ไดเมอไรเซชันของไอโซบิวทีนเป็นไอโซออกทีนบนตัวเร่งปฏิกิริยานิกเกิลออกไซด์-ทังสเตนออกไซด์บนอะลูมินา

นางสาวกรรณรา เกิดผล

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2559

Dimerization of isobutene to isooctene over NiO-WO_3/Al_2O_3 catalysts

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2016

Thesis Title	Dimerization of isobutene to isooctene over NiO-WO_3/Al_2O_3 catalysts
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กรรณรา เกิดผล : ไดเมอไรเซชันของไอโซบิวทีนเป็นไอโซออกทีนบนตัวเร่งปฏิกิริยานิกเกิลออกไซด์-ทังสเตนออกไซด์บนอะลูมินา (Dimerization of isobutene to isooctene over NiO-WO_3/Al_2O_3 catalysts) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. จูงใจ ปั้นประณต, 80 หน้า.

เตรียมตัวเร่งปฏิกิริยานิกเกิลออกไซด์-ทังสเตนออกไซด์บนอะลูมินาด้วยวิธีเคลือบฝังและประสิทธิภาพของตัวเร่งปฏิกิริยาในปฏิกิริยาไดเมอไรเซชันของไอโซบิวทีนภายใต้อุณหภูมิ 150 องศาเซลเซียสและความดันบรรยากาศ จากการศึกษาผลกระทบของร้อยละน้ำหนักของนิกเกิลและทังสเตนที่แตกต่างกันต่อประสิทธิภาพในการเร่งปฏิกิริยาของตัวเร่งปฏิกิริยา ผลการทดสอบพบว่าตัวเร่งปฏิกิริยานิกเกิลออกไซด์-ทังสเตนออกไซด์บนอะลูมินาให้ร้อยละการเปลี่ยนของไอโซบิวทีนและร้อยละการเลือกเกิดไอโซออกทีนสูงกว่าตัวเร่งปฏิกิริยานิกเกิลออกไซด์บนอะลูมินา ทังสเตนออกไซด์เพิ่มความเป็นกรดของตัวเร่งปฏิกิริยาและปรับปรุงร้อยละการเลือกเกิดไอโซออกทีน โดยตัวเร่งปฏิกิริยา 1Ni-4W/Al_2O_3 เป็นอัตราส่วนของนิกเกิลและทังสเตนที่ดีที่สุดที่ให้ประสิทธิภาพของตัวเร่งปฏิกิริยาสูงที่สุด จากนั้นใช้อัตราส่วนของนิกเกิลและทังสเตนนี้ในการศึกษาร้อยละน้ำหนักของซิลิกาในตัวรองรับซิลิกา-อะลูมินาและวิธีการเตรียมอะลูมินาที่แตกต่างกัน ผลการทดสอบพบว่าตัวรองรับซิลิกา-อะลูมินาที่ไม่มีโลหะให้ร้อยละผลได้เป็นไอโซออกทีนสูง เนื่องจากซิลิกา-อะลูมินามีปริมาณกรดแก่สูงและความเป็นกรดทั้งหมดของตัวเร่งปฏิกิริยาสูงซึ่งเพิ่มร้อยละการเปลี่ยนของไอโซบิวทีน ตัวเร่งปฏิกิริยา 40SiO_2-Al_2O_3 ให้ประสิทธิภาพของตัวเร่งปฏิกิริยาสูงที่สุด สำหรับผลกระทบของวิธีการเตรียมอะลูมินาที่แตกต่างกันประกอบด้วยวิธีโซลโวเทอร์มอล วิธีตกตะกอนร่วม และวิธีการเผาจากกิบไซต์ ตัวเร่งปฏิกิริยา 1Ni-4W/Al_2O_3-GIB ให้ประสิทธิภาพของตัวเร่งปฏิกิริยาสูงที่สุด เนื่องจากการเผาจากกิบไซต์ปรับปรุงโครงสร้างและความเป็นกรดของตัวเร่งปฏิกิริยาซึ่งให้ประสิทธิภาพของตัวเร่งปฏิกิริยาสูงและการก่อตัวของคาร์บอนต่ำ

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5870105921 : MAJOR CHEMICAL ENGINEERING

KEYWORDS: ISOBUTENE DIMERIZATION / NICKEL-TUNGSTEN OXIDE / IMPREGNATION METHOD

KANNARA KERDPHOL: Dimerization of isobutene to isooctene over NiO-WO_3/Al_2O_3 catalysts. ADVISOR: ASSOC. PROF. JOONGJAI PANPRANOT, Ph.D., 80 pp.

NiO-WO_3/Al_2O_3 catalysts were prepared by incipient wetness impregnation method. The catalytic performance was determined in the dimerization of isobutene under 150 °C and atmospheric pressure. The effect of different weight percents of nickel and tungsten on the catalytic activity were investigated. The results showed that NiO-WO_3/Al_2O_3 catalysts gave higher isobutene conversion and selectivity to isooctene than NiO/Al_2O_3 catalysts. Tungsten oxide increased the acidity of catalyst and improved the selectivity to isooctene. The 1Ni-4W/Al_2O_3 catalyst was the best ratio of nickel and tungsten that gave the highest catalytic performance. This ratio of nickel and tungsten was used in the study of different weight percents of silica in SiO_2-Al_2O_3 supports and different preparation methods of alumina. The results in this part showed that the SiO_2-Al_2O_3 support without metal gave higher yield to isooctene because silica-alumina possessed strong acid sites and higher total acidity of catalyst which increased the isobutene conversion. The 40SiO_2-Al_2O_3 Al_2O_3 catalyst gave the highest catalytic performance. For the effect of different preparation methods of alumina including solvothermal, co-precipitation, and calcination from gibbsite, the 1Ni-4W/Al_2O_3-GIB catalyst gave the highest catalytic performance because calcination from gibbsite method improved the structure and acidity of catalyst that gave the high catalytic performance with low coke formation.

Department: Chemical Engineering Student's Signature ....

Field of Study: Chemical Engineering Advisor's Signature ....

Academic Year: 2016

ACKNOWLEDGEMENTS

First of all, the author would like to express her gratefulness and appreciation to her advisor, Assoc. Prof. Dr. Joongjai Panpranot for her valuable suggestions, useful knowledge, and constant encouragement throughout this thesis. The author would also be grateful to Prof. Bunjerd Jongsomjit as the chairman of the committee, Chutimon Satirapipathkul and Asst. Prof. Dr. Okorn Mekasuwandumrong as a member of the thesis committee and for your brilliant comments and suggestions. Moreover, the author would like to express her gratefulness to Prof. Dr. Piyasan Praserthdam for useful guidance and knowledge.

Besides, the author would like to be thankful her parents for their attention and suggestions for solving problems. Furthermore, the author would like to thank all her friends, members of the Center of Excellent on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Chulalongkorn University for their support throughout the times of research.

Lastly, the author would like to be grateful the Thailand Research Fund and Department of Chemical Engineering, Chulalongkorn University for financial support to this work.

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

Nowadays, many countries have concern about the effect of methyl tert-butyl ether (MTBE) [1]. MTBE is used as gasoline additive but it is soluble in water and causes the ground water and surface water contamination [2, 3]. There are many substances to substitutes for MTBE such as tert-butyl ethyl ether (ETBE), tert-amyl methyl ether (TAME) and isooctane [4]. Isooctane is the branched paraffin with carbon numbers in the range of 8 to 12. It can increase octane number of gasoline and has a zero content of aromatics and sulphur. All of that are reasons which suggest that isooctane is one of the leading contenders as a replacement of MTBE.

Two processes are available for producing isooctane: direct alkylation and indirect alkylation [4]. Direct alkylation of isobutane with C_4 olefin has been practiced in commercial for several years. This process mainly uses homogeneous strong acids as a catalyst which are environmentally hazardous and hard disposal [5]. For indirect alkylation, isooctane is produced from hydrogenation of isooctene which is the product of isobutene dimerization. Diisobutylene or isooctene is the desired product of this process and byproducts are triisobutylene and tetraisobutylene. This process is particularly attractive because it makes use of the existing MTBE feedstocks and is ecologically friendly process [6]. The major reactant of MTBE reaction is isobutene and plant for producing isooctane can be follow the MTBE plant which reduces the construction cost. The C_4 olefin as a feed can be used from fluid catalytic cracking process, steam cracking process and dehydrogenation process which has wider feedstock flexibility and increases the value of the products [7, 8]. Moreover, the mainly catalysts in dimerization are heterogeneous catalysts which are safer than homogeneous catalyst in direct alkylation process [6].

The catalysts for isobutene dimerization that have been studied consist of phosphoric acid catalysts [9], Ziegler-Natta-based catalysts [10], zeolites [11, 12], ion-exchange resins [2, 13, 14], sulfated titania [8], and nickel-based catalysts [15-18]. Most of the catalysts gave low selectivity to diisobutylene and had an undesirable formation of high molecular weight byproducts, which was not suitable as a gasoline additive and promoted the deactivation problems [4, 6]. Nickel compound supported on oxide catalysts have been studied in dimerization for many years [19]. It shows higher activity for a lower olefin dimerization, especially ethylene. It has been reported that the catalytic activity of dimerization is related to the acidic properties of catalyst. Nickel-based catalysts and nickel modified with tungsten have been also considered in isobutene dimerization which shows that nickel oxide and tungsten oxide increase the acid sites of catalyst [17, 18]. In addition, nickel oxide can increase the stability of reaction.

The aim of this research is to study the catalytic performances of NiO-WO_3/Al_2O_3 catalysts in the dimerization of isobutene. The catalysts were synthesized by different preparation methods of alumina with different weight percents of nickel and tungsten.

1.2 Research Objectives

1. To investigate the characteristics and the catalytic performances of NiO/Al_2O_3 and NiO-WO_3/Al_2O_3 catalysts in the dimerization of isobutene to isooctene.

1.3 Research Scope

1. Synthesis of the NiO-WO_3/Al_2O_3 catalysts by varying nickel loading at 1, 5 wt% and tungsten loading at 4, 20 wt% on commercial Al_2O_3 using incipient wetness impregnation method.
2. Determining the best weight percent ratio of NiO-WO_3/Al_2O_3 catalysts which gives the highest isooctene yield.
3. Modification of the chosen NiO-WO_3/Al_2O_3 catalysts with alumina prepared by different preparation methods including solvothermal method, co-precipitation, method and calcination from Gibbsite.

4. Modification of the chosen NiO-WO_3/SiO_2-Al_2O_3 catalysts with different weight percents of silica (20,40 wt%).
5. Catalyst performances were tested in dimerization of isobutene at 150 °C and atmosphere pressure.
6. The catalysts were characterized by using N_2 physisorption, X-ray diffraction (XRD), Ammonia temperature program desorption (NH_3-TPD), X-ray photoelectron spectroscopy (XPS), Thermal gravimetric and differential thermal analysis (TG/DTA) and Scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX).

1.4 Research Benefits

1. To obtain suitable percents weight of nickel and tungsten in NiO-WO_3/Al_2O_3 catalysts on the dimerization of isobutene.
2. To obtain suitable method for synthesize alumina supports in NiO-WO_3/Al_2O_3 catalysts on the dimerization of isobutene.
3. To obtain suitable percents weight of silica in NiO-WO_3/SiO_2-Al_2O_3 catalysts on the dimerization of isobutene.

1.5 Research Methodology

The research methodology consist of 2 parts.

Part I : Study the effect of different weight percents of nickel and tungsten in $NiO-WO_3/Al_2O_3$ catalysts on the catalytic activity of isobutene dimerization

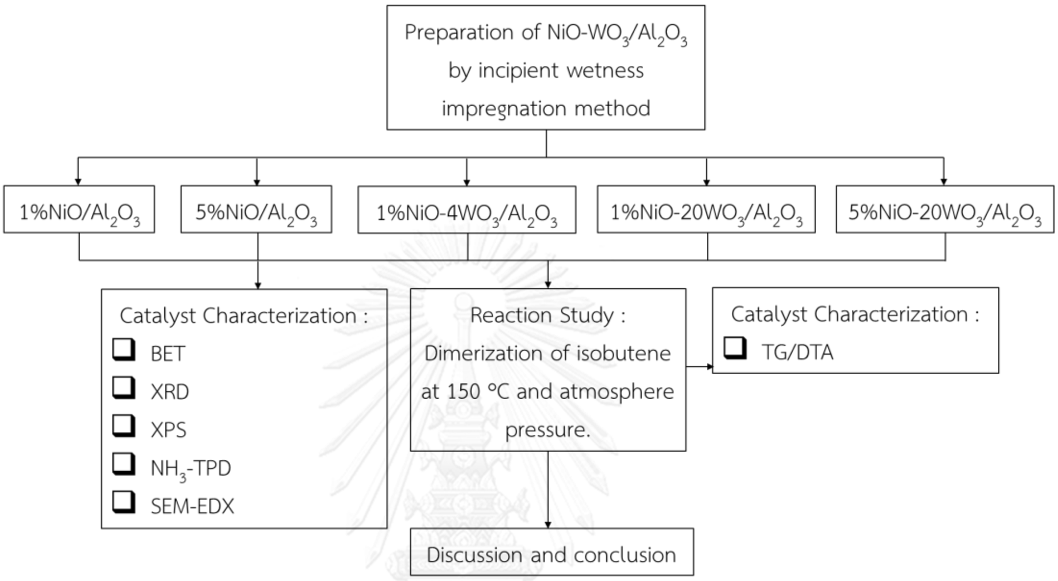

Figure 1.1 Flow diagram of research methodology of part I

Part II : Study the effect of modified alumina in NiO-WO_3/Al_2O_3 catalysts and NiO-WO_3/SiO_2-Al_2O_3 catalysts on the catalytic activity in dimerization of isobutene

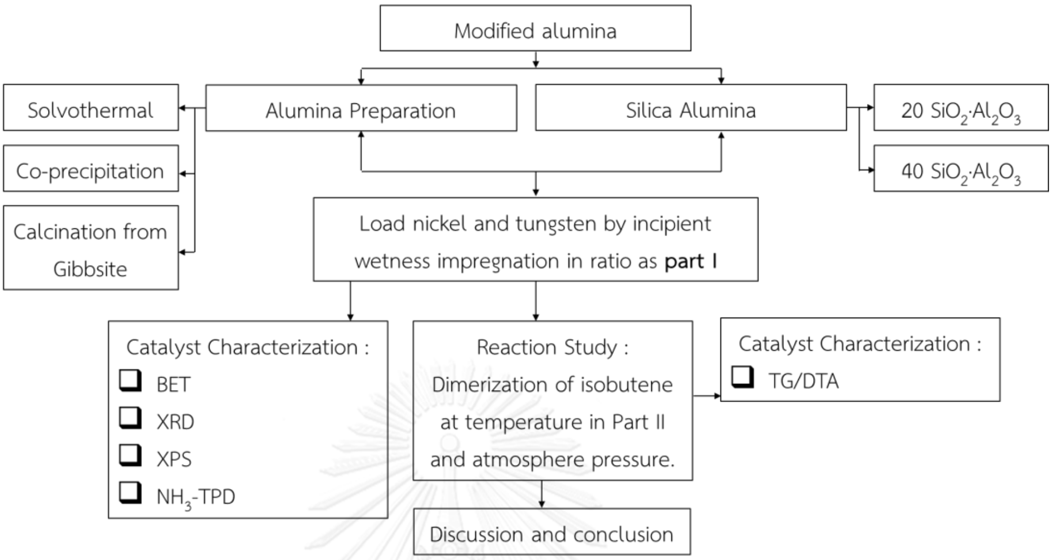

Figure 1.2 Flow diagram of research methodology of part II

CHAPTER 2

THEORY AND LITERATURE REVIEWS

2.1 Dimerization of isobutene reaction

Dimerization is the combination of two identical molecules to form a new single molecule [20]. It is widely used in the industry for converting light olefins to heavier olefins such as motor fuels, plasticizers, pharmaceuticals, dyes, resins, detergents, additives, lubricants and freezing point depressants [13]. Examples of reactant are ethylene, propylene, butene, isobutene (IB) and etc. In this research, dimerization of isobutene is interested in producing isooctene.

Dimerization of isobutene is an exothermic reaction with ΔH = -19.8 kcal/mol [21]. Consecutive reactions of isobutene dimerization are depicted as follows [13];

$$2C_4H_8 \longrightarrow C_8H_{16} \qquad (1)$$

$$C_8H_{16} + C_4H_8 \rightarrow C_{12}H_{24} \qquad (2)$$

$$C_{12}H_{24} + C_4H_8 \rightarrow C_{16}H_{32} \qquad (3)$$

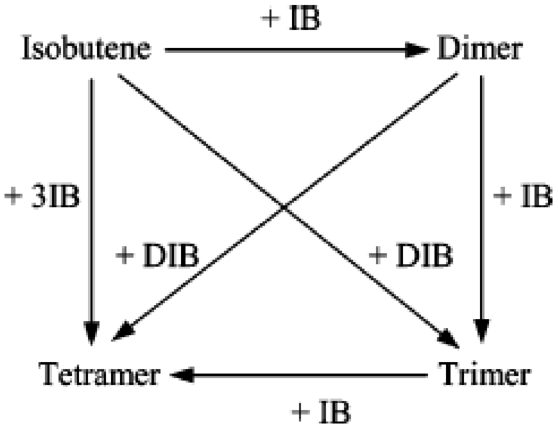

Figure 2.1 Reaction scheme isobutene dimerization and oligomerization

Figure 2.1 represents the reaction scheme for isobutene dimerization and oligomerization [6]. Isobutene combines with another as a consecutive step to form dimer, trimer and tetramer, respectively. Furthermore, trimers and tetramers can also form directly from isobutene through parallel reaction. The distribution of oligomerization products is also influenced by reaction operating conditions such as temperature and pressure. In addition, C_4 feedstock sources, catalyst and solvent also have an effect on the formation of products.

The mechanism of isobutene dimerization is explained in a “push and pull” mechanism for solid acid catalyst [13]. This mechanism is divided to three step as follows;

1.olefin protonation to form alkylcarbenium

2.chain propagation by reaction of a carbenium ion with olefin

3.deprotonation of the carbenium ion with chain growth ending

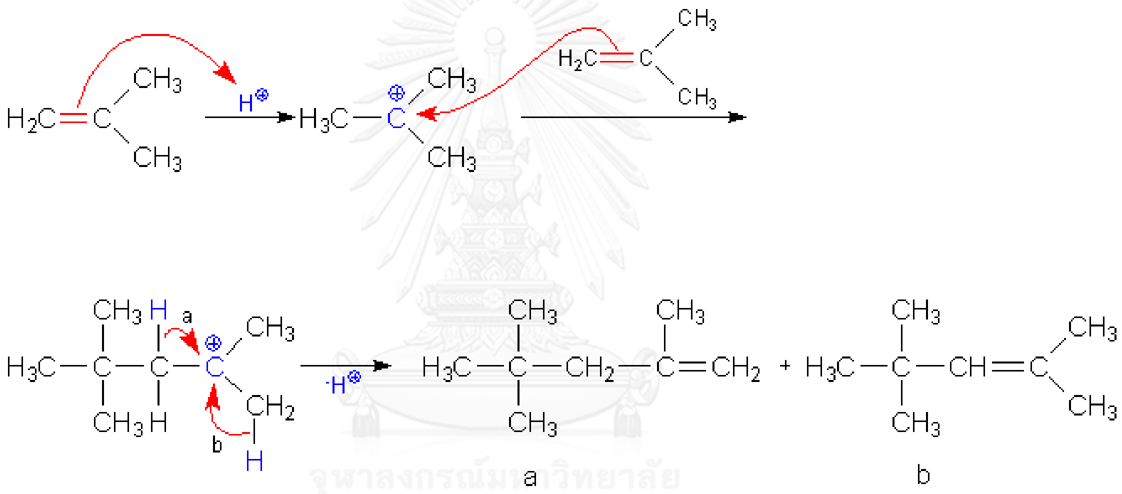

Figure 2.2 Mechanism for dimerization of isobutene [20]

The mechanism of isobutene dimerization to is shown in Figure 2.2. At first, an acid site in the solid acid catalyst protonates the proton to isobutene and form the tertiary carbocation. Then, the carbocation reacts with another molecule of isobutene to form an unstable complex which releases a proton and form two isomers. These isomers are 2,4,4-trimethyl-1-pentene (a) and 2,4,4-trimethyl-2-pentene (b) which commonly are called diisobutylene (DIB) or isooctene.

