การสังเคราะห์และวิเคราะห์คุณลักษณะของตัวเร่งปฏิกิริยาอะลูมินาที่ปรับปรุงด้วยโบรอนสำหรับเอทานอลดีไฮเดรชันเป็นเอทิลีน

นางสาวนพรัตน์ บุญสินวโรทัย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2557

Synthesis and characterization of boron modified alumina catalyst for ethanol dehydration to ethylene

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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 2014

Thesis Title	Synthesis and characterization of boron modified alumina catalyst for ethanol dehydration to ethylene
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Field of Study	Chemical Engineering
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นพรัตน์ บุญสินวโรทัย : การสังเคราะห์และวิเคราะห์คุณลักษณะของตัวเร่งปฏิกิริยาอะลูมินาที่ปรับปรุงด้วยโบรอนสำหรับเอทานอลดีไฮเดรชันเป็นเอทิลีน (Synthesis and characterization of boron modified alumina catalyst for ethanol dehydration to ethylene) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.บรรเจิด จงสมจิตร, 71 หน้า.

ตัวเร่งปฏิกิริยาอะลูมินาเป็นที่น่าสนใจเนื่องจากเสถียรภาพทางความร้อนที่ดีเยี่ยม พื้นที่ผิวสูงและขนาดอนุภาคละเอียด ในงานวิจัยนี้ตัวเร่งปฏิกิริยาอะลูมินาที่มีเฟสต่าง ๆ ถูกสังเคราะห์โดยวิธีโซลโวเทอร์มอล วิธีนี้จะให้ความเป็นผลึกสูง พื้นที่ผิวสูงและรูปร่างเหมือนกัน เมื่ออะลูมินาเฟสแกมมาถูกปรับปรุงด้วยอะลูมินาเฟสไคก็จะส่งผลในการปรับปรุงความเป็นกรดเป็นตัวเร่งปฏิกิริยา ดังนั้นอะลูมินาเฟสผสมให้ร้อยละการเปลี่ยนแปลงเอทานอลสูงสุด การผลิตเอทิลีนจากปฏิกิริยาเอทานอลดีไฮเดรชันต้องใช้ตัวเร่งปฏิกิริยาของแข็งที่ประกอบด้วยกรดบรอนสเตดบนพื้นผิว ความเป็นกรดของตัวเร่งปฏิกิริยาอะลูมินามีผลต่อความสามารถในปฏิกิริยาดีไฮเดรชัน เพื่อปรับปรุงความเป็นกรดเป็นตัวเร่งปฏิกิริยา มันสามารถปรับปรุงได้โดยการใส่โบรอน ในงานวิจัยนี้ตรวจสอบผลของตัวเร่งปฏิกิริยาอะลูมินาที่มีการปรับปรุงด้วยโบรอนต่อเอทานอลดีไฮเดรชัน กลุ่มตัวอย่างทั้งหมดถูกวิเคราะห์คุณลักษณะด้วยการกระเจิงรังสีเอ็กซ์ การวิเคราะห์สารด้วยอินฟาเรด การดูดซับทางกายภาพด้วยไนโตรเจน กล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด กล้องจุลทรรศน์อิเล็กตรอนแบบส่องผ่าน และการคายแอมโมเนีย ตัวเร่งปฏิกิริยาอลูมิเนียมที่มีโบรอนร้อยละ 2 โดยน้ำหนัก ให้ตำแหน่งความเป็นกรดอ่อนมากขึ้นซึ่งเป็นสิ่งที่ดีสำหรับเอทานอลดีไฮเดรชัน เมื่อโบรอนถูกนำเข้าสู่ตัวเร่งปฏิกิริยาอะลูมินาเฟสแกมมา-ไค ที่อุณหภูมิ 400 องศาเซลเซียส ตัวเร่งปฏิกิริยาจะให้ร้อยละการเปลี่ยนแปลงที่สมบูรณ์ นอกจากนี้เสถียรภาพของตัวเร่งปฏิกิริยาถูกตรวจสอบที่ 400 องศาเซลเซียสเป็นเวลา 72 ชั่วโมง

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต ....

