\text{C}_2\text{H}_5}}{dt} \) approximately equal to zero.

\[ k_1^+ P_{H_2} \theta_H^2 - k_1^- \theta_H^2 = 0 \quad \rightarrow \quad \theta_H = \sqrt{K_1 P_{H_2} \theta_{\text{C}_2\text{H}_5}} \]
\[ k_2^+ P_{C_2H_6} \theta_s - k_2^- \theta_{C_2H_6} = 0 \quad \Rightarrow \quad \theta_{C_2H_6} = K_2 P_{C_2H_6} \theta_s \]

\[ k_3^+ \theta_{C_2H_6} \theta_s - k_3^- \theta_{C_2H_5} \theta_H = 0 \quad \Rightarrow \quad \theta_{C_2H_5} = \frac{K_3 \theta_{C_2H_6} \theta_s}{\theta_H} = \frac{K_3 K_2 P_{C_2H_6} \theta_s}{\sqrt{K_1 P_{H_2}}} \]

The rate equation for the reaction could be considered as the same with the rate equation for the rate limiting step: \( r = k_{C-C} \theta_{C_2H_6} \theta_s \).

To solve \( \theta_s \), the most abundant surface intermediate needs to be assumed for the simplification. First of all, if the surface hydrogen is the most abundant surface intermediate, which means that \( \theta_H \gg \theta_s, \theta_{C_2H_6} \) and \( \theta_{C_2H_5} \), then \( \theta_H = \sqrt{K_1 P_{H_2}} \theta_s \approx 1 \). After solving it, \( \theta_s = \frac{1}{\sqrt{K_1 P_{H_2}}} \), and if the \( \theta_s \) and \( \theta_{C_2H_5} \) terms are plugged in the rate equation, then \( r = k_{C-C} \frac{K_3 \theta_{C_2H_6} \theta_s^2}{\theta_H} = k_{C-C} \frac{K_3 K_2 P_{C_2H_6} \theta_s^3}{\sqrt{K_1 P_{H_2}} \theta_s} = k_{C-C} \frac{K_3 K_2 P_{C_2H_6}}{(K_1 P_{H_2})^{1.5}} \). Therefore, the \( H_2 \) order is -1.5 and the ethane order is 1.

It could also be assumed that the most abundant surface intermediate is the \(*C_2H_6\) species instead of the surface hydrogen. So in this case, \( \theta_{C_2H_6} = K_2 P_{C_2H_6} \theta_s \approx 1 \), thus, \( \theta_s = \frac{1}{K_2 P_{C_2H_6}} \). So the rate equation could be expressed as \( r = k_{C-C} \frac{K_3 \theta_{C_2H_6} \theta_s^2}{\theta_H} = k_{C-C} \frac{K_3 K_2 P_{C_2H_6} \theta_s^2}{\sqrt{K_1 P_{H_2}}} = k_{C-C} \frac{K_3 K_2 P_{C_2H_6}}{(K_1 P_{H_2})^{0.5}} \). Therefore, the \( H_2 \) order is -0.5, and the ethane order is -1.

When it is assumed that the C-C bond cleavage on the \(*C_2H_5\) is the rate determining step, and both of the surface hydrogen and adsorbed \(*C_2H_6\) species are most abundant surface intermediates, then \( \theta_H + \theta_{C_2H_6} \approx 1 \), which means that \( (\sqrt{K_1 P_{H_2}} + K_2 P_{C_2H_6}) \times \theta_s = 1 \), so \( \theta_s = \frac{1}{\sqrt{K_1 P_{H_2}} + K_2 P_{C_2H_6}} \). Therefore, the rate equation could be presented as \( r = k_{C-C} \frac{K_3 K_2 P_{C_2H_6}}{(K_1 P_{H_2})^{1.5} + 2 K_1 P_{H_2} K_2 P_{C_2H_6} + (K_2 P_{C_2H_6})^2 \sqrt{K_1 P_{H_2}}} \). As there are more than one intermediate as the most abundant surface species, no simplification could be applied to the denominator of the rate equation in this case. As a consequence, the reaction orders obtained from experiments are very
probably a combination of different reaction mechanisms such as the coexisting surface intermediates, since the particle size distribution within the catalyst utilized in this study is not very uniform.