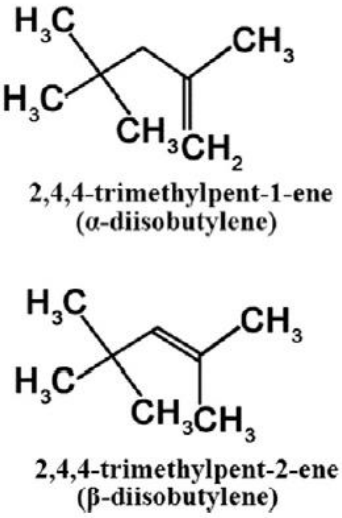

Figure 2.3 Structure of diisobutylene (isooctene) [13]

The structure of DIB is shown in Figure 2.3. the tertiary carbocation can react with n-butene which form the other isomers of DIB such as 5,5-methylhexane-3-yl and 3,4,4-trimethyl-2-pentene as shown in Figure 2.4.

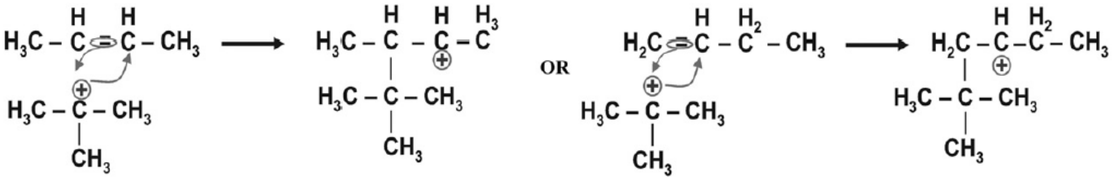

Figure 2.4 Isobutene dimerization with 2-butene (left) or 1-butene (right)

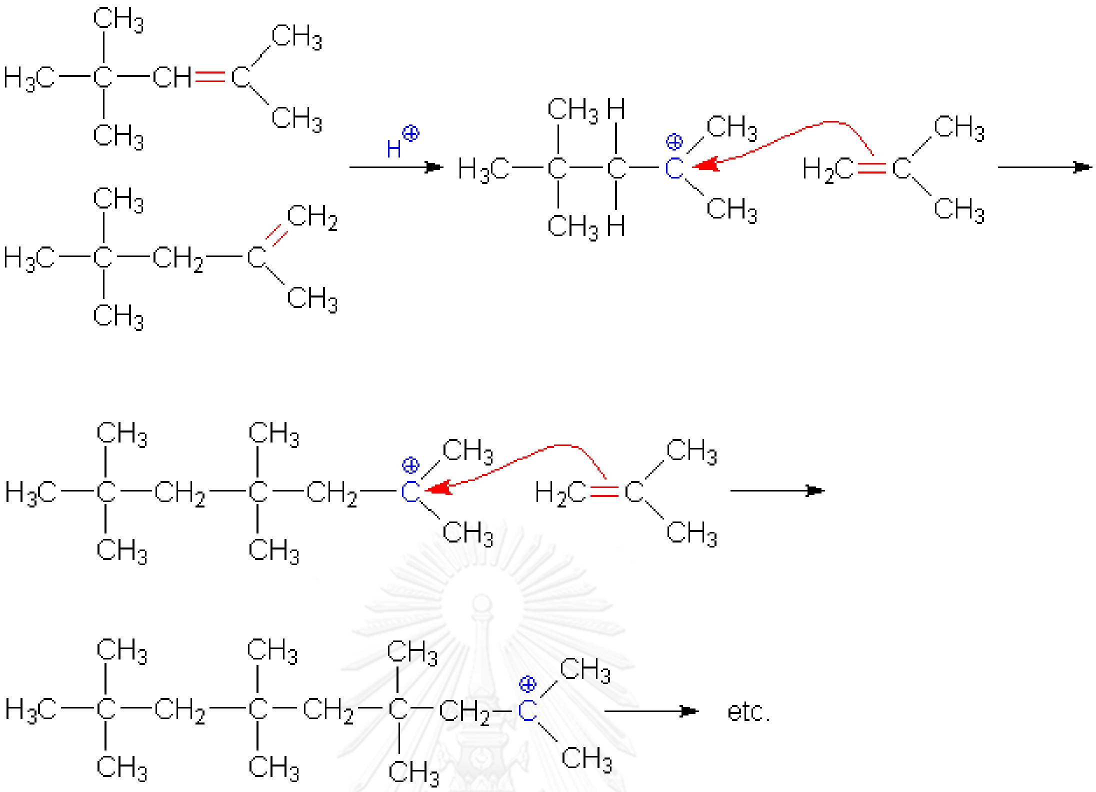

Figure 2.5 Mechanism for oligomerization of isobutene

The mechanism for oligomerization of isobutene is described in Figure 2.5. DIB can further oligomerize to C_{12} (trimer), C_{16} (tetramer) or higher molecule is a similar way. These high molecule of oligomers are the byproducts which are not suitable with reaction and enhance the deactivation rate.

2.2 Reactant and Products

2.2.1 Isobutene

Isobutene (IB) or 2-methylpropene is one of the butene isomers [22]. The structure of IB is shown in Figure 2.6. It is an important chemical in the petrochemical industry and a known component of transportation fuels. Moreover, it is an important intermediate of pyrolysis and reactant of dimerization in industry. It is the major component in naphtha C_4 cuts. N-butene and butadiene can be found as a minor component [13]. Isobutene is more reactive than the other C_4 component. It is more suitable than n-butene for dimerization to obtain isooctene [9]. The low volatile isooctene can be easily hydrogenated to isooctane (2,4,4-trimethylpentane) which has a high octane number and better quality.

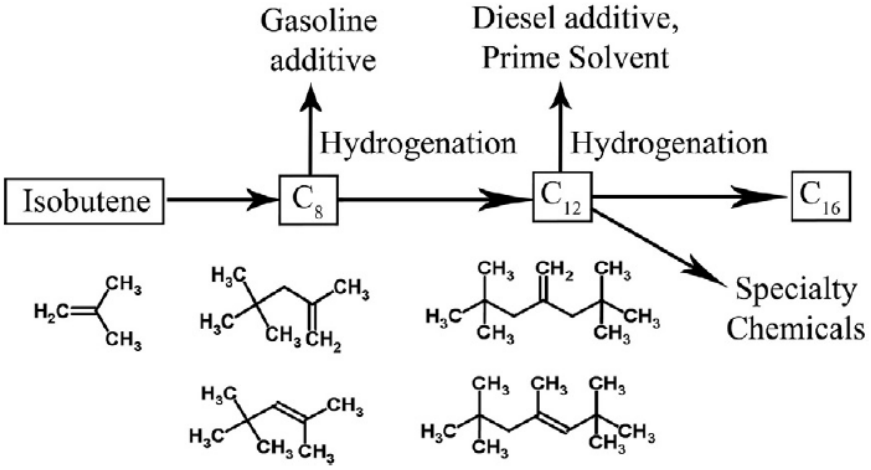

Figure 2.6 Range of products attainable from isobutene oligomerization

2.2.2 Diisobutylene or isooctene

Diisobutylene (DIB) or isooctene is the product of isobutene dimerization. The structure of DIB is shown in Figure 2.6. There are two isomers which are 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene. DIB can be used as a feedstock to produce high-octane component like isooctane or ether like 2-methoxy-2,4,4-trimethylpentane [1]. Isooctane is popularly used as gasoline additive because it is the branched paraffin with carbon numbers in the range of 8 to 12 (H/C < 2.25) [13]. It has a low volatile about 3-5 psi [21] and has a zero content of aromatics and sulphur [4]. Significantly, isooctane are less soluble in water than MTBE.

2.2.3 Triisobutylene

Triisobutylene (TIB) is another product of isobutene dimerization. It is the promising materials for the synthesis of special chemicals such as dodecylbenzene, antirust, lubricants, gas oil additives and solidifying agents for epoxy resins [13]. As depicted in Figure 2.6, hydrogenated triisobutylene is useful diesel additives for kerosene and jet fuel and premium solvents because it is odorless solvents without aromatics.

2.2.4 Tetraisobutylene

Tetraisobutylene (TEB) is a byproduct of isobutene dimerization. The structure of TEB is shown in Figure 2.6. It is not useful for reaction because of high molecular weight oligomer. On the other hand, it is the coke precursor and promote the deactivation problem.

2.3 Alumina

Alumina (Al_2O_3) or aluminum oxide is the one of most important ceramics. It usually occurs in nature as the minerals such as corundum (Al_2O_3), diaspora ($Al_2O_3{\cdot}H_2O$), gibbsite ($Al_2O_3{\cdot}3H_2O$) and most commonly as bauxite which is an impure form of gibbsite [23]. Al_2O_3 is a white solid and has a molar mass of 101.96 g/mol and density of 3.95-4.1 g/cm^3 [24]. It also has high melting and boiling points of 2072 °C and 2977 °C, respectively. Moreover, it has advantages such as high compression strength, high abrasion resistance, high chemical resistance and high dielectric strength. All of those advantages are reasons which suggest that Al_2O_3 usually used in a variety of applications. It widely used for insulating materials, electronics, military uses, bio-medical, glass, fillers and catalyst support [23].

Alumina can exist in many metastable crystalline structures: $\eta-, \gamma-, \delta-, \theta-, \beta-, \kappa-, \chi-$ and $\alpha-$ alumina [24]. These aluminas are called transition aluminas [25]. The crystalline hydroxides can be synthetic or natural. The structure of each alumina depends on the calcination temperature, heating rate and structure of starting or precursor hydroxide through the thermal dehydration reaction. There are different precursor hydroxide for gibbsite, boehmite, bayerite, nordstrandite, and diaspore. The thermal transformation sequence of the aluminum hydroxides is shown in Figure 2.7.

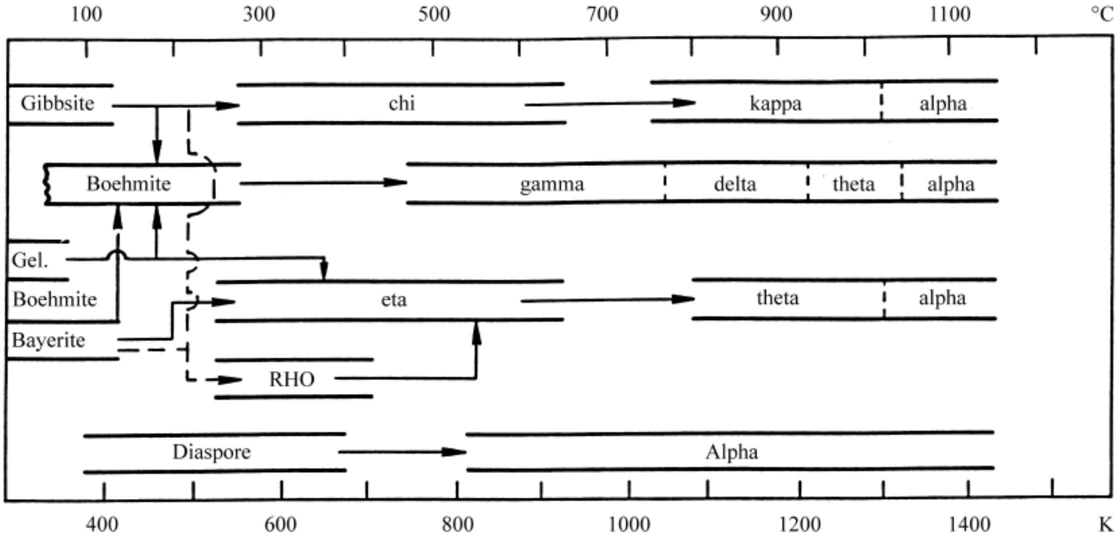

Figure 2.7 Thermal transformation sequence of the aluminum hydroxides [25]

From Figure 2.7, it may be concluded that all transition aluminas may be synthesized from gibbsite. That is one reason that more industry interest in gibbsite production. The thermal transformation sequence can be concluded in the below:

$$\text{Aluminum hydroxide} \rightarrow \text{transition aluminas} \rightarrow \alpha - Al_2O_3$$

There are several techniques to synthesize alumina such as precipitation, sol-gel, solvothermal and calcination method [26]. There are three techniques which is picked up as an interesting method descripted in below;

The solvothermal method is a technique for performing chemical reaction in solvents contained in sealed vessels in high temperature and pressure [27]. The process is referred to hydrothermal when water is used as solvent. For solvothermal, organics are used as solvent. Material synthesize from hydrothermal or solvothermal methods is a crystallization process directly from solutions. It can control size, shape distribution, crystallinity of particle and morphologies same as the sol-gel method by changing parameter condition. The processing variables are precursor, solvent, reaction temperature and reaction time.

The precipitation method is a technique for synthesize material by creating a solid from a liquid mother solution [26]. The solid form is called precipitate and the liquid above a solid is called supernate. The advantages of this process are low cost, easy to acquire apparatus and a simple synthesize process [28]. It can control shape and size particle by changing condition. Condition variables are pH value, precursor and calcination temperature. The pH should be adjusted and kept constant during the operation in order to make the well-establish catalyst.

The calcination method is a further pretreatment beyond drying [26]. It is not considered in preparation procedure because several methods have calcination after drying for some objectives. Examples are chemical bonding, modification of the texture through sintering, modification of the structure, active phase generation and stabilization of the mechanical properties. It is simple method to change the structure or surface catalyst. Alumina can be example of changing phase by calcination in air as shown in Figure 2.8. It can control phase alumina by controlling the calcination temperature and heating rate.

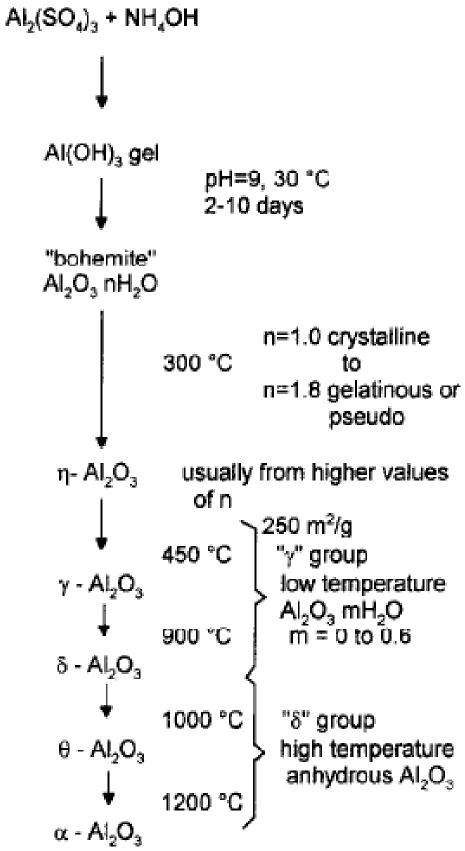

Figure 2.8 Alumina modification upon calcination [26]

2.4 Nickel

Nickel (Ni) is the transition metal and have atomic number of 28. It is a silvery-white lustrous metal with a slight golden tinge which is hard and ductile. There are two electronic configurations of Ni: [Ar] 3d8 4s2 or [Ar] 3d9 4s1. Ni is one of four elements (iron, cobalt, nickel and gadolinium) which are ferromagnetic around room temperature. The more properties of nickel are descripted in Table 2.1.

Table 2.1 The properties of nickel [29]

Properties	Specification
Atomic Weight	58.6934
Phase	Solid
Density	Near room temperature 8.908 g/cm^3 Liquid at melting point 7.81 g/cm^3
Melting point	1455 °C
Boiling point	2730 °C
Heat of fusion	17.48 kJ/mol
Heat of vaporization	379 kJ/mol
Molar heat capacity	26.07 J/(mol·K)

The most common oxidation state of Ni are Ni^{2+}, Ni^0 and Ni$^+$ and unknown oxidation state are Ni^{3+}, Ni^{2-}, Ni^{1-} and Ni^{4+}.

1.Ni^0: it is a volatile, highly toxic liquid at room temperature and decomposes to nickel at high temperature founded in purifying nickel.

2.Ni$^+$: Example is the tetrahedral complex NiBr(PPh$_3$)$_3$ which has a Ni-Ni bonding. This compound is uncommon and oxidized in water.

3.Ni^{2+}: This compound is common in anions such as sulfide, sulfate, carbonate, hydroxide, carboxylates, and halides. Nickel(II) sulfate is useful for electroplating nickel. Nickel(II) chloride is most common and usually encountered as the green hexahydrate. The tetracoordinate nickel(II) complexes exist in both of tetrahedral and square planar geometries. The tetrahedral complexes are paramagnetic but the square planar complexes are diamagnetic.

4.Ni^{3+}: Examples are Nickel(III) trihalophosphines which forms simple salts with fluoride or oxide ions.

5.Ni^{4+}: It is present in the $BaNiO_3$. It remains a rare oxidation state of nickel and very few compounds are known to date.

Transition metal is considered as a good catalyst for several reaction [30]. Nickel is the one of transition metal which is attractive. It is cheaper and more sufficiently active than other metals such as Platinum and Ruthenium. It has found in widely application because of its specific properties [31]. It has a low electrical resistivity, good corrosion resistance and good thermal conductivity. Nickel is useful in chemical processing, electronics, food and synthetic fibers. Several years ago, Ni-based catalyst is usually used as a catalyst in dimerization of olefins. Most of Ni^{2+} displays as active site of catalyst on the variety support such as alumina, silica-alumina and zeolite [32].

2.5 Tungsten

Tungsten (W) is the transition metal and have atomic number of 74. It also known as wolfram and is a hard steel-grey metal that is often brittle and hard to work. In general, tungsten exists in two major crystalline form: α and β. The crystalline form is a body-centered cubic structure. The β structure is a metastable and can coexist with α phase at ambient condition. The more properties of tungsten are descripted in table 2.2.

Table 2.2 The properties of tungsten [33]

Properties	Specification
Atomic Weight	183.84
Phase	Solid
Density	Near room temperature 19.25 g/cm^3
	Liquid at melting point 17.6 g/cm^3
Melting point	3422 °C
Boiling point	5930 °C
Heat of fusion	35.3 kJ/mol
Heat of vaporization	774 kJ/mol
Molar heat capacity	24.27 J/(mol·K)

Tungsten is known in various application such as electrical conductor, pigments, lubricants and chemical application. The major of chemical application is in the area of catalyst. Tungsten is used as catalyst in several reaction such as hydrocracking, hydrogenation, isomerization and aromatization reaction [34]. Recently, tungsten is used as solid acid catalyst in dimerization [17].

2.6 Literature reviews

Several catalysts have been studied for dimerization of isobutene reaction. They can be divided into five main groups, which are phosphoric acid catalysts, ion-exchange resins, zeolites, sulfated titania, and nickel-based catalysts.

2.6.1 Solid phosphoric acid catalysts (SPA)

Solid phosphoric acid catalysts (SPA) has been a commercial process for 80 years. It is used distinctively for the production of polymer gasoline, kerosene and diesel fuel compounds [9]. This type of catalyst is used at the temperatures of 150-250 °C and pressures of 2-8 MPa. Controlling the temperature and the degree of hydration of phosphoric acid on the catalyst can increase the selectivity to isooctene.

SPA catalysts can contain a number of modifiers such as iron, cobalt, nickel, copper, chromium and magnesium. However, SPA catalyst has limitations which were short life time, destruction of catalyst grains, acid entrainment, equipment corrosion and non-regenerable.

2.6.2 Ion exchange resins catalysts

Table 2.3 Summary of the research of isobutene dimerization on ion exchange resins

Researchers	Purposes of study	Catalysts	Solvents	Results
Honkela, M. et al. 2003 [2]	The effect of polar component in the dimerization of isobutene	Ion exchange resin of a styrene-divinylbenzene-based with sulfonic acid group	-Isopentane as solvent -methanol and TBA as polar component	-Polar component decreased the conversion but increased the selectivity. -TBA gave the highest selectivity to isooctene.
Ouni, T., et al. 2006 [3]	The catalytic activity of isobutene dimerization under various condition	Ion exchange resin of a styrene-divinylbenzene-based with sulfonic acid group	Mixture of TBA and isooctane	-Increasing the TBA content and reaction temperature increased the selectivity but decreased the conversion.