สาขาวิชา วิศวกรรมเคมี ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

ปีการศึกษา 2557

5670242021 : MAJOR CHEMICAL ENGINEERING

KEYWORDS: MIXED PHASE ALUMINA; ETHANOL DEHYDRATION; BORON PROMOTER; GAMMA AND CHI ALUMINA

NOPPARAT BOONSINVAROTHAI: Synthesis and characterization of boron modified alumina catalyst for ethanol dehydration to ethylene. ADVISOR: ASSOC. PROF. BUNJERD JONGSOMJIT, Ph.D., 71 pp.

Alumina catalyst is interesting due to its excellent thermal stability, high surface area and fine particle size. In this research, the alumina catalysts having different phases were synthesized by the solvothermal method. This method possesses high crystallinity, high surface area and uniform morphology. When γ-phase alumina is adjusted with χ-phase alumina, it results in the improvement of catalyst acidity. So, the mixed phase alumina gave the highest ethanol conversion. Ethylene production from ethanol dehydration reaction requires solid acid catalysts consisting of Brønsted acid site on surface. Acidity of alumina catalyst affected on dehydration activity. To improve catalyst acidity, it can be modified by boron loading. In this research, we investigated the effect of alumina catalysts with boron modification on ethanol dehydration. All samples were characterized by XRD, FTIR, N_2 physisorption, SEM, TEM and NH_3-TPD analysis. The alumina catalyst containing 2wt% boron content gave more weak acid sites, which is good for ethanol dehydration. When boron was introduced into γ-χ Al_2O_3 catalyst, at temperature 400°C, the catalyst gave a complete conversion. Besides, the stability of catalysts was investigated at 400°C for 72 hours.

Department:	Chemical Engineering	Student's Signature	....
Field of Study:	Chemical Engineering	Advisor's Signature	....
Academic Year:	2014		

ACKNOWLEDGEMENTS

I would like to impressively thank my thesis advisor, Associate Professor Bunjerd Jongsomjit, Ph.D. for his advice and guidance in order to solve the problem in this research as well as invaluable help, understanding and continued support. I realize the teachings of his. This thesis cannot be achieved without my advisor.

Furthermore, I also have to thank Associate Professor Muenduen Phisalaphong, Ph.D, as a chairman, Dr. Chutimon Satirapipathkul, D.Eng and Dr. Eakrachan Chaichana, D.Eng as the members of the thesis committee for suggestions and taking valuable time to review this thesis.

The author would like to thank the Ratchadaphiseksomphot Endowment Fund 2013 of Chulalongkorn University (CU-56-654-AM), the Thailand research fund (TRF) and the National Research Council of Thailand (NRCT) for the financial support of this project.

Finally, I most gratefully acknowledge my parents, Dr. Mingkwan Wannaborworn, co-worker and my friends in Center of Excellence on Catalysis and Catalytic Reaction Engineering laboratory for all support and carefulness.

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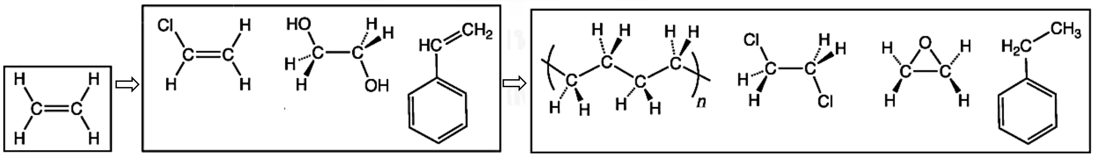
CHAPTER I

INTRODUCTION

1.1 General introduction

Ethylene is the most important primary product in petroleum industry. It can be transformed to many products such as LDPE, HDPE, PVC, ethylene glycol and acetic acid as shown in **Scheme 1.1**. Ethylene is made from ethane and hydrocarbon (propane, LPG, naphtha and gas-oil) by steam thermal cracking, which is called pyrolysis process. Ethane and hydrocarbon are obtained from oil refinery. Nowadays, the oil price increases which causes ethane and hydrocarbon’s price increasing. For steam cracking, this reaction is conducted via too many complex steps at high temperature range (600°C-1000°C). A lot of energy and money are consumed for making ethylene, therefore the other method for making ethylene must be considered.



Scheme 1.1 Products from ethylene [1].

The process for producing ethylene by ethanol is another good option because of its green alternatives to reduce greenhouse gas emissions and dependency on limited fossil fuels. According to ethanol, it can be made from bio-chemical reaction, which uses agricultural materials or biomass such as corn, sorghum, cassava, sugar cane, algae, and etc. So, this method is very popular and also easy to find the material for the process.