Honkela, M. et al. (2003) [2] studied the effect of polar component in the dimerization of isobutene on an ion exchange resin catalyst. The polar components were methanol and tert-butyl ether alcohol (TBA). The results showed that addition of polar component gave the higher selectivity to isooctene and lower conversion of isobutene than without polar component. TBA gave the best selectivity which was concluded to be due to the higher polarity of TBA. Moreover, this research also studied the effect of alcohol content on the catalytic activity. The alcohol content is 0-20 mol%. The results showed the same trend of methanol and TBA. Alcohol content increase gave the selectivity increase and conversion decrease. The best performance was experiment with TBA which gave 53% conversion of isobutene with 86% selectivity and 46% yield to isooctene at 0.9 mol% of TBA.

Ouni, T., et al. (2006) [3] studied the catalyst performance of isobutene dimerization on an ion exchange resin catalyst under various conditions. The condition variables were reaction temperature and TBA content. The catalytic testing operated in the liquid phase with different temperature. The results showed the same trend of two variables that was increasing the TBA content and reaction temperature increased the selectivity to isooctene but decreased the conversion of isobutene. The best performance gave 62.9% conversion of isobutene with 93.3% selectivity to isooctene at 2.53 wt% of TBA and 348.15 K.

In summary, ion exchange resins were widely used in dimerization catalyst as well as the SPA [9]. This type of catalyst was used under milder conditions than SPA. The temperatures was no more than 100 °C and pressures were in the range of 1-2 MPa. Most of this catalyst usually add the alcohol as a polar component into reaction medium. Addition of alcohol increased the selectivity to isooctene but it was expensive. Moreover, ion exchange resin has low thermal stability at temperature above 130 °C. A resin decomposed with the release of sulfuric acid, which had an effect on the feedstock component and oligomerization products, and the loss of its catalytic activity.

2.6.3 Zeolites catalysts

Table 2.4 Summary of the research of isobutene dimerization on zeolites

Researchers	Purposes of study	Catalysts	Results
Yoon, J. W. et al. 2009 [12]	The effect of different zeolite catalyst	-USY zeolite -Al/USY zeolite	-USY gave the lower conversion and higher selectivity to isooctene than Al/USY.
Koskinen, R. et al. 2012 [11]	The impact of the solvent on the catalyst behavior	-ZSM-5 -ZSM-23 -CO_2 -propane	-ZSM-23 with CO2 gave the best catalytic performance

Yoon, J. W. et al. (2009) [12] studied the effect of different zeolite catalyst on the catalytic activity in the dimerization of isobutene. The catalysts are ultra stable Y (USY) zeolite and USY modified with $AlCl_3$ (Al/USY). Dimerization of isobutene were testing in the liquid phase at 70 °C under 15 bar. N-butane was used as a diluent. The results showed that USY catalyst gave the higher yield to isooctene than Al/USY catalyst. The best performance was 85.3% conversion of isobutene and 59.6% selectivity to isooctene with USY catalyst. Al/USY catalyst gave the high conversion (99.2%) and selectivity to trimer(21.0) and tetramer (31.1) which might be due to the increasing lewis acid site to bronsted acid site ratio.

Koskinen, R. et al. (2012) [11] studied the effect of solvent on the zeolite catalyst in the dimerization of isobutene. Zeolite catalysts, which were ZSM-5 and ZSM-23, had a different structure. Solvents in the reaction were carbon dioxide (CO_2) and propane. The results showed that ZSM-23 gave the higher conversion than ZSM-5. The conversion of ZSM-23 with CO_2 was approximate 56% and the conversion of ZSM-23 with propane was approximate 32%. Zeolite catalyst made the coke formation which limited selectivity to isooctene. CO_2 had an ability to remove the heavier molecule which it can reduce the coke formation and increase the conversion of zeolite catalyst.

In summary, zeolites were a promising catalyst. However, this type of catalyst required the high temperatures and pressures than other catalysts [9]. High temperatures caused the side reactions which deactivated the catalyst. The conversion of isobutene and selectivity to isooctene were affected by silicon to aluminum ratio and other factors. Zeolites were easily regenerable and can operate at higher feed. In addition, zeolites were sensitive to the presence of sulphur compound in feedstocks.

2.6.4 Sulfated titania catalysts

Mantilla, A. et al. (2005) [8] studied the effect of operating conditions on the activity, selectivity and stability in dimerization of isobutene. Operating conditions were temperature, pressure and weight hourly space velocity (WHSV). Catalyst was a sulfated titania prepared by gelling titanium alkoxide in a sulfuric acid medium. Dimerization of isobutene was tested in the liquid phase under different temperatures and pressures. Isobutene was used as a diluent in the feed. From the results, when WHSV was increased from 2.5 to 10 h^{-1}, conversion and selectivity to isooctene decreased but selectivity to triisobutene and tetraisobutene increased. For the effect of pressure, when pressure was decreased from 600 to 400 psi, conversion decreased but selectivity to isooctene increased. For the effect of temperature, conversion of isobutene and selectivity to isooctene and tetraisobutene increased but selectivity to triisobutene decreased when temperature was decreased from 140 to 28 °C. The best performance was 100% conversion of isobutene with 66.7% selectivity to isooctene at WHSV of 5 h^{-1} under 28 °C and 400 psi. Moreover, this research group had studied the effect of diluent in the feed. The results showed that diluent can be remove the adsorbed high molecular weight olefins deposited on the active sites and diminish the contact time for reactants. This effect can increase the stability of reaction.

Sulfated titania was an acidic metal oxide. It was highly active in the oligomerization but the stability was low.

2.6.5 Nickel-based catalysts

Table 2.5 Summary of the research of isobutene dimerization on nickel-based catalysts

Researchers	Purposes of study	Catalysts	Results
Jeon, J. K. et al. 2004 [15]	The effect of 1,3-butadiene in C_4 feedstock and promoter on the catalytic activity and branching index over Ni/Al_2O_3 catalyst.	Ni/Al_2O_3 -impregnation -H_3PO_4 and TPPO as a promoter	-1,3-butadiene in C_4 gave the lower conversion than pure C_4. -Ni-P-TPPO/Al_2O_3 catalyst gave the lower conversion and higher selectivity. -The branching index of product over Ni-P-TPPO/Al_2O_3 catalyst was higher than other catalysts.
Yaocíhuatl, M. G. et al. 2006 [1]	The effect of nickel precursor salt, the role of the acidity and the zeolites structures in the dimerization of isobutene	Ni/Zeolite -HY-zeolite, -Hβ-zeolite, -H-modernite, -$NiCl_2 \cdot 6H_2O$, -$NiCO_3 \cdot 2Ni(OH) \cdot 4H_2O$, -$NiSO_4 \cdot 6H_2O$ -impregnation	-HY-zeolite modified with nickel carbonate showed high selectivity -Addition of nickel resulted in an enhancement of acid sites. -Nickel loading between 3-6% showed the best selectivity to isooctene.
Tzompantzi, F. J. et al. 2008 [16]	The effect of nickel loading in NiO/ZrO_2-SO_4 catalyst on the catalytic activity.	-ZrO_2-SO_4 -3%NiO/ZrO_2-SO_4 -5%NiO/ZrO_2-SO_4 -10%NiO/ZrO_2-SO_4	-10%NiO/ZrO_2-SO_4 catalyst gave the highest selectivity to isooctene and deactivation rate.

Researchers	Purposes of study	Catalysts	Results
Tzompantzi, F. et al. 2009 [18]	The effect of different catalysts on the catalytic activity.	-W_2O_3/Al_2O_3 -$NiO-W_2O_3/Al_2O_3$ -impregnation	- $NiO-W_2O_3/Al_2O_3$ gave the high yield to isooctene at 150 °C.
Tzompantzi, F. et al. 2009 [17]	The effect of different catalysts preparation on the catalytic activity.	-W_2O_3/Al_2O_3 -$NiO-W_2O_3/Al_2O_3$ -impregnation -sol-gel	- $NiO-W_2O_3/Al_2O_3$ from impregnation method gave the high yield to isooctene at 150 °C.
Tong, L. et al. 2015 [4]	The effect of condition parameters on the conversion and selectivity	-Ni/Al_2O_3 -impregnation	-Ni loading, temperature and isobutene concentration gave the same trend of result which conversion increased and selectivity decreased at high value of condition parameter.

Jeon, J. K. et al. (2004) [15] studied the the effect of 1,3-butadiene in C_4 feedstock and promoter on the conversion,selectivity and branching index over Ni/Al_2O_3 catalyst in the dimerization of butene. The catalyst were 10 wt% Ni/Al_2O_3 prepared by impregnation method and modified with phosphorus acid (H_3PO_4,P) and triphenyl phosphine oxide (TPPO) as a promoter. The reaction conditions were 70 °C and 700 psig. The results found that 1,3-butadiene in C_4 feedstock caused the lower conversion than pure C_4 feedstock. The researchers suggested that deactivation caused by reaction between butadiene and active nickel site and blocking the catalyst pores with long chain oligomer. Ni-P-TPPO/Al_2O_3 catalyst gave the lower conversion and higher selectivity than other catalyst because the presence of TPPO made the easy desorption of octene. Moreover, the branching index of product over Ni-P-TPPO/Al_2O_3 catalyst was higher than other catalysts because of a strong steric hindrance effect of TPPO.

Yaocíhuatl, M. G. et al. (2006) [1] studied the effect of nickel precursor salt, the role of the acidity and the zeolites structures on the activity and selectivity in the isobutene dimerization under mild condition. Catalytic testing operated in the liquid phase at 298 K under 140 psig and gas phase at 298 K under 5 psig. From result of liquid phase, HY-zeolite modified with nickel carbonate showed high selectivity to isooctene. Addition of nickel resulted in an enhancement of acid sites which decrease the weak acid site and increase the strong acid site. It presented both of leiws acid sites and bronsted acid sites. From result of gas phase, nickel loading between 3-6% showed the best selectivity to isooctene. The best performance was 28% conversion of isobutene with 87% selectivity to isooctene at nickel loading of 3.2%.

Tzompantzi, F. J. et al. (2008) [16] studied the effect of nickel loading in NiO/ZrO_2-SO_4 catalyst on the conversion and selectivity in the isobutene dimerization. The NiO/ZrO_2-SO_4 catalysts were prepared by sol-gel method in appropriate amounts to get 3, 5 and 10 wt% of nickel. The temperature was 28 °C and mixture of isobutene/isobutene (50:50 w/w) was fed into reactor under atmospheric pressure. The results showed the conversion of 20, 29, 33 and 36% for ZrO_2-SO_4, 10%NiO/ZrO_2-SO_4, 5%NiO/ZrO_2-SO_4 and 3%NiO/ZrO_2-SO_4, respectively. The catalyst with lower nickel content were more active. 10%NiO/ZrO_2-SO_4 catalyst gave the highest selectivity to isooctene and deactivation rate because of the highest acidity of catalyst.

Tzompantzi, F. et al. (2009) [18] studied the effect of different catalyst on the catalytic activity in the dimerization of isobutene. The catalysts were W_2O_3/Al_2O_3 and NiO-W_2O_3/Al_2O_3 which were prepared by impregnation method. Both of catalysts obtained NiO and W_2O_3 contents of 5 and 20 wt%, respectively. The catalytic activity for isobutene dimerization was testing in gas phase. A mixture of isobutane/isobutene (40:60 wt/wt %) was fed to the reactor at GHSV = 9.0 h^{-1} under different temperature and atmospheric pressure. The temperature was in the range of 50-150 °C. For W_2O_3/Al_2O_3 catalyst, increasing temperature gave the high selectivity to isooctene but the low conversion of isobutene. This behavior was due to the fast deactivation. For

NiO-W_2O_3/Al_2O_3 catalyst, the result showed the opposite effect, the conversion was increased at high temperature. NiO-W_2O_3/Al_2O_3 catalyst gave the higher conversion and selectivity than W_2O_3/Al_2O_3 catalyst. The best performance was 14.8% conversion of isobutene with 82% selectivity to isooctene with NiO-W_2O_3/Al_2O_3 catalyst at 150 °C. it can be due to the increasing acidity of the catalyst from better dispersion of W_2O_3. The smaller crystallite size the higher number of acid sites.

Tzompantzi, F. et al. (2009) [17] studied the effect of different catalyst preparation on the catalytic activity in the dimerization of isobutene. The catalysts were NiO-W_2O_3/Al_2O_3 which were prepared by impregnation and sol-gel method. The catalytic activity for isobutene dimerization was similar to previous research. The result showed that NiO-W_2O_3/Al_2O_3 catalyst from impregnation method gave the higher yield to isooctene than NiO-W_2O_3/Al_2O_3 catalyst from sol-gel method. Because of the similar acidity of catalyst, this research suggested that the high selectivity to isooctene with impregnation catalyst was due to the distribution improvement of the acid site on the surface catalyst.

Tong, L. et al. (2015) [4] studied the effect of condition parameters on the conversion and selectivity in the isobutene dimerization. Catalytic testing operated in the liquid phase with different temperature under 2.0 MPa. Catalyst was Ni/Al_2O_3 and solvent was n-pentane. Major reaction conditions are temperature, Ni loading and isobutene concentration. For Ni loading, it was studied in the range of 0.5-3% Ni by mass. At high Ni loading, the conversion increased but selectivity decreased because Ni promoted the dimerization and side reaction which isooctene is consumed in consecutive side reaction to triisobutene and tetraisobutene. For temperature, it was studied in the range of 338-383 K.Isooctene selectivity was maximum (85%) at 353 K and declined at high temperature. The activation energy of triisobutene was less than activation energy of isooctene which easily occur side reaction at high temperature. For isobutene concentration, it was studied at 30% and 50% by mass. High isobutene concentration led the isobutene to be adsorbed on the catalyst surface which lead to side reaction and triisobutene and tetraisobutene were produced. 30 wt% of isobutene concentration gave the best catalytic activity. The best performance was 40%

conversion of isobutene with 75% selectivity to isooctene at nickel loading of 1% and isobutene concentration of 30 wt% under 353 K and 2.0 MPa.

In summary, nickel-based catalyst had been widely studied in the dimerization reaction, especially ethylene dimerization. The study found that the catalytic activity was related to the acidity of catalyst and nickel played important role in the reaction. All of nickel-based catalysts in the isobutene dimerization, alumina modified with nickel and tungsten is interesting because of high thermal stability, important role of nickel and acidity of tungsten.

Table 2.6 Summary of the research of ethylene dimerization on nickel-based catalysts

Ref NO.	Catalysts	Acidity	Catalytic activity
[19]	20%$NiSO_4/Al_2O_3$	540 μmol/g	4.5 mmol/g
[35]	20%$NiSO_4/SiO_2$	137 μmol/g	0.42 mmol/g
[35]	15% $NiSO_4$/66-SiO_2-Al_2O_3	374 μmol/g	2.4 mmol/g
[35]	15% $NiSO_4$/82-SiO_2-Al_2O_3	353 μmol/g	2.61 mmol/g
[36]	10%$NiSO_4/ZrO_2$	132 μmol/g	1.35 mmol/g
[36]	10% $NiSO_4$/5-Al_2O_3-ZrO_2	176 μmol/g	1.95 mmol/g
[37]	10% $NiSO_4$/5-FeO-ZrO_2	257 μmol/g	1.5 mmol/g

Most of Nickel-based catalyst had been studied in the ethylene dimerization. The catalysts, from Table 2.6, were the best catalytic performance in each research. Sohn, J. R. studied the effect of Al_2O_3 in the nickel-based catalysts on the catalytic activity of ethylene dimerization. The catalytic activity was determined at 20 °C and initial pressure of 290 Torr. The amount of ethylene consumed in the initial 5 minutes was determined as catalytic activity. The best performance was 20%$NiSO_4/Al_2O_3$ with acidity 540 μmol/g and catalytic activity 4.5 mmol/g. The second highest performance was $NiSO_4/SiO_2$-Al_2O_3. 15% $NiSO_4$/66-SiO_2-Al_2O_3 and 15% $NiSO_4$/82-SiO_2-Al_2O_3, which had slightly differences in catalytic activity. The addition of Al_2O_3 to $NiSO_4/SiO_2$-Al_2O_3 catalyst improved thermal stability and increased the number of acid sites on the surface catalyst. For the $NiSO_4/ZrO_2$ catalyst, the addition of Al_2O_3 increased the acidity, surface area, thermal stability and catalytic activity because of the interaction between Al_2O_3 and ZrO_2 and the formation of Al-O-Zr bond. For 10% $NiSO_4$/5-FeO-ZrO_2 catalyst, FeO was a good promotor for $NiSO_4$ supported on ZrO_2. The addition of FeO had a similar effect of Al_2O_3 but catalytic activity was not equal to 20%$NiSO_4$/Al_2O_3.

From the above mentioned works, it can be concluded that Al_2O_3 was a good support and promoter for ethylene dimerization. Moreover, SiO_2–Al_2O_3 also gave the good performances. The results of ethylene dimerization may be similar to dimerization of isobutene. Therefore, the effect of NiO-W_2O_3/Al_2O_3 catalyst and SiO_2 addition on catalytic activity over dimerization of isobutene are needed for further study.

CHAPTER 3

MATERIALS AND METHODS

This chapter explains the method for synthesis catalyst and catalytic testing in dimerization of isobutene. There are 3 parts including 3.1) catalyst preparation 3.2) catalytic testing and 3.3) catalyst characterization. The techniques described in part 3.3 were used to analyze the properties of catalyst consisting of N_2 physisorption, X-ray diffraction (XRD), NH_3-temperature program desorption (NH_3-TPD), H-temperature program reduction (H_2-TPR), X-ray photoelectron spectroscopy (XPS), Thermal gravimetric and differential thermal analysis (TG/DTA) and scanning electron microscope and energy dispersive X-ray spectroscopy (SEM-EDX)

3.1 Catalyst Preparation

3.1.1 Synthesis of Al_2O_3 supports

For solvothermal method, alumina supports was obtained following the procedure reported by Wannaborworn, M. et al [38]. 25 g of aluminium isopropoxide (AIP) was dissolved into 100 mL of 1-butanol in a small test tube and 30 mL of 1-butanol was added into a large test tube. Then, both of test tubes were put into autoclave and purged with nitrogen gas. The autoclave was heated up to 300 °C at heating rate 2.5 °C/min and held constant at that temperature 2 h. After the autoclave was cooled down to room temperature, the obtained solid was washed with ethanol 5 times by centrifugation. Finally, the solid was dried at 120 °C overnight and calcined at 600 °C for 6 h.

For co-precipitation method, alumina supports was obtained following the procedure reported by Lili Zhang et al [39]. Ammonium aluminium sulfate ($NH_4Al(SO_4)_2$) and ammonium hydrogen carbonate (NH_4HCO_3) were dissolves into distilled water to obtain 0.2 mol/L and 2 mol/L, respectively. 250 ml of $NH_4Al(SO_4)_2$ solution was gradually dropped into 100 ml of NH_4HCO_3 solution under stirring at 60 °C. Then, ammonium hydroxide was added into the solution to obtain pH = 9.5 and the solution was filtered by vacuum filtration. After filtration, the obtained solid was washed with hot distilled water 4 times, followed by drying at 110 °C for 2 h and calcination at 500 °C for 4 h at a heating rate of 2 °C/min.

For calcination method, fine gibbsite was calcined in air at 500 °C for 3 h to acquire the γ-Al_2O_3 support.

The chemicals used to synthesized alumina supports are shown in Table 3.1 as follows:

Table 3.1 The chemicals used for synthesis Al_2O_3 supports

Chemical	Formula	Supplier
Aluminium isopropoxide	$((CH_3)_2CHO)_3Al$	Sigma - Aldrich
1-Butanol	$C_4H_{10}O$	Fluka
Ethanol	CH_3OH	Merck
Ammonium aluminium sulfate	$NH_4Al(SO_4)_2$	Sigma - Aldrich
Ammonium hydrogen carbonate	NH_4HCO_3	Sigma - Aldrich
Ammonium hydroxide	NH_4OH	Sigma - Aldrich
Fine gibbsite	$Al(OH)_3$	Merck

3.1.2 Metal loading on support

The NiO/Al_2O_3, NiO-WO_3/Al_2O_3 and NiO-$WO_3/SiO_2{\cdot}Al_2O_3$ catalysts were prepared by incipient wetness impregnation. For commercial Al_2O_3 and SiO_2-Al_2O_3, the support samples were calcined at 500 °C for 4 h before impregnation. Nickel nitrate hexahydrate and ammonium metatungstate hydrate were dissolve in deionized water which contained a specific amount of Ni and W. For NiO/Al_2O_3 catalysts, only Nickel nitrate hexahydrate was dissolve in deionized water. The Al_2O_3 supports were impregnated with aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$ and $(NH_4)_6H_2W_{12}O_{40}{\cdot}xH_2O$ which the volume equal to pore volume of Al_2O_3 support. After that, the catalysts were dried at 120 °C for 12 h and calcined at 500 °C for 4 h.

The chemicals used to synthesized the NiO/Al_2O_3 and NiO-WO_3/Al_2O_3 catalysts are shown in Table 3.2 as follows:

Table 3.2 The chemicals used for synthesis NiO/Al_2O_3 and NiO-WO_3/Al_2O_3 catalysts

Chemical	Formula	Supplier
Nickel nitrate hexahydrate	$Ni(NO_3)_2 \cdot 6H_2O$	Sigma - Aldrich
Ammonium metatungstate hydrate	$(NH_4)_6H_2W_{12}O_{40} \cdot xH_2O$	Fluka
Aluminium Oxide	Al_2O_3	Merck
Silica Alumina	$SiO_2 \cdot Al_2O_3$	AOC

3.2 Catalytic testing

The chemicals used in dimerization of isobutene are shown in Table 3.3. The catalytic testing of isobutene dimerization was tested in a fixed-bed reactor, with dimensions of 1 cm inside diameter. A fresh catalyst of 0.8 g and 0.03 g of quartz wool were placed in the reactor on the same apparatus as Figure 3.1 and heated to 150 °C under atmosphere pressure. For part II, 0.28 g of catalyst was placed in the reactor. Then, a mixture of Isobutene/Argon (10:90 v/v %) was fed into the reactor at total flow rate 60 ml/min. The products were analyzed by using a gas chromatograph – mass spectrometry (GC-MS). The operating conditions are shown in the Table 3.4

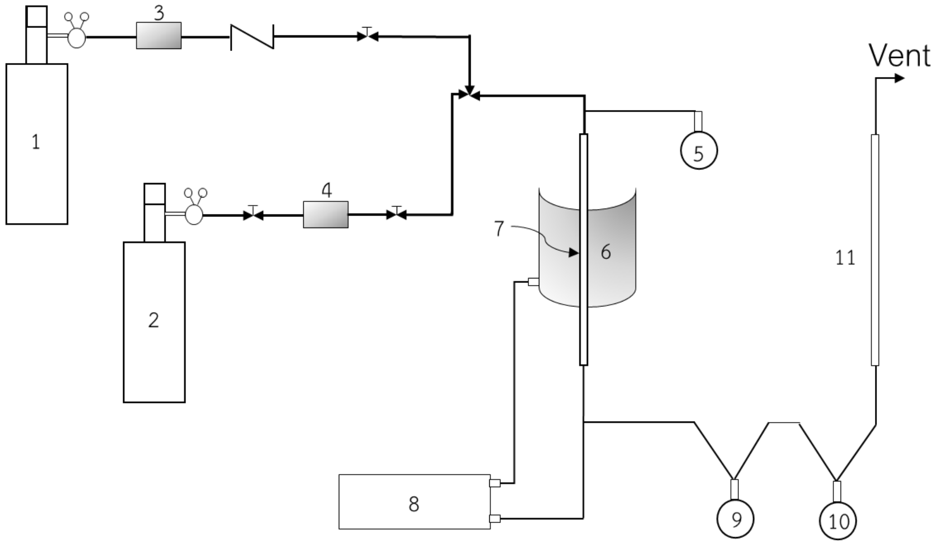

Figure 3.1 Flow diagram of isobutene dimerization

1. Isobutene gas cylinder
2. Argon gas cylinder
3. Mass flow controller of isobutene
4. Mass flow controller of argon
5. Inlet gas sampling
6. Furnace
7. Glass tube reactor
8. Temperature controller
9. Outlet gas sampling
10. Saturator
11. Bubble Flow

Table 3.3 The chemicals used for dimerization of isobutene reaction

Chemical	Supplier
Isobutene	TIG
Argon	TIG

Table 3.4 The operating conditions in gas chromatograph – mass spectrometry (GC-MS)

GC-MS	SHIMADZU 2010 – QP2010 PLUS
Capillary Column	RTX-5
Carrier Gas	Helium
Column Temperature	Initial Temperature : 35 °C
	Final Temperature : 280 °C
Injector Temperature	300 °C
Ion Source Temperature	250 °C
Interface Temperature	250 °C
Time Analysis	35min

3.3 Catalyst Characterization

3.3.1 N_2 physisorption

The BET surface area, average pore size (BJH desorption), average pore volume (BJH desorption) and pore size distribution of the catalysts were investigated by N_2 physisorption on a Micromeritrics ASAP 2000 automated system. The samples were pretreated at 110 °C for 24 h before analysis.

3.3.2 X-ray diffraction (XRD)

The bulk crystalline phase and crystalline size of the catalysts were determined by X-ray diffraction (XRD) on a SIEMENS D500 X-ray diffractometer with CuK_α radiation (λ=1.54439 Å) in scanning range from 10° to 80°.

3.3.3 Ammonia temperature program desorption (NH_3-TPD)

The acid sites of the catalysts were measured by ammonia temperature program desorption on a Micromeritics Pulse Chemisorp 2750 automated system with chemisoft TPX software. Approximately 0.1 g of sample and quartz wool were packed in quartz tube. Each sample was degassed at 350 °C for 1 h with helium (25 ml/min) at heating rate 10 °C/min and cooled down to 40 °C. The sample was saturated with 15%NH_3 in Helium (25 ml/min) at 40 °C for 60 minutes. After that, the samples were heated to 800 °C with helium at heating rate 10 °C/min.

3.3.4 X-ray photoelectron spectroscopy (XPS)

The binding energy of the each element on the catalysts were analyzed by X-ray photoelectron spectroscopy on an AMICUS photoelectron spectrum spectrometer equipped with an MgKα X-ray as primary excitation and KRATOS VISION2 software. The samples were pretreated at 110 °C for 24 h before analysis.

3.3.5 Thermal gravimetric and differential thermal analysis (TG/DTA)

The thermal decomposition of catalysts and the amount of carbon (coke) in catalysts after catalytic testing were characterized by Thermal gravimetric and differential thermal analysis on a TA instruments SDTQ 600 analyzer.

3.3.6 Scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX)

The element distribution and percent metal on the catalyst were characterized by JEOL mode JSM-6400 Scanning electron microscope and Link Isis Series 300 program energy dispersive X-ray spectroscopy. The samples were pretreated at 110 °C for 24 h before analysis.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter describes the characteristics and catalytic activity of NiO/Al_2O_3, NiO-WO_3/Al_2O_3, and modification of NiO-WO_3/Al_2O_3 catalysts in the isobutene dimerization reaction. There are 2 parts including 4.1) the effect of different weight percents of nickel and tungsten and 4.2) the effects of SiO_2 in SiO_2-Al_2O_3 supports and preparation methods of alumina. The first part, the catalysts were prepared with different weight percents of nickel (1,5 wt%) and tungsten (4,20 wt%) by incipient wetness impregnation. The second part, the catalysts were modified with different weight percents of silica (20,40 wt%). The alumina supports were prepared by different preparation methods including solvothermal, co-precipitation, and calcination from gibbsite. The characterization of catalysts include XRD, N_2 physisorption, SEM-EDX, XPS, NH_3-TPD, and TG/DTA.

4.1 The effect of different weight percents of nickel and tungsten in NiO-WO$_3$/Al$_2$O$_3$ catalysts on the catalytic activity of isobutene dimerization

The catalysts nomenclatures are shown in below as follows;

1Ni/Al$_2$O$_3$ presents the 1%NiO/Al_2O_3 catalysts which were prepared 1 wt% nickel on commercial Al_2O_3.

5Ni/Al$_2$O$_3$ presents the 5%NiO/Al_2O_3 catalysts which were prepared 5 wt% nickel on commercial Al_2O_3.

1Ni-4W/Al$_2$O$_3$ presents the 1%NiO-4%WO_3/Al_2O_3 catalysts which were prepared 1 wt% nickel and 4 wt% tungsten on commercial Al_2O_3.

1Ni-20W/Al$_2$O$_3$ presents the 1%NiO-20%WO_3/Al_2O_3 catalysts which were prepared 1 wt% nickel and 20 wt% tungsten on commercial Al_2O_3.

5Ni-20W/Al$_2$O$_3$ presents the 5%NiO-20%WO_3/Al_2O_3 catalysts which were prepared 5 wt% nickel and 20 wt% tungsten on commercial Al_2O_3.

4.1.1 X-ray diffraction

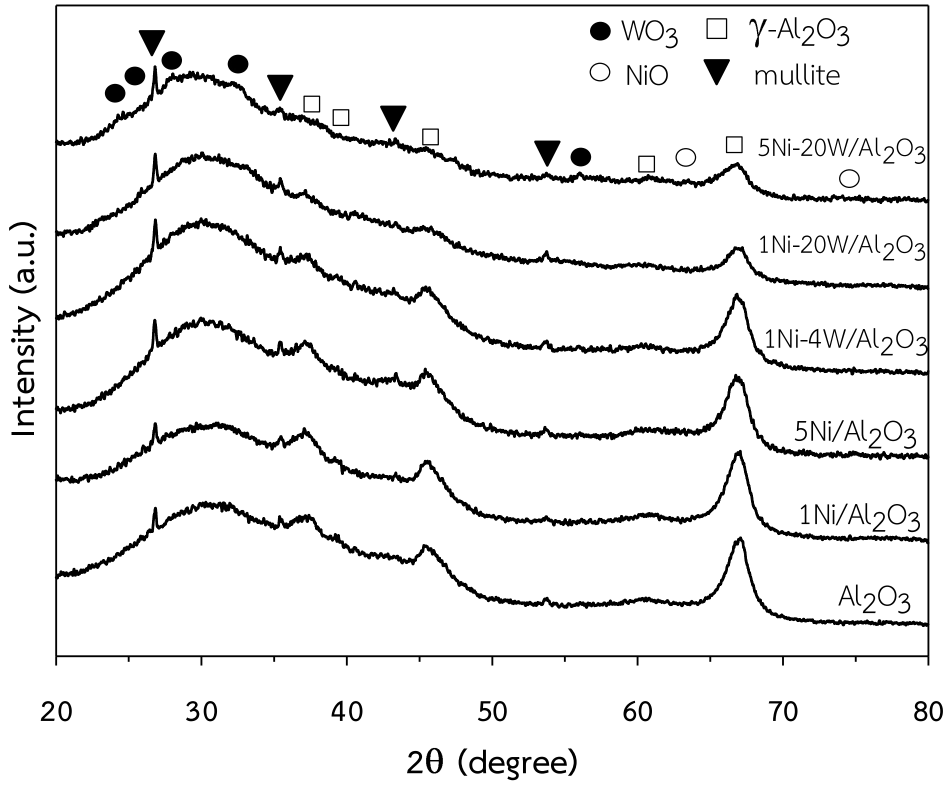

Figure 4.1 XRD patterns of Al_2O_3 and Ni-W/Al_2O_3 catalysts

The crystalline structures of NiO-WO_3/Al_2O_3 catalysts were investigated by X-ray diffraction and the results are shown in Figure 4.1. From the XRD patterns, the diffraction peaks at 2θ = 36.8°, 39.4°, 45.7°, 60.7° and 66.6° represented the γ-Al_2O_3 support and 2θ = 62.9° and 75.5° represented the NiO [40]. For the WO_3, the XRD peaks for WO_3 were detected at 2θ of 23.6°, 24.6°, 29.0°, 33.5° and 55.6° as reported by Wang et al [41]. In addition, there was mullite as impurity from commercial Al_2O_3 catalysts. The diffraction peaks at 2θ = 26.4°, 35.5°, 43.5° and 53.9° were attributed to the mullite crystal as specified in Talou et al [42]. There were γ-Al_2O_3, and mullite in all the catalysts. The diffraction peaks corresponding to NiO and WO_3 were not observed at low NiO (5 wt%) and WO_3 (20 wt%) because of their good dispersion or small crystallite size [40].

4.1.2 N_2 physisorption

Table 4.1 The surface area, pore volume and average pore size of Al_2O_3 and Ni-W/Al_2O_3 catalysts

Catalyst	Surface Area [a] (m^2/g)	Pore Volume [b] (cm^3/g)	Average Pore [b] Diameter (°A)
Al_2O_3	145	0.28	50.1
1Ni/ Al_2O_3	140	0.28	50.1
5Ni/ Al_2O_3	118	0.23	49.3
1Ni-4W/Al_2O_3	142	0.26	49.0
1Ni-20W/Al_2O_3	134	0.22	46.4
5Ni-20W/Al_2O_3	86	0.14	45.4

[a] determined from BET method

[b] determined from BJH desorption method

The surface area, pore volume, and average pore diameter were measured by N_2 physisorption and the results are shown in Table 4.1. From the results, there were no significant differences in the pore diameter and pore volume except for the 5Ni-20W/Al_2O_3 catalysts. The surface area decreased when metal loading increased because of deposition of oxides on the surface of catalyst blocking the alumina pores [18]. However, the 1Ni-4W/Al_2O_3 catalyst had surface area similar to the Al_2O_3 support. The presence of nickel oxide had more effect on the decrease of surface area than tungsten oxide. Increasing of nickel loading from 1% to 5% resulted in a significant decrease in the surface area of the catalysts while the presence of tungsten (4 wt%) had little effect. The surface area was further decreased by increasing loading of tungsten to 20%.

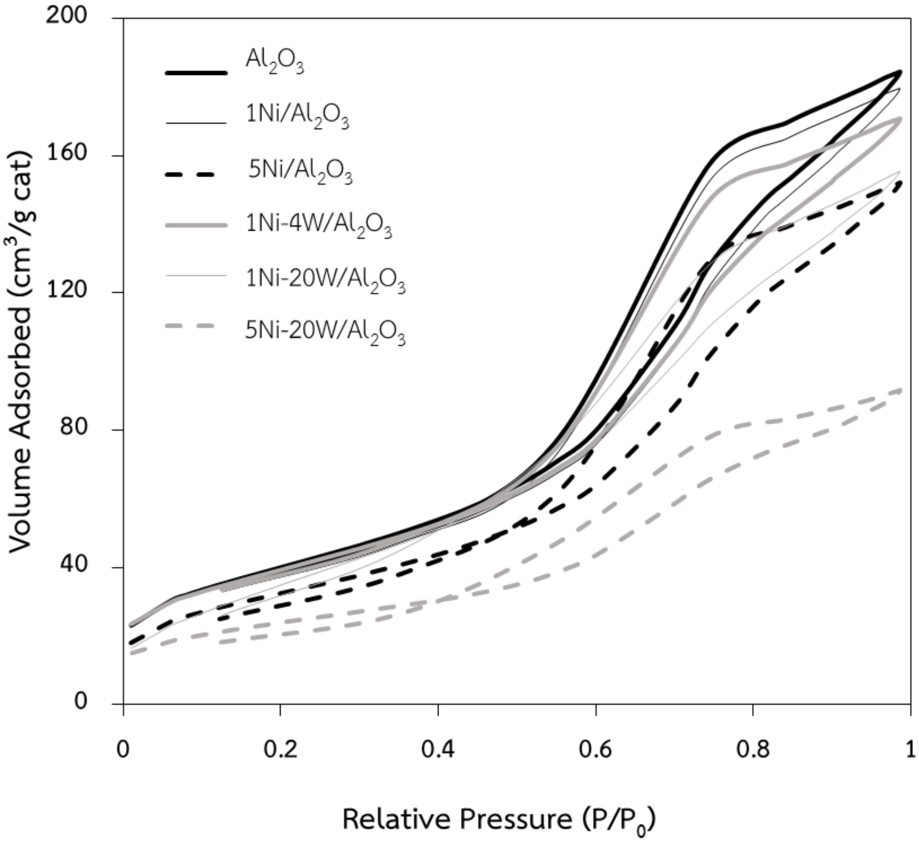

Figure 4.2 Nitrogen adsorption-desorption isotherm of Al_2O_3 and Ni-W/Al_2O_3 catalysts

The nitrogen adsorption-desorption isotherms of all catalysts are shown in Figure 4.2. From the results, all catalysts exhibited the type IV isotherms (IUPAC classification) which was the characteristic of mesoporous materials and displayed a hysteresis loop [43]. The pore size of mesoporous material was in the range of 2-50 nm that corresponded to the results. The hysteresis loop was type H1. It can be assumed that the characteristic of pore consisted of well-defined cylindrical pores or uniform spherical pores. In addition, the results showed that 5Ni-20W/Al_2O_3 catalyst had the lowest volume adsorbed which associated to the lowest pore volume.

4.1.3 Scanning electron microscopy and energy dispersive X-ray spectroscopy

Table 4.2 The amount of element distribution on the catalyst surface

Catalysts	Amount of element (wt %)					Amount of element (at %)				
	O	Al	Si	Ni	W	O	Al	Si	Ni	W
Al_2O_3	40.1	59.4	0.5			53.1	46.6	0.3		
$1Ni/Al_2O_3$	39.4	57.8	0.8	2.0		52.8	45.9	0.6	0.7	
$5Ni/Al_2O_3$	35.5	53.8	0.4	10.3		50.4	45.3	0.4	3.9	
$1Ni\text{-}4W/Al_2O_3$	35.3	54.0	0.4	3.1	7.2	51.1	46.5	0.3	1.2	0.9
$1Ni\text{-}20W/Al_2O_3$	32.8	39.2	0.5	3.1	24.4	55.3	39.2	0.5	1.4	3.6
$5Ni\text{-}20W/Al_2O_3$	29.3	37.3	0.8	7.0	25.6	52.3	39.5	0.9	3.4	3.9

The amount of element distribution on the catalyst surface are shown in Table 4.2. The results showed that amount of nickel and tungsten from EDX were more than the amount from calculation because EDX results randomly depends on the measurement position. In addition, all catalyst had a little amount of silicon contamination which may come from the composition of mullite.

4.1.4 X-ray photoelectron spectroscopy

The oxidation state of each element in the catalysts were determined by XPS. The Ni 2p XPS spectra of catalysts are shown in Figure 4.3. The catalysts with 1 wt% nickel did not exhibit any peak of nickel. When increase the nickel loading from 1 to 5 wt%, the peak of Ni $2p_{3/2}$ and shakeup satellites (850-870 eV) were found, corresponding to charge-transfer transitions [40]. The Ni 2p peaks for $5Ni/Al_2O_3$ catalyst can be deconvoluted into two peaks at 854.8 eV and 856.5 eV, attributed to Ni^{2+} and Ni^{3+}, respectively. The peaks of Ni $2p_{3/2}$ in $5Ni\text{-}20W/Al_2O_3$ catalyst shifted to higher binding energy at 855.2 eV and 856.6 eV. Addition of tungsten enhanced the electron density of NiO that led to the formation of NiO and the higher binding energy. The relative content of Ni is shown in Table 4.3. The results were similar to the research of

Huang et al. [40] and Lu et al [44]. The research reported that the addition of metal to Ni/Al_2O_3 can increase the binding energy of Ni.