In the catalytic dehydration of ethanol to ethylene, this reaction is endothermic reaction and needs temperature ranging from 180°C to 500°C. The main product is ethylene, whereas diethyl ether (DEE), acetaldehyde and light olefins are byproducts. Each of products is produced at the different temperatures. For example, the high temperature (400°C-450°C) is suitable to produce ethylene, while the byproduct is gained at lower temperature (< 300°C). In chemical reactions, the catalysts are an important factor because they control and accelerate the rate of reaction. The catalysts have many types and have been used in different chemical reactions. The ethanol dehydration to ethylene requires acid catalysts because active site of this reaction has to desire acidity. Acidity of catalyst is an important in the ethanol dehydration. One of the most popular acid solid for catalyst is HZSM-5 zeolite catalyst, silicoaluminophosphates (SAPO), heteropolyacid catalysts and γ-alumina catalyst [1].

γ-Alumina has been used as a catalyst for dehydration reaction because it can be easily synthesized and it possesses excellent thermal stability, fine particle size, high surface area. However, γ-alumina requires the high reaction temperature of 450°C and the ethylene yield was relatively low of 80% [2]. To make it more economically efficient, it needs to modify the alumina catalyst to reduce the reaction temperature and enhance ethylene yield. The mixed γ- and χ- phase Al_2O_3 catalysts was interesting. Because the products obtained by solvothermal synthesis show uniform morphology, narrow size distribution and well-controlled chemical composition by varying process conditions [3-7]. Also, the chi phase may be possible to make a dispersed metal catalyst, including the acidity of mixed γ- and χ- phase Al_2O_3.

In order to improve the catalyst acidity, alumina catalyst was modified by boron. Thongpradab et al. (2014) [8] investigated effect of boron modified boehmite catalysts on ethanol dehydration. The results show that adding boron on boehmite catalyst gave a high ethanol conversion (100%) when compared with undoped boehmite catalyst (70.9%). Previous research studied an acidity of boron oxide on alumina catalyst and reported that an addition of boron oxide onto alumina possessed non-selective strongly acidic sites as a result of the bond formation between boron oxide and alumina. The boron oxide gave the medium Brønsted acid strength [9], which favors for the ethanol dehydration reaction [10]. Therefore, it is possible that the alumina catalysts which are modified with boron will increase the ethanol dehydration activity.

In this research, we investigated the effect of mixed gamma-chi phase alumina catalysts with boron modification on ethanol dehydration. The catalysts were characterized by X-ray diffraction (XRD), N_2 physisorption (BET), scanning electron microscopy (SEM), transmission electron microscopy (TEM), NH_3-tempearture programmed desorption (NH_3-TPD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA).

1.2 Research objectives

- To improve the properties of alumina catalysts for ethanol dehydration to ethylene.
- To investigate the characteristics and catalytic properties of modified alumina catalysts for ethanol dehydration to ethylene.
- To study effect of modified alumina catalysts for ethanol dehydration to ethylene.
- To investigate the stability of modified alumina catalysts for ethanol dehydration to ethylene.