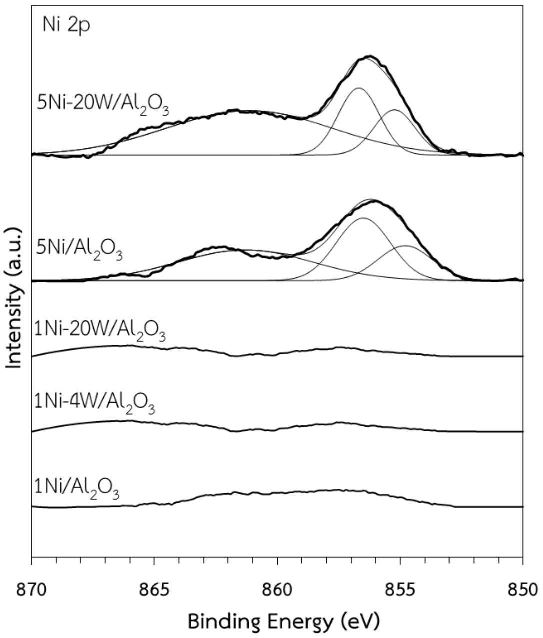

Figure 4.3 Ni 2p XPS spectra of $Ni\text{-}W/Al_2O_3$ catalysts

Table 4.3 Relative content and binding energy of Ni 2P XPS spectra of $Ni\text{-}W/Al_2O_3$ catalysts

Catalysts	Binding energy (eV)		Relative content (%)		
	$Ni^{3+}(Ni_2O_3)$	$Ni^{2+}(NiO)$	$Ni^{3+}(Ni_2O_3)$	$Ni^{2+}(NiO)$	Ni^{3+}/Ni^{2+}
$5Ni/Al_2O_3$	856.5	854.8	64.1	35.9	1.78
$5Ni\text{-}20W/Al_2O_3$	856.6	855.2	59.7	40.3	1.48

The W 4f XPS spectra of all $Ni\text{-}W/Al_2O_3$ catalysts are shown in Figure 4.4. From the result, the $1Ni\text{-}4W/Al_2O_3$ catalyst can be fitted to two peaks at 35.9 eV and 38 eV, attributed to $W4f_{7/2}$ and $W4f_{5/2}$ level for W^{6+} [41]. The W 4f peaks shifted to lower binding energy and the formation of W^{4+} was found with increasing of tungsten loading. This indicated that W^{6+} was converted to W^{4+}. It was similar to that W^{6+} was converted to W^{5+} as reported by Zhiqing et al [45]. In addition, increase of nickel loading can promote the formation of WO_3 which make the curve peak of W^{4+} shifted to higher binding energy.

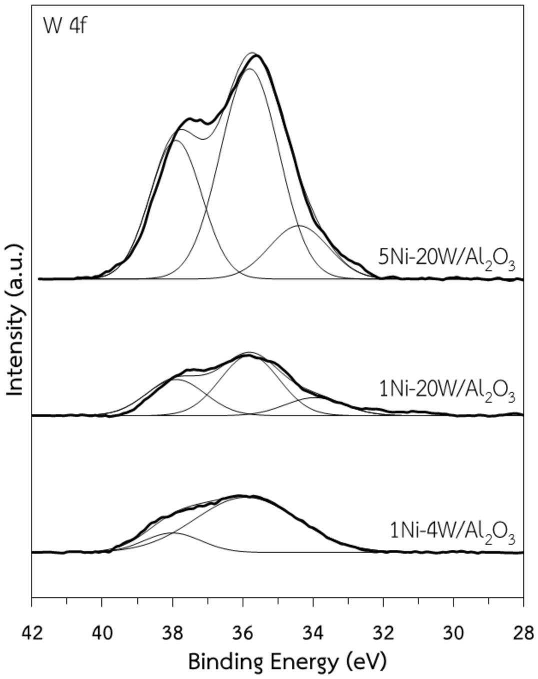

Figure 4.4 W 4f XPS spectra of Ni-W/Al_2O_3 catalysts

Table 4.4 Relative content and binding energy of W 4f XPS spectra of Ni-W/Al_2O_3 catalysts

Catalysts	Binding energy (eV)			Relative content (%)		
	$W^{4+}(4f_{5/2})$	$W^{6+}(4f_{7/2})$	$W^{6+}(4f_{5/2})$	W^{4+}	W^{6+}	W^{6+}/W^{4+}
1Ni-4W/Al_2O_3	-	35.9	38	-	100	-
1Ni-20W/Al_2O_3	33.9	35.8	37.9	15.7	84.3	5.35
5Ni-20W/Al_2O_3	34.4	35.8	37.9	13.8	86.2	6.23

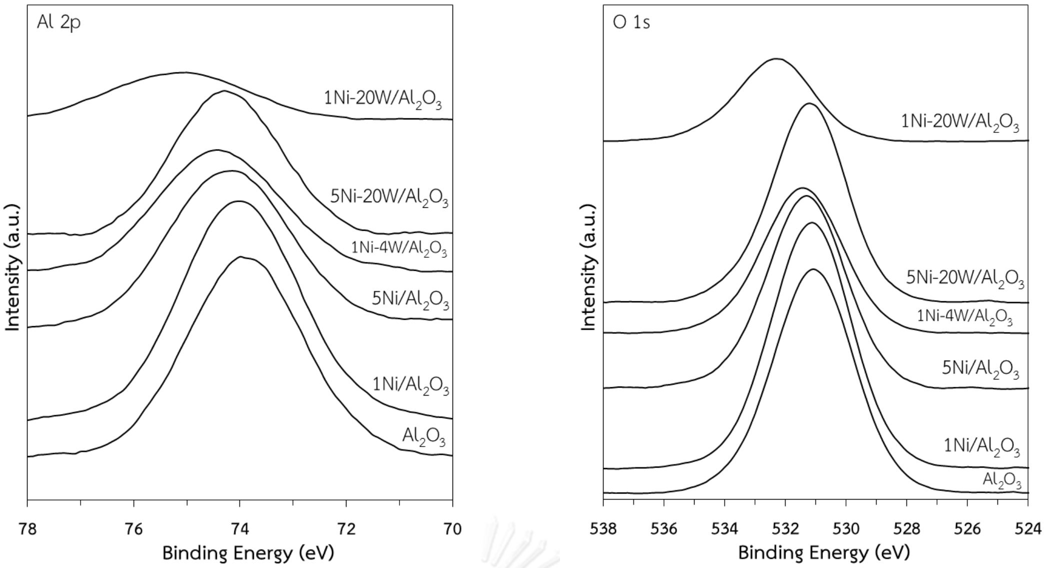

Figure 4.5 Al 2p and O 1s XPS spectra of Al_2O_3 and Ni-W/Al_2O_3 catalysts

Table 4.5 Binding energy of Al 2p and O 1s XPS spectra of Al_2O_3 and Ni-W/Al_2O_3 catalysts

Catalysts	Binding energy (eV)	
	Al 2p	O 1s
Al_2O_3	74.0	531.1
1Ni/Al_2O_3	74.0	531.1
5Ni/Al_2O_3	74.1	531.3
1Ni-4W/Al_2O_3	74.4	531.4
1Ni-20W/Al_2O_3	75.1	532.4
5Ni-20W/Al_2O_3	74.3	531.2

The Al 2p and O 1s XPS spectra of Al_2O_3 and Ni-W/Al_2O_3 catalysts are shown in Figure 4.5. The binding energy of aluminium and oxygen are shown in Table 4.5. The results showed that characteristic peak of aluminium and oxygen shifted to higher binding energy when metal was added. This indicated that addition of nickel resulted in a slight shift because nickel did not incorporate with alumina. On the other hand, more tungsten loading led the peak shift to higher binding energy because tungsten had bonding with alumina, especially for the 1Ni-20W/Al_2O_3 catalyst. It was similar to those reported by Reddy et al. that the shift of aluminum and oxygen resulted in the removal of negative charge density and the formation of Mo-Al-O bonds [46]. For 5Ni-20W/Al_2O_3 catalyst, there was lower binding energy of aluminium and oxygen than 1Ni-20W/Al_2O_3 catalyst because of poor dispersion of tungsten. Table 4.6 shows the atomic ratio of element on the surface catalysts. For atomic ratio of W/Al, 5Ni-20W/Al_2O_3 catalyst had a higher W/Al than 1Ni-20W/Al_2O_3 catalyst that indicated the poor dispersion of tungsten corresponding to lower binding energy.

Table 4.6 Atomic ratio of element on the surface catalysts

Catalysts	Atomic ratio		
	Ni/Al	W/Al	Ni/W
Al_2O_3	-	-	-
1Ni/Al_2O_3	0.011	-	-
5Ni/Al_2O_3	0.031	-	-
1Ni-4W/Al_2O_3	0.027	0.024	1.125
1Ni-20W/Al_2O_3	0.021	0.077	0.279
5Ni-20W/Al_2O_3	0.035	0.121	0.290

4.1.5 Ammonia temperature program desorption

The total acidity of catalysts were measured by ammonia temperature program desorption. The NH_3-TPD profiles for all catalysts are shown in Figure 4.6 and the amount of acidity are shown in Table 4.7. The acid strength can be determined from the desorption temperature. The weak, medium, and strong acid sites were assigned to the desorption peak of NH_3-TPD curves at below 250 °C, 250-500 °C, and above 500 °C, respectively as described in the report of Pudi et al. [47].

From Figure 4.6, the NH_3-TPD profiles of all the catalysts are shown by two desorption peaks which consisted of weak and strong acid sites. It was found that the total acidity is decreased after metal loading via impregnation. It was due to the pore blocking and the decrease of surface area as descripted in the report by Huang et al

[40]. This inhibited the adsorption of ammonia and obscured the acid of Al_2O_3. Comparing the catalysts with different tungsten loadings, it was found that the total acidity increased with increase of tungsten loading because WO_3 played a role as acid site [41]. The tungsten oxide improved acidity by formation of weak acid more than strong acid.

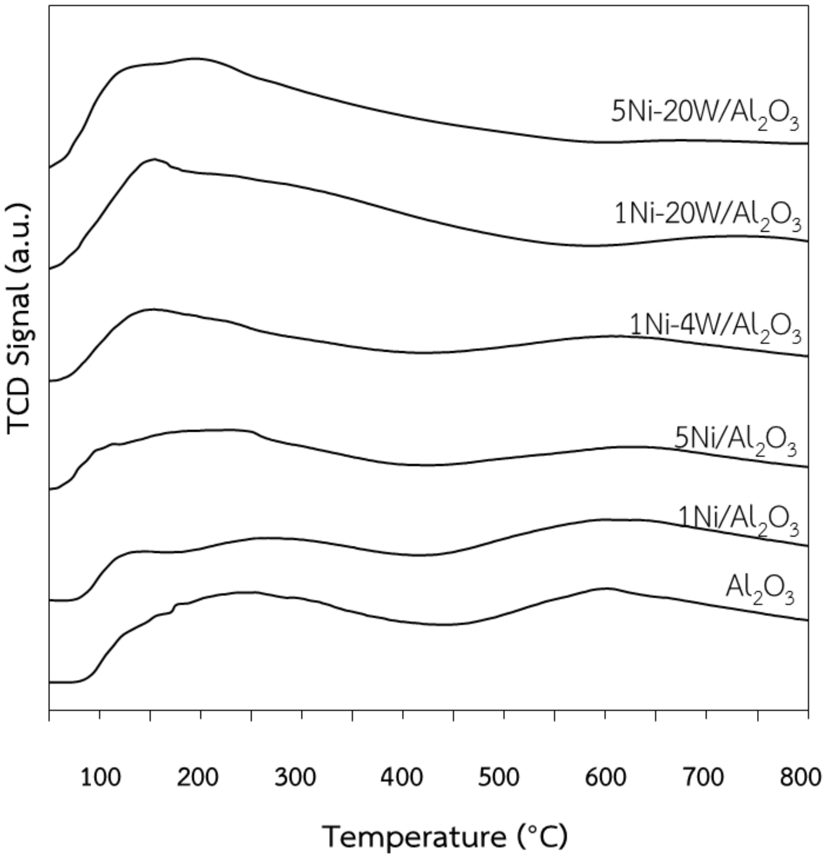

Figure 4.6 NH_3-TPD profiles of Al_2O_3 and Ni-W/Al_2O_3 catalysts

Table 4.7 Amount of acidity of Al_2O_3 and Ni-W/Al_2O_3 catalysts

Catalysts	Amount of acidity (mmol/g)			
	Weak	Strong	Total	Strong / Weak
Al_2O_3	0.72	0.86	1.58	1.18
1Ni/Al_2O_3	0.54	0.88	1.42	1.62
5Ni/Al_2O_3	0.49	0.44	0.93	0.91
1Ni-4W/Al_2O_3	0.57	0.32	0.89	0.56
1Ni-20W/Al_2O_3	0.87	0.18	1.05	0.20
5Ni-20W/Al_2O_3	1.0	0.12	1.12	0.12

4.1.6 Catalytic activity

Table 4.8 Conversion of isobutene and selectivity to isooctene of Ni-W/Al_2O_3 catalysts at 1 h

Catalysts	Conversion (%)	Selectivity to $C_8^=$ (%)	Selectivity to $C_{12}^=$ (%)	Selectivity to $C_{16}^=$ (%)	$C_8^=$ Yield (%)
1Ni/Al_2O_3	12.3	43	0	57	5.3
5Ni/Al_2O_3	4.0	27	0	73	1.1
1Ni-4W/Al_2O_3	12.7	85	15	0	10.8
1Ni-20W/Al_2O_3	15.2	97	3	0	14.7
5Ni-20W/Al_2O_3	14.1	68	32	0	9.6

Table 4.9 Conversion of isobutene and selectivity to isooctene of Ni-W/Al_2O_3 catalysts at 4 h

Catalysts	Conversion (%)	Selectivity to $C_8^=$ (%)	Selectivity to $C_{12}^=$ (%)	Selectivity to $C_{16}^=$ (%)	$C_8^=$ Yield (%)
1Ni/Al_2O_3	3.1	20	0	80	0.6
5Ni/Al_2O_3	0.05	27	0	73	0.01
1Ni-4W/Al_2O_3	9.6	90	10	0	8.6
1Ni-20W/Al_2O_3	12.1	75	25	0	9.0
5Ni-20W/Al_2O_3	5.8	82	18	0	4.8

Catalytic activity was determined in the dimerization of isobutene under similar conditions (150 °C and atmosphere pressure). Diisobutylene or isooctene (or $C_8^=$) is the desired product and by-products are triisobutylene (or $C_{12}^=$) and tetraisobutylene (or $C_{16}^=$). From the reaction results at 1 h as shown in Table 4.8, it was found that the conversion and selectivity to isooctene of Ni/Al_2O_3 catalyst was lower than $Ni-W/Al_2O_3$ catalyst and the Al_2O_3 support did not exhibit any catalytic activity. It is suggested that the addition of WO_3 improved the catalyst performance in terms of both conversion and selectivity.

Comparing the selectivity to isooctene, it was found that Ni/Al_2O_3 catalyst gave lower isooctene selectivity and higher tetraisobutylene selectivity but without the formation of triisobutylene. On the other hand, $Ni-W/Al_2O_3$ catalyst gave higher isooctene selectivity as well as triisobutylene, and tetraisobutylene as by-products. It is suggested that the addition of WO_3 decreased the formation of high molecular of olefins.

Moreover, increasing amount of nickel oxide to 5% led to lower conversion and selectivity. On the contrary, the higher amount of tungsten increased the catalytic performance of the catalyst. The best catalyst performance was obtained over $1Ni-20W/Al_2O_3$ catalyst. The isobutene conversion of $1Ni-20W/Al_2O_3$ catalyst was 15.2% and selectivity to isooctene was 97% that gave 14.7% yield to isooctene.

The conversion of isobutene and selectivity to isooctene of all catalysts at 4 h are shown in Table 4.9. It was found that the conversion of all catalyst decreased because of deactivation of catalyst. The selectivity to isooctene of Ni/Al_2O_3 catalyst also decreased but the selectivity to isooctene of $Ni-W/Al_2O_3$ catalyst slightly increased except $1Ni-20W/Al_2O_3$ catalyst that made yield to isooctene of $1Ni-20W/Al_2O_3$ catalyst was similar to $1Ni-4W/Al_2O_3$ catalyst

4.1.7 Thermal gravimetric and differential thermal analysis

The amount of coke formation was determined by thermal gravimetric and differential thermal analysis. TGA curve and derivative weight of spent catalysts are shown in Figure 4.7 and 4.8. From the results, it could be seen that all spent catalysts has two steps of weight loss. The first step, the loss of weight at below 200 °C was assigned to the removal of moisture according to Rad et al [48]. The second step, the loss of weight at around 300-700 °C was suggested to be the decomposition of coke on the surface catalyst. It was calculated from the different weight percent between 200-800 °C of catalyst after catalytic testing. The amount of coke formation are shown in Table 4.10.

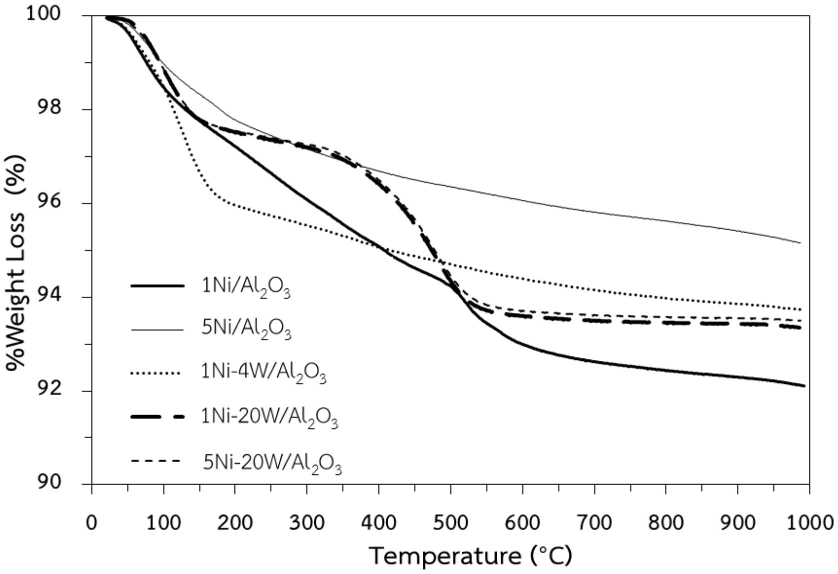

Figure 4.7 TGA curve of spent Ni-W/Al_2O_3 catalysts

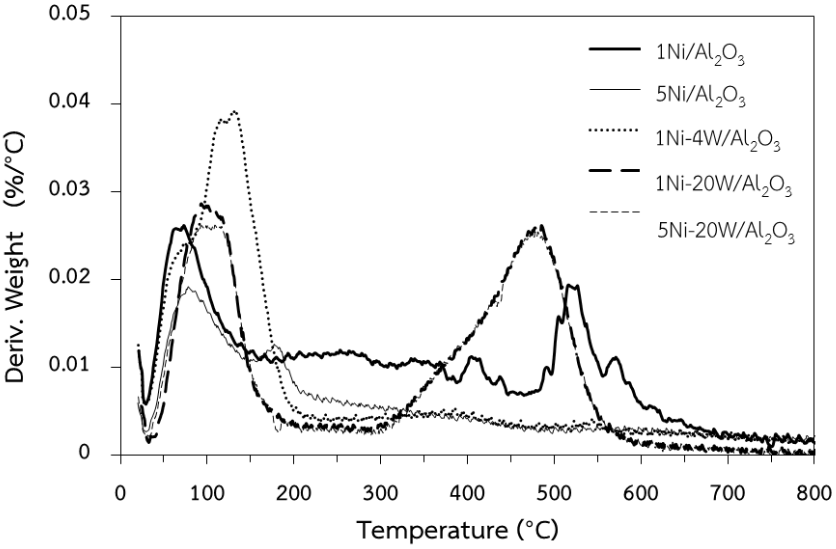

Figure 4.8 Derivative weight of spent Ni-W/Al_2O_3 catalysts

Table 4.10 Amount of coke formation of Ni-W/Al_2O_3 catalysts [a]

Catalysts	Amount of coke formation (%)
1Ni/Al_2O_3	4.79
5Ni/Al_2O_3	2.16
1Ni-4W/Al_2O_3	1.98
1Ni-20W/Al_2O_3	4.05
5Ni-20W/Al_2O_3	3.96

[a] Determined from TG/DTA method

From the results described in Table 4.10, it could be seen that 1Ni/Al_2O_3 catalyst gave the highest coke formation. The amount of coke formation could be related to the amount of acidity in Table 4.7. The higher amount of acidity led to the catalyst with higher activity and coke formation.

From the results described in Table 4.8 and 4.9, it was found that the 1Ni-20W/Al_2O_3 catalyst gave the highest yield to isooctene during reaction study. However, yield to isooctene of 1Ni-20W/Al_2O_3 catalyst was similar to 1Ni-4W/Al_2O_3

catalyst after 4 h reaction. Furthermore, 1Ni-20W/Al_2O_3 catalyst gave a low selectivity to isooctene and more amount of coke. On the other hand, the 1Ni-4W/Al_2O_3 catalyst gave amount of coke less than 1Ni-20W/Al_2O_3 catalyst. It also had a high and stable selectivity to isooctene. Therefore, 1Ni-4W/Al_2O_3 catalyst would be chosen to study in part2.

4.1.8 Purposed mechanism and pathway of dimerization reaction

The mechanism of isobutene dimerization as reported by Tzompantzi, F et al. is shown in Figure 4.9. According to report of Tzompantzi, F et al., the active sites are Ni^{2+} and acid site [16]. The presence of Ni^{2+} is responsible for adsorption of isobutene. Ni^{2+} bonds with isobutene to form carbocation. Then, carbocation reacts with another molecule of isobutene to form unstable complex which releases Ni^{2+} and form two isomers of isooctene. This step occurs on the acid site which is formed by WO_3. From the results of catalytic activity as shown in Table 4.8, it can be assumed that the mechanism is similar to the report of Tzompantzi, F et al. but the pathway of reaction is different because Ni/Al_2O_3 and Ni-W/Al_2O_3 catalyst gave different products. The possible reaction pathway of isobutene dimerization is shown in Figure 4.10 [6]. Therefore, discussion of results may divide the mechanism into two steps including adsorption and surface reaction.

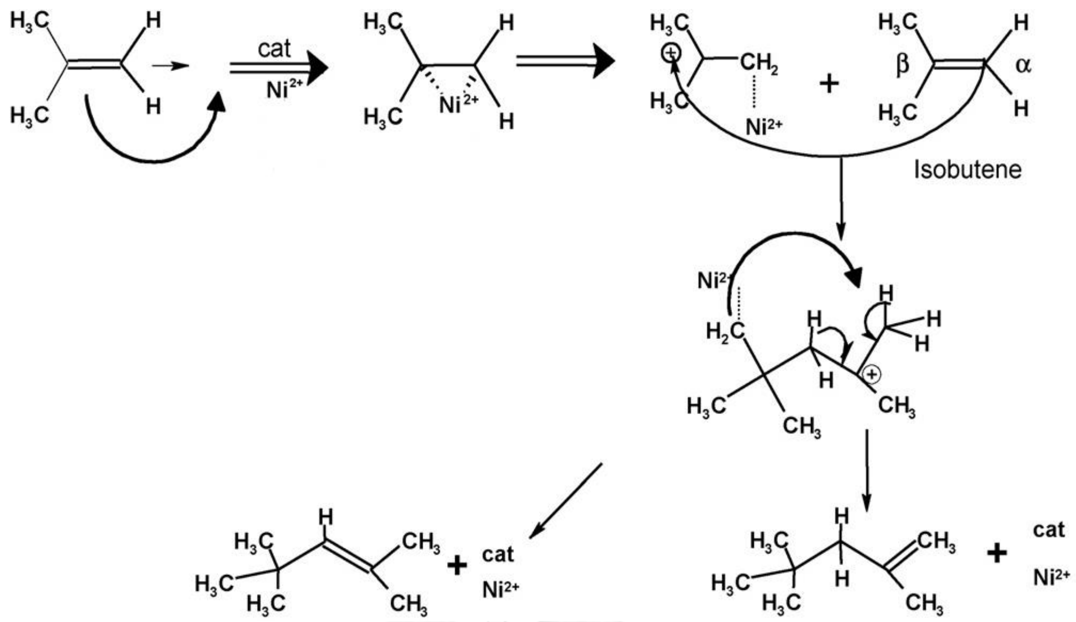

Figure 4.9 Mechanism of isobutene dimerization on Ni-based catalysts

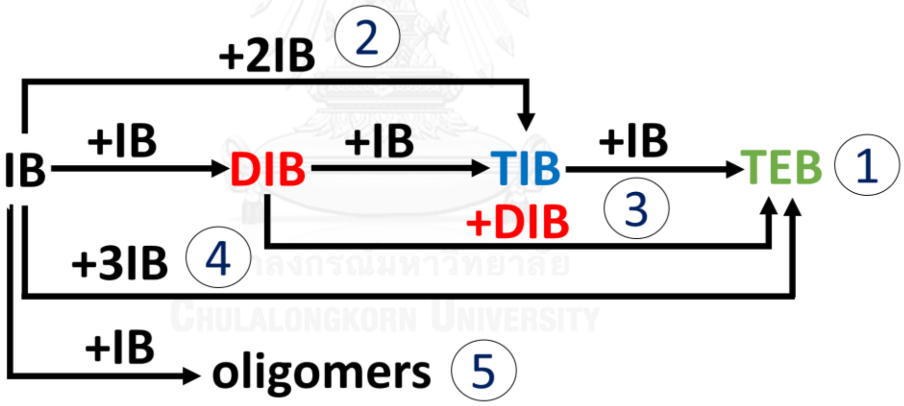

Figure 4.10 Reaction pathway of isobutene dimerization

For discussion of Al_2O_3 support, Al_2O_3 did not exhibit any catalytic activity because it was not suitable for adsorption of isobutene. Therefore, addition of nickel is necessary in order to start the reaction. For Ni/Al_2O_3 catalyst, there was adsorption of isobutene but surface reaction on the surface catalyst was slow that caused the slow desorption of isooctene (DIB). Then, isooctene on the surface catalyst continued to react with another isooctene and formed tetraisobutylene by parallel reaction as shown in pathway 3. Isobutene adsorbed more when nickel loading was increased that increased the formation of tetraisobutylene, corresponding to the results in Table 4.8. In addition, the conversion of isobutene decreased with increasing of nickel loading because more nickel obscured the acid of alumina that reduced acid site for surface reaction.

For Ni-W/Al_2O_3 catalysts, it can be assumed that tungsten oxide inserted between molecules of nickel which improved the catalyst performance. It enhanced the amount of acid sites for surface reaction which increased the conversion of isobutene. Moreover, it reduced the dimerization of isooctene to tetraisobutylene but isooctene can also react with isobutene to formed triisobutylene. Considering the results in Table 4.8, the results confirmed that Ni-W/Al_2O_3 catalyst made consecutive reaction as pathway 1 because selectivity to isooctene was high and tetraisobutylene was not found. Thus, addition of tungsten increased the catalyst performance in terms of both conversion and selectivity.

4.2 The effect of modified alumina in NiO-WO_3/Al_2O_3 catalysts and NiO-WO_3/SiO_2-Al_2O_3 catalysts on the catalytic activity in dimerization of isobutene

In this part, the catalysts were divided into two group. There were addition of silica to NiO-WO_3/Al_2O_3 catalysts and varying alumina preparation method.

4.2.1 The effect of NiO-WO_3/SiO_2-Al_2O_3 catalysts on the catalytic activity in dimerization of isobutene

The catalysts nomenclatures are shown in below as follows;

40SiO_2-Al_2O_3 presents the catalysts which contained 40 wt% of SiO_2 in commercial Al_2O_3.

1Ni-4W/20SiO_2-Al_2O_3 presents the catalysts which were prepared 1 wt% nickel and 4 wt% tungsten on commercial 20%SiO_2-Al_2O_3.

1Ni-4W/40SiO_2-Al_2O_3 presents the catalysts which were prepared 1 wt% nickel and 4 wt% tungsten on commercial 40%SiO_2-Al_2O_3.

4.2.1.1 X-ray diffraction

Figure 4.11 presents the crystalline structures of NiO-WO_3/SiO_2-Al_2O_3 catalysts. In all catalysts, there was a board peak around 20-30 ° which presented an amorphous solid [49]. The diffraction peaks at $2\theta = 54.0°$ and 66.0° represented the WO_3 crystal and γ-Al_2O_3 support. There were no diffraction peaks of NiO species because they were highly dispersed on the catalyst surface or due to their small crystallite sizes [40].

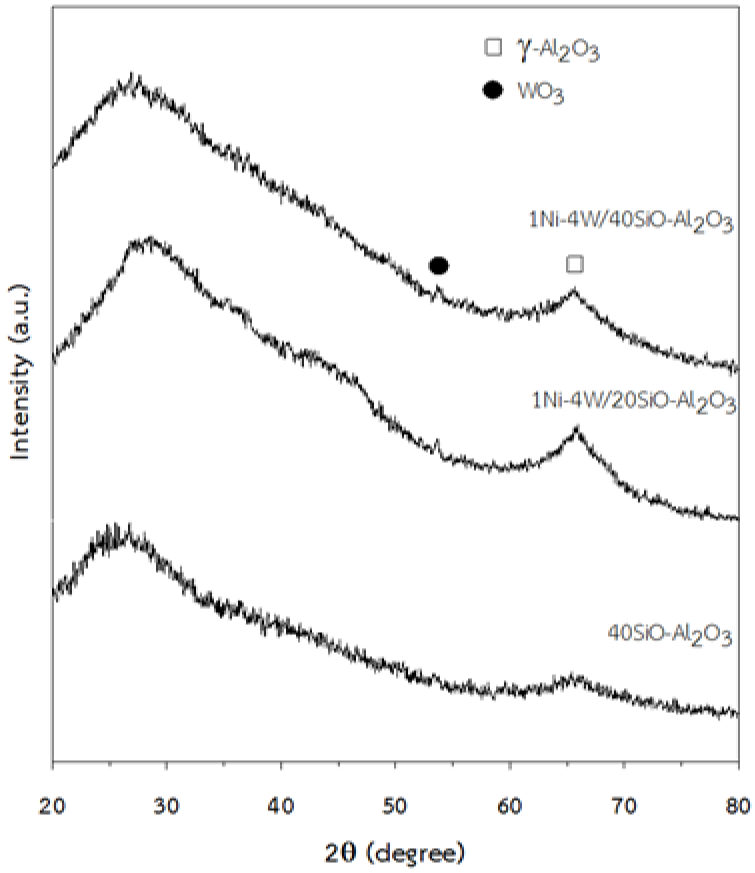

Figure 4.11 XRD patterns of SiO_2-Al_2O_3 and Ni-W/SiO_2-Al_2O_3 catalysts

4.2.1.2 N_2 physisorption

Table 4.11 The surface area, pore volume and average pore size of SiO_2-Al_2O_3 and Ni-W/SiO_2-Al_2O_3 catalysts

Catalyst	Surface Area [a] (m^2/g)	Pore Volume [b] (cm^3/g)	Average Pore [b] Diameter (nm)
40SiO_2-Al_2O_3	500	1.42	8.0
1Ni-4W/40SiO_2-Al_2O_3	422	1.29	7.8
1Ni-4W/20SiO_2-Al_2O_3	408	0.96	5.8

[a] determined from BET method

[b] determined from BJH desorption method

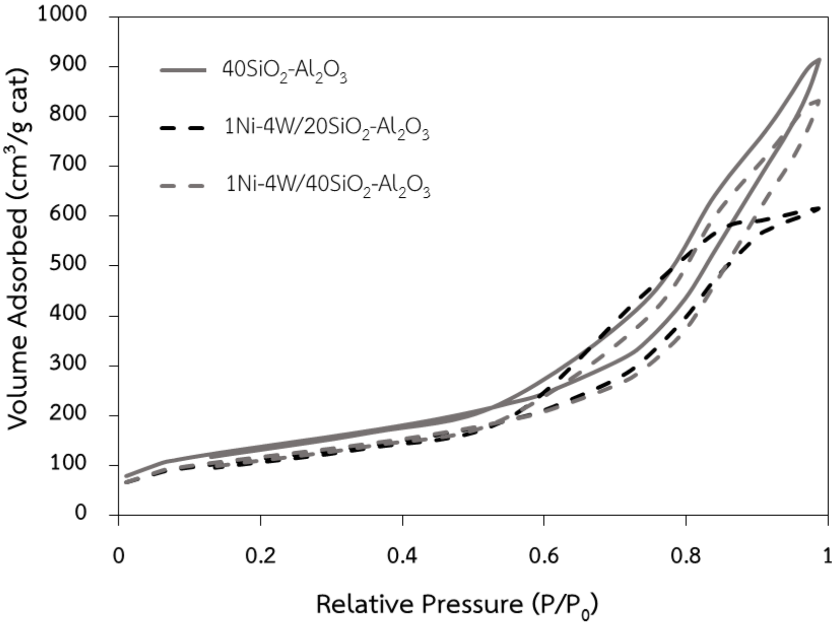

Figure 4.12 Nitrogen adsorption-desorption isotherm of SiO_2-Al_2O_3 and Ni-W/SiO_2-Al_2O_3 catalysts

Table 4.11 presents the surface area, pore volume, and average pore diameter of SiO_2-Al_2O_3 and Ni-W/SiO_2-Al_2O_3 catalysts. It was found that the surface area and pore volume decreased when metal was loaded because of deposition of oxides on the surface of catalyst blocking the pores [18]. The catalyst with 40 wt% silica gave higher surface area, larger pore volume and average pore diameter than 20 wt% silica as shown in Figure 4.12 with the 1Ni-4W/20SiO_2-Al_2O_3 catalyst had the lowest pore volume. All catalysts exhibited the type IV isotherms with a H1-type hysteresis loop in the IUPAC classification [43]. This type is associated with a typical mesoporous material with well-defined cylindrical pores or uniform sphere pores. From the results, pore diameter of all catalysts was in the range 2-50 nm that confirmed they was mesoporous material.

4.2.1.3 X-ray photoelectron spectroscopy

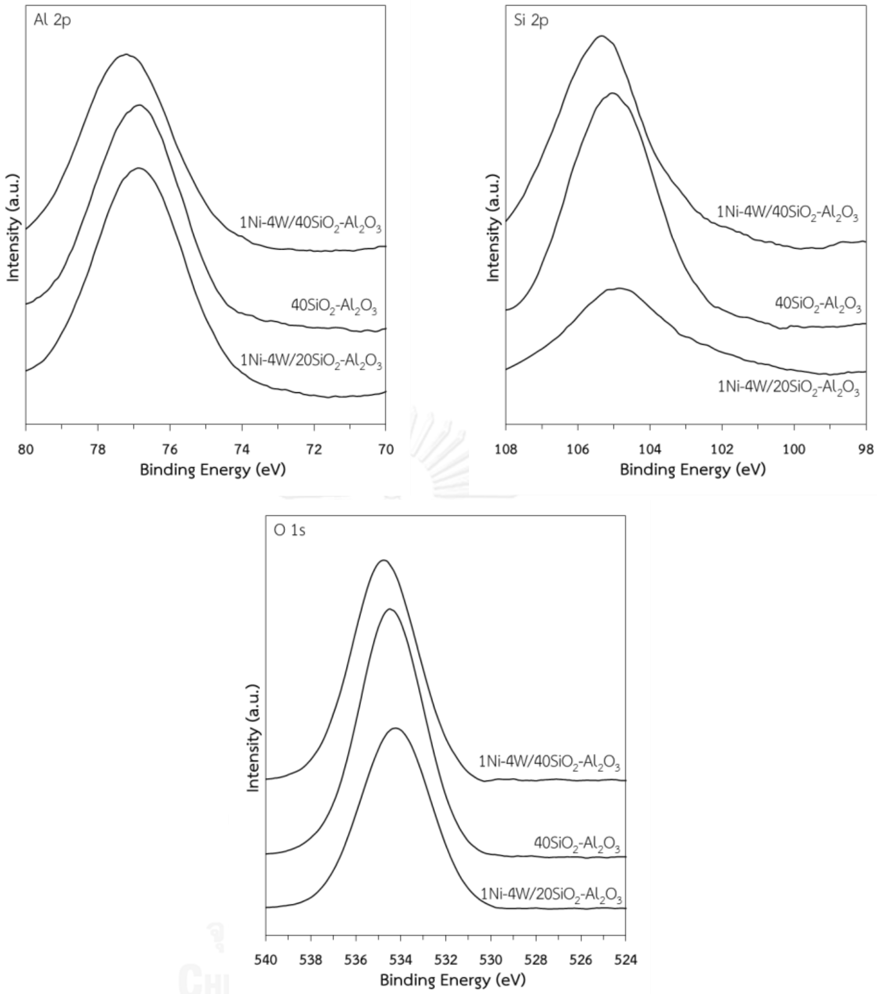

Figure 4.13 Al 2p, O 1s, and Si 2p of XPS spectra of SiO_2-Al_2O_3 and Ni-W/SiO_2-Al_2O_3 catalysts

Table 4.12 Binding energy of Al 2p, O 1s, and Si 1p of XPS spectra of Al_2O_3 and Ni-W/Al_2O_3 catalysts

Catalysts	Binding energy (eV)		
	Al 2p	O 1s	Si 2p
40SiO_2-Al_2O_3	76.8	534.4	105.0
1Ni-4W/20SiO_2-Al_2O_3	76.9	534.2	104.8
1Ni-4W/40SiO_2-Al_2O_3	77.2	534.8	105.3

The XPS spectra of SiO_2-Al_2O_3 and Ni-W/SiO_2-Al_2O_3 catalysts are shown in Figure 4.13 and binding energy of all elements are shown in Table 4.12. In the report of Ahmad et al., the peak of Si at binding energy of 104.6 eV were attributed to SiO_2 [50]. From the results, peak of all elements shifted toward higher binding energy values for Ni-W/SiO_2-Al_2O_3 catalysts. The catalysts with more silica also shifted to higher binding energy. It may be due to formation of strong interaction between oxides. Grundling et al. reported that it was attributed to the formation of Si-O-Al bonds which increased the electron density on silicon and oxygen [51]. It was confirmed that the binding energy for O and Si decreased with increasing aluminum content.

4.2.1.4 Ammonia temperature program desorption

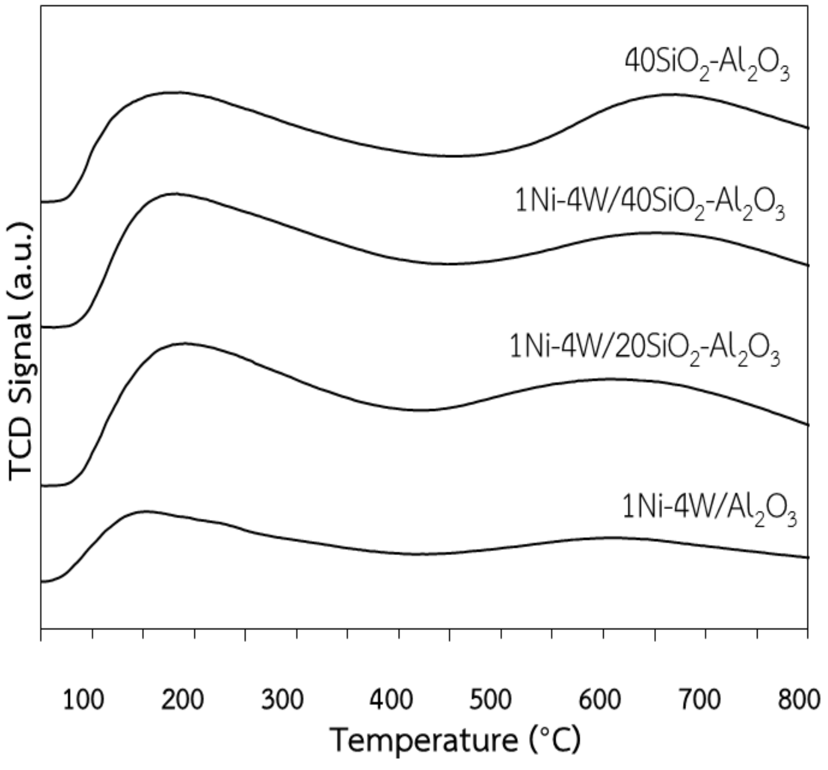

Figure 4.14 NH_3-TPD profiles of SiO_2-Al_2O_3 and Ni-W/SiO_2-Al_2O_3 catalysts

Table 4.13 Amount of acidity of SiO_2-Al_2O_3 and Ni-W/SiO_2-Al_2O_3 catalysts

Catalysts	Amount of acidity (mmol/g)			
	Weak	Strong	Total	Strong / Weak
40SiO_2-Al_2O_3	1.42	1.72	3.14	1.21
1Ni-4W/20SiO_2-Al_2O_3	1.86	2.05	3.91	1.09
1Ni-4W/40SiO_2-Al_2O_3	1.98	1.53	3.51	0.77
1Ni-4W/Al_2O_3	0.57	0.32	0.89	0.56

The NH_3-TPD profiles of SiO_2-Al_2O_3 and Ni-W/SiO_2-Al_2O_3 catalysts are shown in Figure 4.14. There were two desorption peaks that indicated to weak and strong acids in all catalysts. Two desorption peaks of SiO_2-doped catalysts shifted to higher temperature. The amount of acidity of all catalysts are shown in Table 4.13. From the results, the acidity of SiO_2-doped catalysts were higher than the non-doped catalyst. The acidity of catalysts and amount of strong acid decreased with increasing of silica loading. Moreover, amount of acidity increased and amount of strong acid decreased after metal was added. It was suggested that metal reduced the strong acid and enhanced the weak acid.