1.3 Research scopes

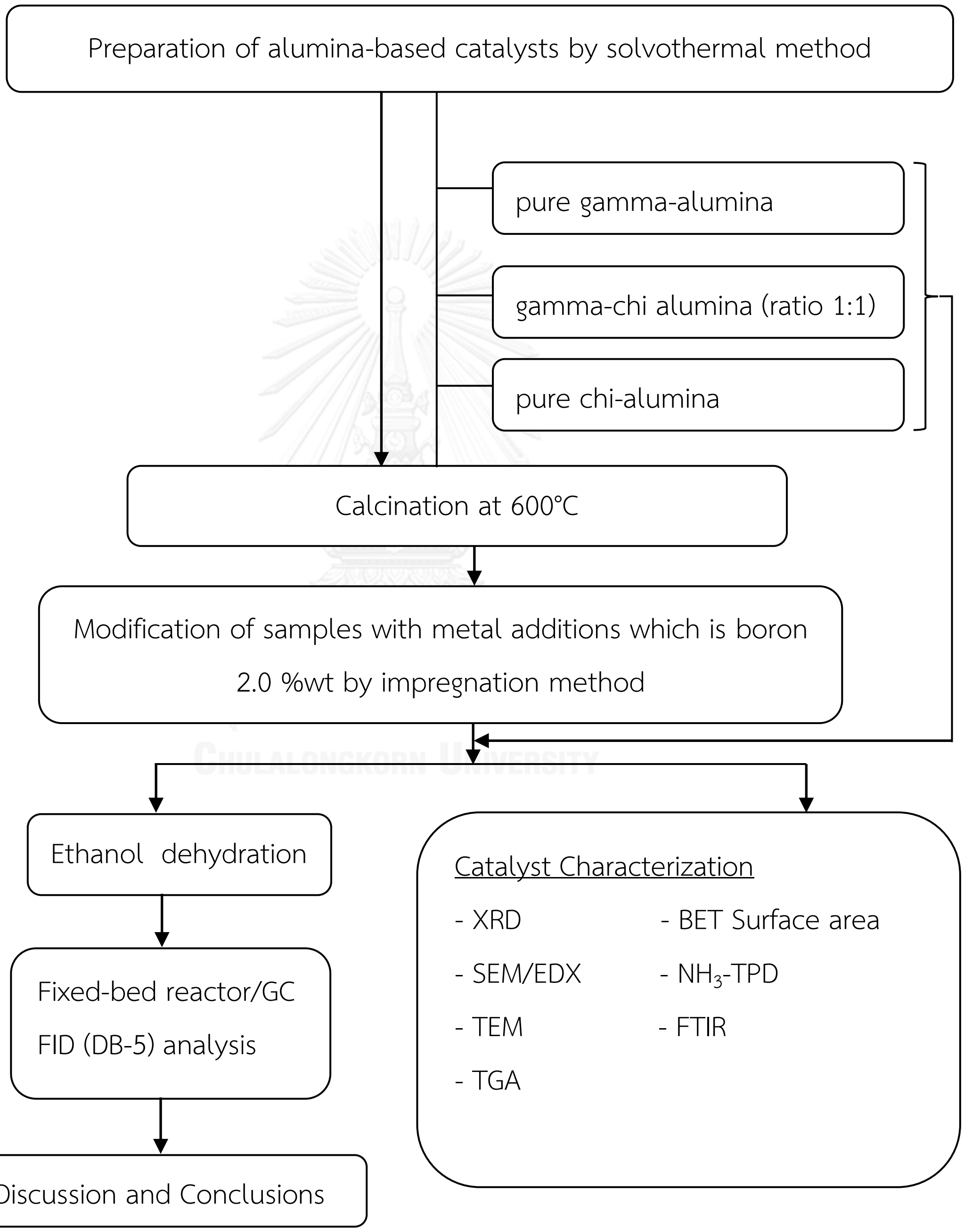
- Investigation the effect of mixed γ- and χ-crystalline phase, γ-phase and χ-phase alumina catalysts synthesized by the solvothermal method on ethanol dehydration reaction.

- Investigation the effect of boron loading over mixed γ- and χ-crystalline phase alumina catalysts by impregnation method on ethanol dehydration reaction.
- Investigation the catalytic performance of all catalysts in ethanol dehydration reaction under atmospheric pressure and temperature between 200°C to 400°C.
- Characterization of the catalysts by the following method; X-ray diffraction (XRD), N_2 physisorption (BET), scanning Electron Microscopy (SEM), transmission electron microscopy (TEM) and NH_3-temperature programmed desorption (NH_3-TPD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA).
- Investigation the stability of catalysts in ethanol dehydration reaction within TOS around 72 hrs.