4.2.1.5 Catalytic activity

Table 4.14 Conversion of isobutene and selectivity to isooctene of Ni-W/SiO_2-Al_2O_3 catalysts at 1 h

Catalysts	Conversion (%)	Selectivity to $C_8^=$ (%)	Selectivity to $C_{12}^=$ (%)	Selectivity to $C_{16}^=$ (%)	$C_8^=$ Yield (%)
40SiO_2-Al_2O_3	27.3	61	39	0	16.6
1Ni-4W/20SiO_2-Al_2O_3	7.9	71	29	0	5.6
1Ni-4W/40SiO_2-Al_2O_3	16.3	78	22	0	12.7
1Ni-4W/Al_2O_3	7.2	93	5	2	6.7

Table 4.15 Conversion of isobutene and selectivity to isooctene of Ni-W/SiO_2-Al_2O_3 catalysts at 4 h

Catalysts	Conversion (%)	Selectivity to $C_8^=$ (%)	Selectivity to $C_{12}^=$ (%)	Selectivity to $C_{16}^=$ (%)	$C_8^=$ Yield (%)
40SiO_2-Al_2O_3	19.6	64	35	1	12.5
1Ni-4W/20SiO_2-Al_2O_3	2.6	74	26	0	1.9
1Ni-4W/40SiO_2-Al_2O_3	8.2	80	20	0	6.5
1Ni-4W/Al_2O_3	1.6	92	5	3	1.5

The catalytic activity of Ni-W/SiO_2-Al_2O_3 catalysts at 1 h and 4 h are shown in Table 4.14 and Table 4.15. From the results, the 1Ni-4W/Al_2O_3 catalyst was tested under the same conditions as other catalysts. The results showed that the catalysts with silica gave higher conversion and lower selectivity to isooctene than the catalyst without silica. Conversion and selectivity to isooctene increased with increasing of silica loading. However, addition of metal led to lower conversion and higher selectivity to isooctene than the catalyst without metal. Therefore, it is suggested that silica improved the conversion and metal improved the selectivity to isooctene.

Comparing the selectivity to isooctene, it was found that the 1Ni-4W/Al_2O_3 catalyst gave high isooctene selectivity with little triisobutylene and tetraisobutylene selectivity. On the other hand, the catalysts with silica gave lower isooctene selectivity and higher triisobutylene selectivity than 1Ni-4W/Al_2O_3 catalyst without tetraisobutylene selectivity. The best catalyst performance was obtained over 40SiO_2-Al_2O_3 catalyst. The isobutene conversion of 40SiO_2-Al_2O_3 catalyst was 27.3% and selectivity to isooctene was 61% that gave 16.6% yield to isooctene.

After 4 h reaction, the conversion of all catalysts decreased because of deactivation of catalyst. The selectivity to isooctene of catalyst with silica slightly increased while the selectivity to isooctene of 1Ni-4W/Al_2O_3 catalyst was stable. From the results, the 40SiO_2-Al_2O_3 catalyst showed the slowest deactivation.

4.2.1.6 Thermal gravimetric and differential thermal analysis

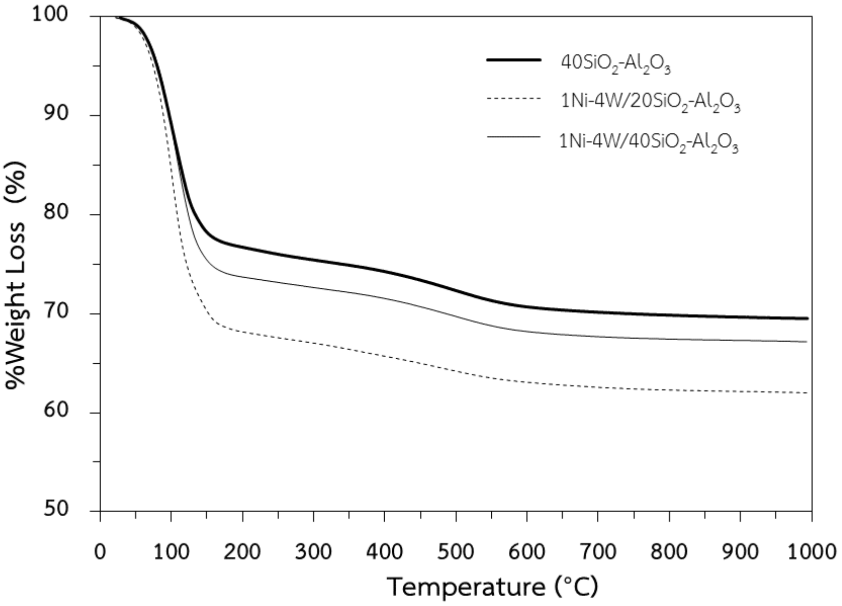

Figure 4.15 TGA curve of spent Ni-W/SiO_2-Al_2O_3 catalysts

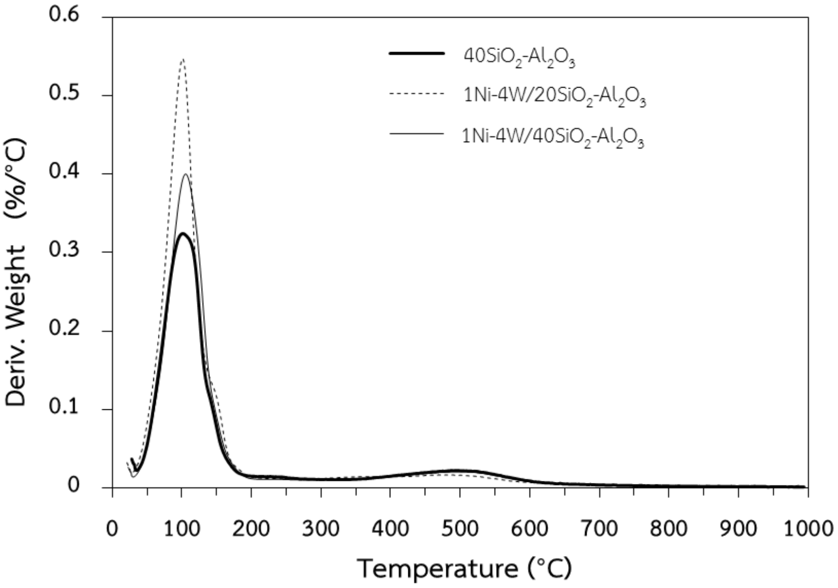

Figure 4.16 Derivative weight of spent Ni-W/SiO_2-Al_2O_3 catalysts

Table 4.16 Amount of coke formation of Ni-W/SiO_2-Al_2O_3 catalysts [a]

Catalysts	Amount of coke formation (%)
40SiO_2-Al_2O_3	6.88
1Ni-4W/20SiO_2-Al_2O_3	5.87
1Ni-4W/40SiO_2-Al_2O_3	6.28

[a] Determined from TG/DTA method

The TGA curve and derivative weight of spent Ni-W/SiO_2-Al_2O_3 catalysts are shown in Figure 4.15 and Figure 4.16. It could be seen that all spent catalysts had two steps of weight loss. The first step, the loss of weight at below 200 °C was assigned to the removal of moisture according to Rad et al [48]. The second step, the loss of weight at around 300-800 °C was suggested to be the decomposition of coke on the surface catalyst. It was calculated from the different weight percent between 200-800 °C of catalyst after catalytic testing. The amounts of coke formation are shown in Table 4.16.

From the results described in Table 4.16, it could be seen that 40SiO_2-Al_2O_3 catalyst gave the highest coke formation. The amount of coke formation had a negative effect on the amount of acidity in Table 4.13 but it was related to the catalytic activity. The higher activity led the catalyst to give higher coke formation.

4.2.1.7 Purposed mechanism and pathway of dimerization reaction

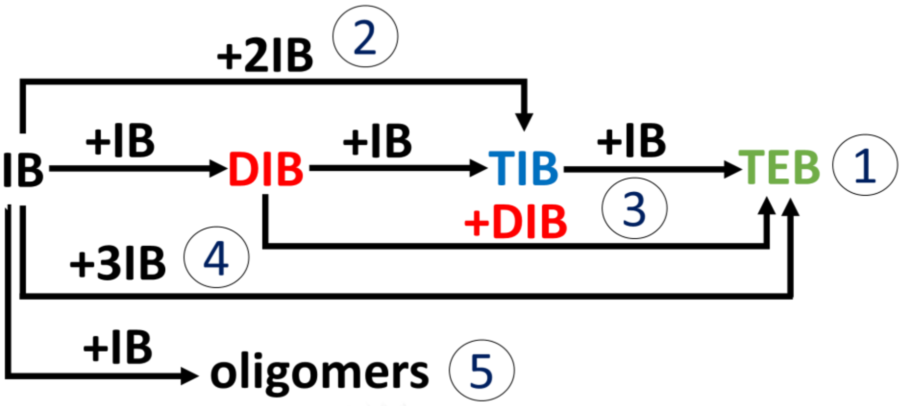

Figure 4.10 Reaction pathway of isobutene dimerization

The mechanism and pathway of isobutene dimerization for discussion of results was similar to part1 as shown in Figure 4.9 and Figure 4.10. For discussion of SiO_2-Al_2O_3 catalysts, it did not have metal to help isobutene adsorption but the strong acid sites may be strong enough to be responsible for isobutene adsorption as well as surface reaction. In addition, there appeared to be more adsorption and surface reaction on the SiO_2-Al_2O_3 catalysts, resulting in higher conversion of isobutene. More isobutene on the catalyst can react to form isooctene and triisobutylene by consecutive and parallel reactions as shown in pathway 1 and 2. Competition of two pathways made the low isooctene and high triisobutylene selectivity.

For the 1Ni-4W/SiO_2-Al_2O_3 catalysts, it is suggested that the reaction formed in the same pathway as SiO_2-Al_2O_3 catalysts. The 1Ni-4W/SiO_2-Al_2O_3 catalysts had lower strong acid sites than SiO_2-Al_2O_3 catalysts that made the low conversion. Addition of metal improved the structure of catalyst that increased selectivity to isooctene as explained in part1. From all the reasons, the 1Ni-4W/SiO_2-Al_2O_3 catalysts had lower conversion and higher isooctene selectivity than SiO_2-Al_2O_3 catalysts.

4.2.2 The effect of different alumina preparation methods of NiO-WO_3/Al_2O_3 catalysts on the catalytic activity in dimerization of isobutene

The catalysts nomenclatures are shown below as follows:

1Ni-4W/Al_2O_3-SV presents the catalysts which were prepared with 1 wt% nickel and 4 wt% tungsten on Al_2O_3 from solvothermal method.

1Ni-4W/Al_2O_3-CP presents the catalysts which were prepared with 1 wt% nickel and 4 wt% tungsten on Al_2O_3 from co-precipitation method.

1Ni-4W/Al_2O_3-GIB presents the catalysts which were prepared with 1 wt% nickel and 4 wt% tungsten on Al_2O_3 from gibbsite calcination method.

4.2.2.1 X-ray diffraction

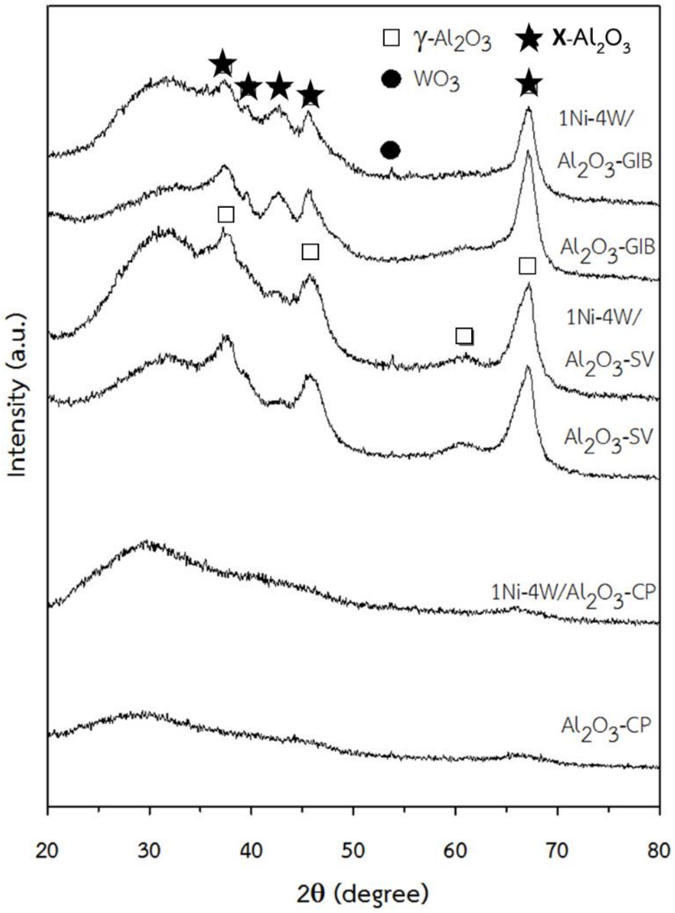

Figure 4.17 XRD patterns of Ni-W/Al_2O_3 catalysts with different alumina preparation method

The XRD patterns of $NiO-WO_3/Al_2O_3$ catalysts with different alumina preparation methods are shown in Figure 4.17. The diffraction peaks at 2θ = 37.0°, 45.9°, 60.0°, and 66.0° represented $\gamma-Al_2O_3$ support [40]. The diffraction peaks at 2θ = 37.0°, 39.8°, 42.7°, 45.9°, and 66.0° represented $\chi-Al_2O_3$ support [52]. The diffraction peaks at 2θ = 54.2° represented the WO_3 crystal [41]. All the catalysts presented the $\gamma-Al_2O_3$ support except the Al_2O_3-GIB and 1Ni-4W/Al_2O_3-GIB catalyst which were observed for χ-phase of Al_2O_3. The diffraction peaks of WO_3 can be detected on the 1Ni-4W/Al_2O_3-SV and 1Ni-4W/Al_2O_3-GIB catalysts. There were no diffraction peaks of NiO in all catalysts because it was highly dispersed on the catalyst surface or their crystallite size were very small [40].

4.2.2.2 N_2 physisorption

Table 4.17 The surface area, pore volume and average pore size of Ni-W/Al_2O_3 catalysts with different alumina preparation methods

Catalyst	Surface Area [a] (m^2/g)	Pore Volume [b] (cm^3/g)	Average Pore [b] Diameter (°A)
1Ni-4W/Al_2O_3-SV	222	0.88	106
1Ni-4W/Al_2O_3-CP	114	0.48	102
1Ni-4W/Al_2O_3-GIB	157	0.23	35

[a] determined from BET method

[b] determined from BJH desorption method

A comparison of the textural properties of the different Ni-W/Al_2O_3 catalysts are shown in Table 4.17. The 1Ni-4W/Al_2O_3-SV catalyst had the highest surface area, pore volume, and the largest average pore diameter. The 1Ni-4W/Al_2O_3-CP catalyst had the lowest surface area while 1Ni-4W/Al_2O_3-GIB catalyst had the lowest pore volume and the smallest pore diameter.

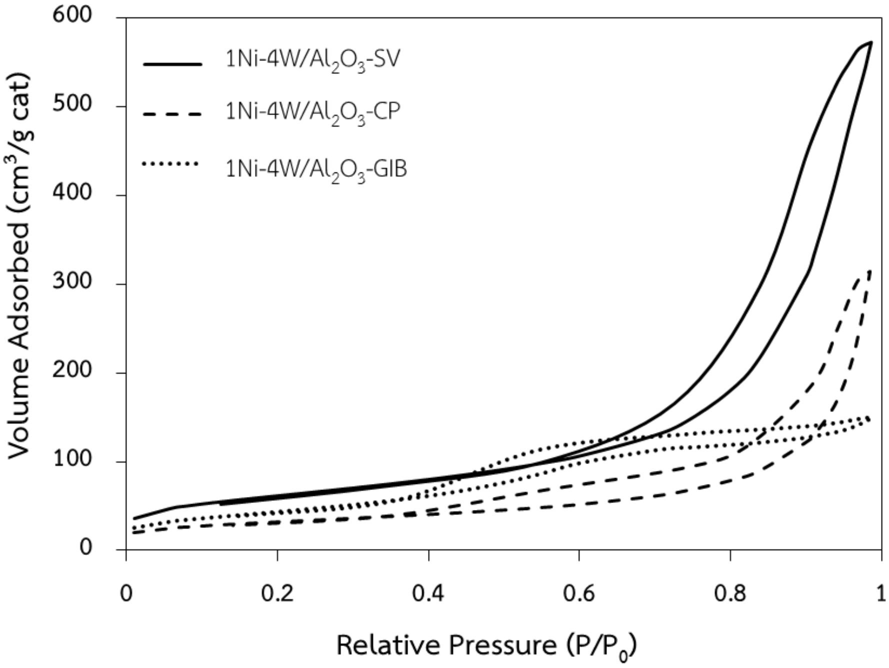

Figure 4.18 Nitrogen adsorption-desorption isotherm of Ni-W/Al_2O_3 catalysts with different alumina preparation method

Figure 4.18 shows the nitrogen adsorption-desorption isotherm of Ni-W/Al_2O_3 catalysts with different alumina preparation methods. All catalysts exhibited the type IV isotherms in the IUPAC classification, indicating they were mesoporous materials [43]. The 1Ni-4W/Al_2O_3-SV and 1Ni-4W/Al_2O_3-CP catalysts presented H1-type hysteresis loop, indicating they were associated with porous material consisting of well-defined cylindrical pores or uniform sphere pores. The 1Ni-4W/Al_2O_3-GIB catalyst presented H4-type hysteresis loop, indicating it was associated with narrow slit pores. From the results, the 1Ni-4W/Al_2O_3-GIB catalyst had the lowest pore volume. It is suggested that 1Ni-4W/Al_2O_3-GIB catalyst had a narrow slit-type pores, which made it had low pore volume.