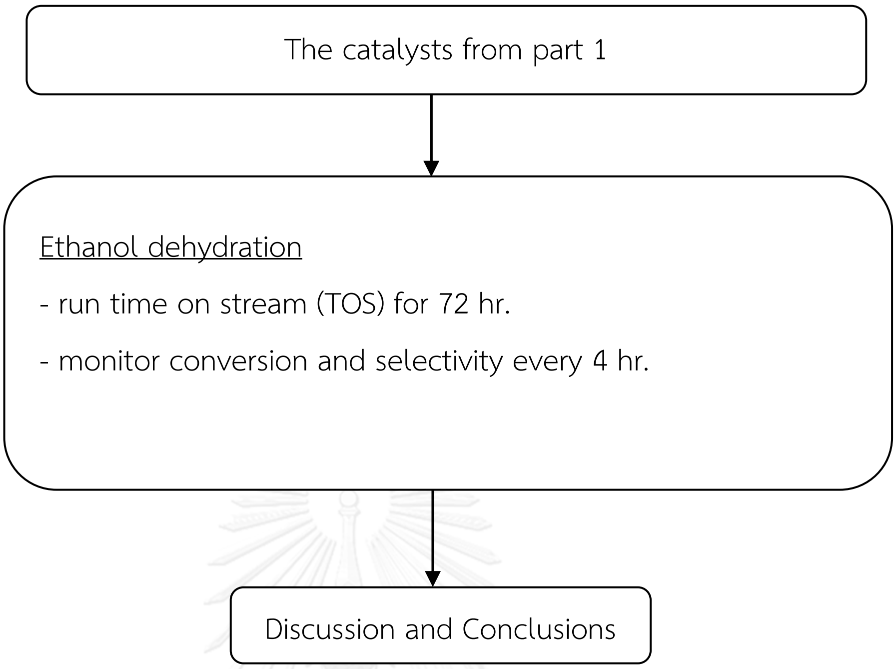
1.4 Research methodology

Research methodology is as shown as follows;

Part 1 The catalytic performance of all catalysts in ethanol dehydration



<u>Part 2</u> The stability of catalysts in ethanol dehydration reaction



1.5 Benefits of this research

- This research is an alternative for catalysts in ethanol dehydration reaction.
- It obtains various new catalysts for ethanol dehydration.
- It can be applied in real industry.
- It can realize the different properties of the catalysts.

CHAPTER II

THEORY AND LITERATURE REVIEWS

This chapter shows the basic knowledge of ethanol dehydration reaction and the solid catalysts used.

2.1 Ethanol dehydration process

The process of ethanol dehydration to ethylene regularly consists of two parts: the ethanol dehydration reaction and the purification of ethylene. The feedstock which is evaporated for ethanol dehydration flows into the reactor to generate the crude ethylene, and then into a water washing tower, alkaline washing tower, dryer, light-ends tower, and heavy-ends tower to remove light byproducts and heavy byproducts, etc. At last, the ethylene is obtained from the upper part of the heavy-ends tower. The process diagram is shown in **Figure 2.1.**

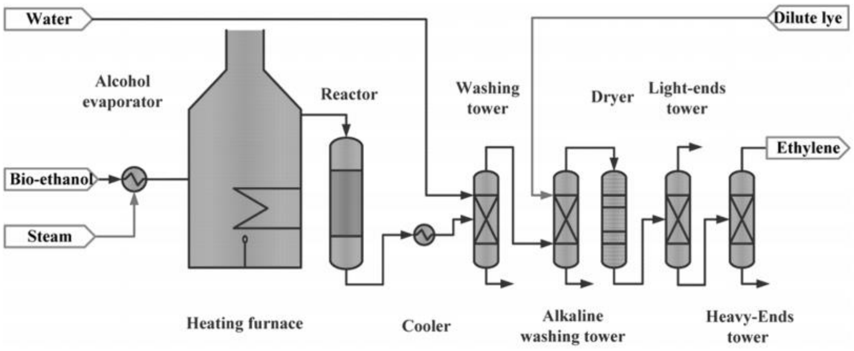


Figure 2.1 A process diagram of ethylene plant [1].

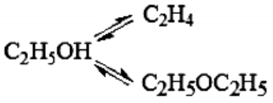
In the catalytic dehydration of ethanol to ethylene, the hydroxyl group in ethanol molecule can be dehydrated by using acid catalysts. The hydroxyl group is converted into water molecule. The water molecule is emitted from ethanol molecule, and the hydrocarbon rearranges into ethylene or diethylether [11]. The temperature of reaction is between 180 to 500°C in gas phase and liquid phase [10]. Two chemical competitive ways for ethanol dehydration reaction is represented by :

$$C_2H_5OH \longrightarrow C_2H_4 + H_2O \qquad \Delta H^{298} = +44.9 \text{ kJ/mole} \quad (1)$$

$$2C_2H_5OH \longrightarrow C_2H_5OC_2H_5 + H_2O \qquad \Delta H^{298} = -25.1 \text{ kJ/mole} \quad (2)$$