4.2.2.3 Ammonia temperature program desorption

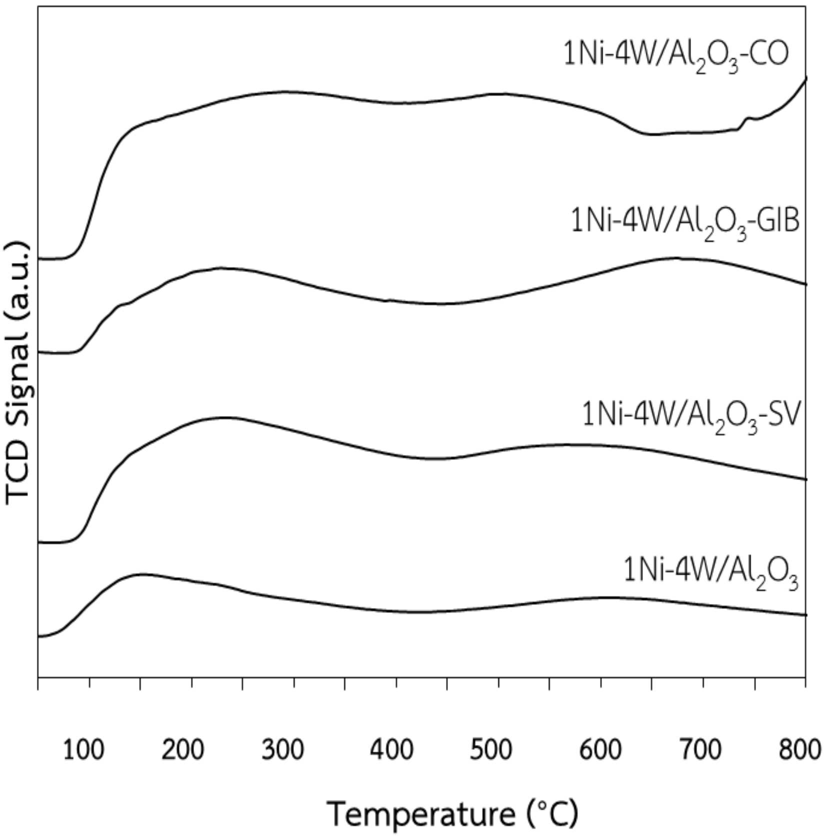

Figure 4.19 NH_3-TPD profiles of Ni-W/Al_2O_3 catalysts with different alumina preparation method

Table 4.18 Amount of acidity of Ni-W/Al_2O_3 catalysts with different alumina preparation method

Catalysts	Amount of acidity (mmol/g)			
	Weak	Strong	Total	Strong / Weak
1Ni-4W/Al_2O_3-SV	1.07	1.31	2.38	1.22
1Ni-4W/Al_2O_3-CP	1.23	2.58	3.81	2.10
1Ni-4W/Al_2O_3-GIB	0.78	1.28	2.06	1.64
1Ni-4W/Al_2O_3	0.57	0.32	0.89	0.56

The NH_3-TPD profiles of SiO_2-Al_2O_3 and Ni-W/SiO_2-Al_2O_3 catalysts are shown in Figure 4.19. Two types of acid sites including weak and strong acid were seen in all the catalysts. The amounts of acidity are provided in Table 4.18. The results showed that strong acid was higher than weak acid for catalysts with different alumina preparation method. The 1Ni-4W/Al_2O_3-CP catalysts had the highest amount of acidity and the highest ratio of strong to weak acid compared to 1Ni-4W/Al_2O_3-SV and 1Ni-4W/Al_2O_3-GIB catalysts.

4.2.2.4 Catalytic activity

Table 4.19 Conversion of isobutene and selectivity to isooctene of Ni-W/Al_2O_3 catalysts with different alumina preparation method at 1 h

Catalysts	Conversion (%)	Selectivity to $C_8^=$ (%)	Selectivity to $C_{12}^=$ (%)	Selectivity to $C_{16}^=$ (%)	$C_8^=$ Yield (%)
1Ni-4W/Al_2O_3-SV	6.6	92	7	1	6.1
1Ni-4W/Al_2O_3-CP	11.7	71	29	0	8.3
1Ni-4W/Al_2O_3-GIB	9.7	91	8	1	8.8
1Ni-4W/Al_2O_3	7.2	93	5	2	6.7

Table 4.20 Conversion of isobutene and selectivity to isooctene of Ni-W/Al_2O_3 catalysts with different alumina preparation method at 4 h

Catalysts	Conversion (%)	Selectivity to $C_8^=$ (%)	Selectivity to $C_{12}^=$ (%)	Selectivity to $C_{16}^=$ (%)	$C_8^=$ Yield (%)
1Ni-4W/Al_2O_3-SV	1.2	91	8	1	1.1
1Ni-4W/Al_2O_3-CP	9.5	75	25	0	7.1
1Ni-4W/Al_2O_3-GIB	3.4	88	9	3	2.9
1Ni-4W/Al_2O_3	1.6	92	5	3	1.5

The catalytic activity of Ni-W/Al_2O_3 catalysts at 1 h and 4 h with different alumina preparation method are shown in Table 4.19 and Table 4.20. From the results, the 1Ni-4W/Al_2O_3 catalyst was tested under the same conditions with similar catalyst loading. The results showed that the catalysts with different alumina preparation method gave higher conversion and lower selectivity to isooctene than the 1Ni-4W/Al_2O_3 catalyst in the same reaction condition. Comparing the selectivity to isooctene, it was found that the 1Ni-4W/Al_2O_3-CP catalyst gave lower isooctene selectivity and higher triisobutylene selectivity than 1Ni-4W/Al_2O_3 catalyst without tetraisobutylene selectivity. On the other hand, the 1Ni-4W/Al_2O_3-SV and 1Ni-4W/Al_2O_3-GIB catalyst gave high isooctene selectivity with a little treiisobutylene and tetraisobutylene selectivity. The catalytic activity was related to the strong to weak acid ratio of catalyst. The higher strong to weak acid ratio led the catalyst gave higher conversion and lower selectivity to isooctene. The best catalyst performance was obtained over 1Ni-4W/Al_2O_3-GIB catalyst. The isobutene conversion of 1Ni-4W/Al_2O_3-GIB catalyst was 9.7% and selectivity to isooctene was 91% that gave 8.8% yield to isooctene.

For discussion of 1Ni-4W/Al_2O_3-CP catalyst, it is suggested that it followed the same mechanism and pathway as SiO_2-Al_2O_3 catalyst. However, 1Ni-4W/Al_2O_3-CP catalyst gave the lower conversion than SiO_2-Al_2O_3 catalyst while acidity was similar because co-precipitation method may improve structure of catalyst which was different from SiO_2-Al_2O_3 catalyst and gave the low conversion. From N_2 physisorption results, the SiO_2-Al_2O_3 catalyst had higher surface area than 1Ni-4W/Al_2O_3-CP catalyst which led the catalyst gave more reaction.

For discussion of 1Ni-4W/Al_2O_3-SV and 1Ni-4W/Al_2O_3-GIB catalyst, it is suggested that it followed the same mechanism and pathway as Ni-W/Al_2O_3 catalyst. Form the results, selectivity to isooctene was similar but conversion was different. The 1Ni-4W/Al_2O_3-GIB catalyst gave the high conversion because it had high acidity. The 1Ni-4W/Al_2O_3-SV catalyst gave the low conversion because solvothermal method may result in different catalyst morphology from the commercial Al_2O_3 catalyst and gave the low conversion.

After 4 h reaction, the conversion of all catalysts decreased because of deactivation of catalyst. The selectivity to isooctene of 1Ni-4W/Al_2O_3-CP catalyst slightly increased while the selectivity to isooctene of 1Ni-4W/Al_2O_3-GIB catalyst decreased. From the results, the 1Ni-4W/Al_2O_3-CP catalyst had the slowest deactivation.

4.2.2.5 Thermal gravimetric and differential thermal analysis

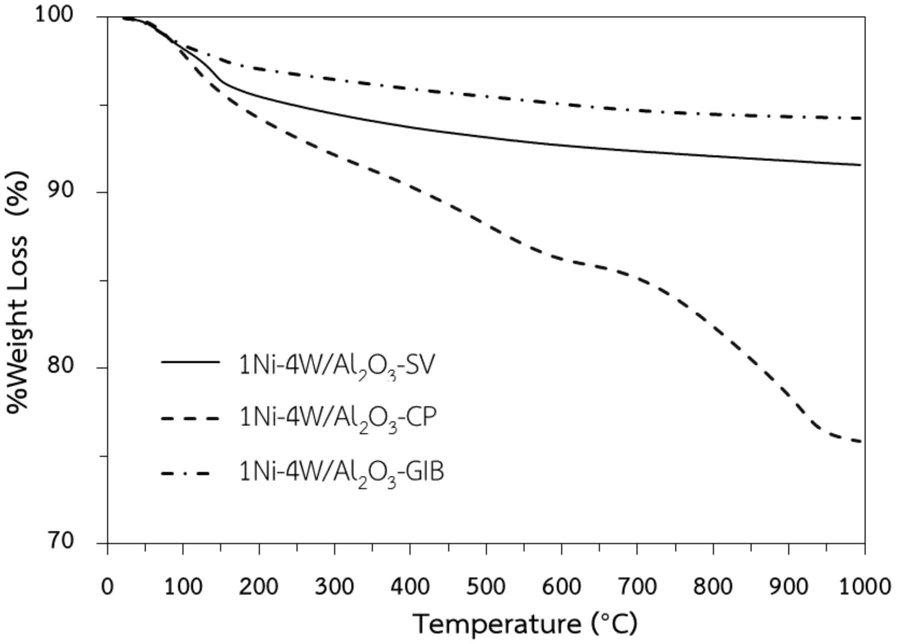

Figure 4.20 TGA curve of spent Ni-W/Al_2O_3 catalysts with different alumina preparation method

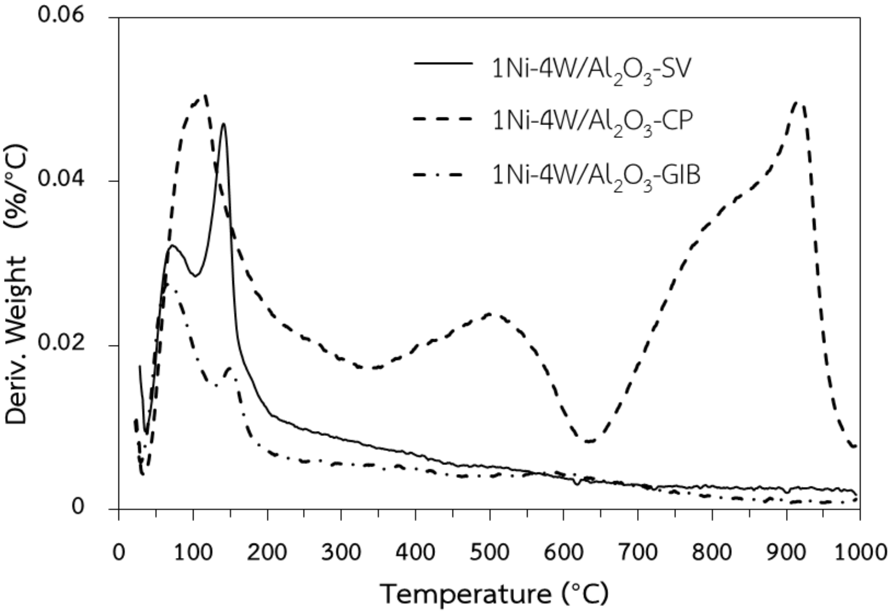

Figure 4.21 Derivative weight of spent Ni-W/Al_2O_3 catalysts with different alumina preparation method

Table 4.21 Amount of coke formation of Ni-W/Al_2O_3 catalysts with different alumina preparation method [a]

Catalysts	Amount of coke formation (%)
1Ni-4W/Al_2O_3-SV	3.89
1Ni-4W/Al_2O_3-CP	18.41
1Ni-4W/Al_2O_3-GIB	2.82

[a] Determined from TG/DTA method

The TGA curves and derivative weights of spent Ni-W/Al_2O_3 catalysts with different alumina preparation methods are shown in Figure 4.20 and Figure 4.21, respectively. It could be seen that all spent catalysts had two steps of weight loss. The first step, the loss of weight at below 200 °C was assigned to the removal of moisture according to Rad et al [48]. The second step, the loss of weight at around 300-650 °C was suggested to be the decomposition of coke on the catalyst surface. For 1Ni-4W/Al_2O_3-CP catalyst, there was third step that may be assigned to another type of coke. Coke formation was calculated from the different weight percent between 200-990 °C of catalyst after catalytic testing. The amount of coke formation are shown in Table 4.21.

From the results described in Table 4.16, it could be seen that 1Ni-4W/Al_2O_3-CP catalyst gave the highest coke formation. The amount of coke formation was related to the amount of acidity in Table 4.18. The higher acidity led the catalyst to give higher conversion and coke formation.

CHAPTER 5

CONCLUSIONS

5.1 Conclusions

1) In the case of Al_2O_3 supported catalysts, Ni-W/Al_2O_3 catalysts gave higher conversion and selectivity than Ni/Al_2O_3 catalysts. Addition of WO_3 increased the acidity of catalyst. Furthermore, tungsten oxide inserted between molecules of nickel which improved selectivity to isooctene. The 1Ni-4W/Al_2O_3 catalyst was the best Ni and W ratio under the conditions used. Although, it gave a slightly lower yield of isooctene than 1Ni-20W/Al_2O_3 catalyst, it gave higher and more stable selectivity with less coke formation. Therefore, 1Ni-4W/Al_2O_3 catalyst was selected as the best catalyst among the catalysts studied.

2) For the case of SiO_2-Al_2O_3 without metal, the 40SiO_2-Al_2O_3 catalyst exhibited the highest catalyst performances. The SiO_2-Al_2O_3 continued strong acid and high total acidity which able to catalyze the dimerization of isobutene with high conversion and high yield of isooctene. Addition of Ni and W metals on the SiO_2-Al_2O_3 on the other hand led to lower catalytic performances due to lower strong acidity presented.

3) For the case of different alumina preparation methods, the 1Ni-4W/Al_2O_3-GIB catalyst exhibited higher catalyst performance than those prepared by co-precipitation and solvothermal methods. The catalytic activity was related to the strong to weak acid ratio of catalyst. The higher strong to weak acid ratio led the catalyst gave higher conversion and lower selectivity to isooctene.

5.2 Recommendation

1) Pyridine adsorption analysis should be investigated to indicate Bronsted and Lewis acid sites.

2) Pathway of isobutene dimerization should be studied further.

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APPENDIX

APPENDIX A

CALCULATION FOR CATALYST PREPARATION

1)Calculation for preparation of Ni/Al_2O_3

Example calculation of 1 wt% of Ni on Al_2O_3 support

Information: Nickel Nitrate Hexahydrate

Molecular weight = 290.79 g/mol

Molecular weight of Ni = 58.69 g/mol

Based on 1 g catalyst used:

There are Ni 0.01 g and Al_2O_3 0.99 g in 1 g catalyst

Ni 58.69 g in $Ni(NO_3)_2{\cdot}6H_2O$ 290.79 g

Ni 0.01 g in $Ni(NO_3)_2{\cdot}6H_2O$ $\frac{290.79 \times 0.01}{58.69} = 0.049$ g

Therefore, used $Ni(NO_3)_2{\cdot}6H_2O$ 0.049 g and Al_2O_3 0.99 g for preparation 1Ni/ Al_2O_3 1 g

2)Calculation for preparation of Ni-W/Al_2O_3

Example calculation of 1 wt% of Ni and 4 wt% of W on Al_2O_3 support

Information: -Nickel Nitrate Hexahydrate

Molecular weight = 290.79 g/mol

Molecular weight of Ni = 58.69 g/mol

-Ammonium metatungstate hydrate

Molecular weight = 2956.3 g/mol

Molecular weight of W = 183.84 g/mol

Based on 1 g catalyst used:

There are Ni 0.01 g, W 0.04 and Al_2O_3 0.95 g in 1 g catalyst

Ni 58.69 g in $Ni(NO_3)_2{\cdot}6H_2O$ 290.79 g

Ni 0.01 g in $Ni(NO_3)_2{\cdot}6H_2O$ $\frac{290.79 \times 0.01}{58.69} = 0.049$ g

W 183.84×12 g in $(NH_4)_6H_{12}O_{40}{\cdot}xH_2O$ 2956.3 g

W 0.04 g in $(NH_4)_6H_{12}O_{40}{\cdot}xH_2O$ $\frac{2956.3 \times 0.04}{183.84 \times 12} = 0.053$ g

Therefore, used $Ni(NO_3)_2{\cdot}6H_2O$ 0.049 g, $(NH_4)_6H_{12}O_{40}{\cdot}xH_2O$ 0.053 g, and Al_2O_3 0.95 g for preparation 1Ni-4W/ Al2O3 1 g

APPENDIX B

CALCULATION FOR THE ACID SITE OF CATALYST

The acid site of catalyst were investigated by ammonia temperature program desorption. The amount of acidity on the surface catalyst was calculated as the following step.

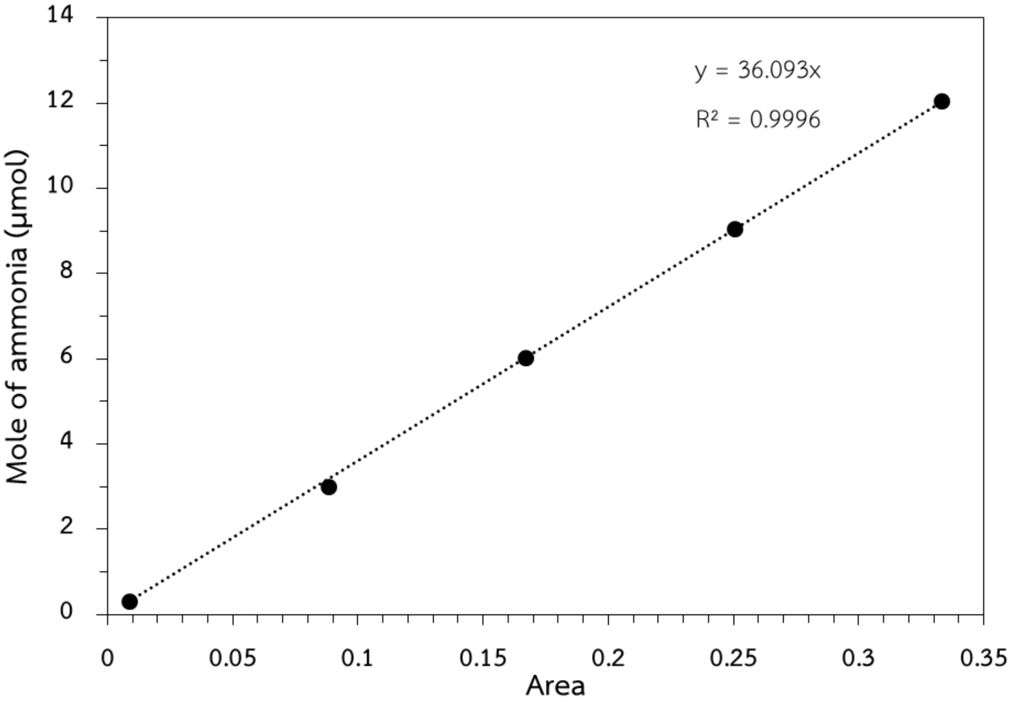

Figure B.1 Calibration curve of ammonia

The acidity of catalyst can be calculated from :

$$\text{The acid of catalyst} = \frac{36.093 \times \text{Area of } NH_3\text{-TPD profile}}{\text{catalyst loading}} \ \mu\text{mol } NH_3/\text{g catalyst}$$

APPENDIX C

CALCULATION FOR CATALYTIC PERFORMANCE

1) Conversion of Isobutene

$$\text{Conversion}\ (\%) = \frac{\text{Area of Isobutene in} \times \text{Area of Isobutene out}}{\text{Area of Isobutene in}} \times 100$$

2) Selectivity to products

$$\text{Selectivity to}\ C_8^{=}\ (\%) = \frac{\text{Area of Isooctene}}{\text{Area of total products}} \times 100$$

$$\text{Selectivity to}\ C_{12}^{=}\ (\%) = \frac{\text{Area of Triisobutylene}}{\text{Area of total products}} \times 100$$

$$\text{Selectivity to}\ C_{16}^{=}\ (\%) = \frac{\text{Area of Tetraisobutylene}}{\text{Area of total products}} \times 100$$

3) Yield to Isooctene

$$\text{Selectivity of}\ C_8^{=}\ (\%) = \frac{\text{Conversion (\%)} \times \text{Selectivity to}\ \mathbf{C_8}^{=}\ (\%)}{100}$$

VITA

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