The first reaction is reaction for dehydration of ethanol to produce main product (ethylene) that is endothermic reaction and it requires relatively more heat, with higher reaction temperature. While the second reaction is side reaction which produce diethylether that is exothermic reaction and occurred at the low temperature. In addition to the main product of ethylene and the main byproduct of diethylether, the ethanol dehydration also generate a small amount of byproducts, such as acetaldehyde, hydrocarbons (methane, ethane, propylene, butylene) and light base-groups (CO_2, CO, H_2, etc.) and so on. But the amount of other byproducts is small, the most of the mechanism research of ethanol dehydration reaction considers mainly the generation of ethylene and diethylether, which can be devided into three kinds of routes: (1) parallel reactions, (2) a series of reactions, and (3) a parallel series reaction, is shown in the following three formulas [12] as follows;

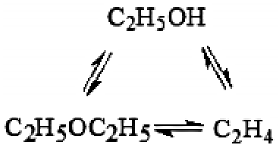
(1) parallel reactions



(2) a series of reactions

$$C_2H_5OH \rightleftharpoons C_2H_5OC_2H_5 \rightleftharpoons C_2H_4$$

(3) a parallel series reaction



The ethanol dehydration reaction required strong acid site or Brønsted acid site on surface of catalyst combining with hydroxyl groups [13]. It generates a water molecule, which is emitted. The mechanism in **Figure 2.2** shows that ethanol dehydration to ethylene is E1 elimination reaction [1]. It can be described into 3 steps: First, the hydroxyl group in ethanol molecule is removed, when protonation of acid catalyst adds into alcoholic oxygen. This step is very fast reversible reaction. Second step, the C-O bond is broken, that is endothermic reaction. It causes the loss of a water molecule resulting in a carbocation intermediate. This step is the rate determining reaction because it is slowly step. Final, The water molecule deprotonates in methyl group leads to rearrange the alkene group (C=C bond).

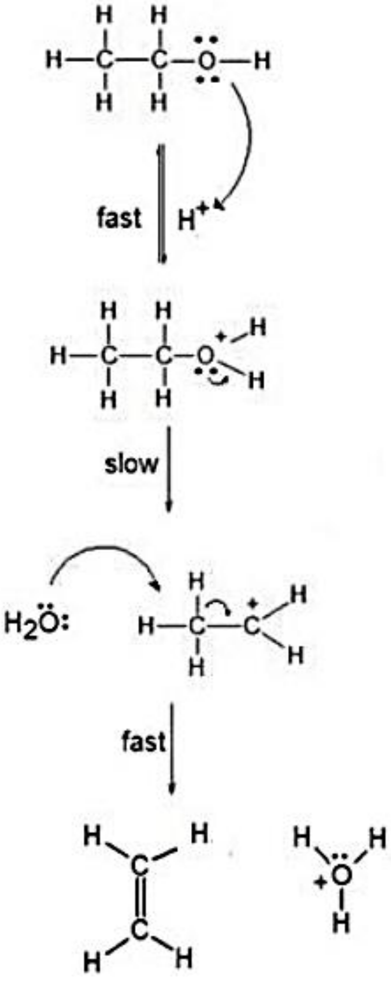


Figure 2.2 The mechanism of ethanol dehydration reaction to ethylene [11].

Ethanol dehydration is not only produce ethylene. It also produces diethylether. Ethanol molecules convert to diethylether through the dehydration of ethanol. This reaction is exothermic, which requires weak acid site and low operating temperature (below 240°C) [10]. During ethanol convert to diethylether, on the surface of the catalyst is found alkoxide. Alkoxide intermediate product is the hydroxyl hydrogen of the ethanol molecule is substituted by the metal compounds. Alkoxide is an important intermediate of the ethanol dehydration to ether. The mechanism of ethanol dehydration to be diethylether is a substitution reaction. The formation of diethylether essentially follows the reaction mechanism of SN_1 (single-molecule nucleophilic substitution reaction) or SN_2 (bimolecular nucleophilic substitution reaction) [14].

The SN_1 reaction is divided into two steps [12]. In the first step, the precursor dissociates to a carbocation and anionic leaving group. This step is a rate determining step. The second step is the carbocations associated with nucleophiles, which is an extremely fast rate. The reaction is a first-order reaction. The SN_1 is shown in **Figure 2.3.** The SN_2 reaction, lone pair electrons of the nucleophile attacks the electrophilic electron at central atom to form the intermediate, and remove the leaving base-group at the same time. Carbocations are not generated in the reaction. Both steps are the rate determining step. This reaction is a second-order reaction. The SN2 mechanisms are shown in **Figure 2.4**.

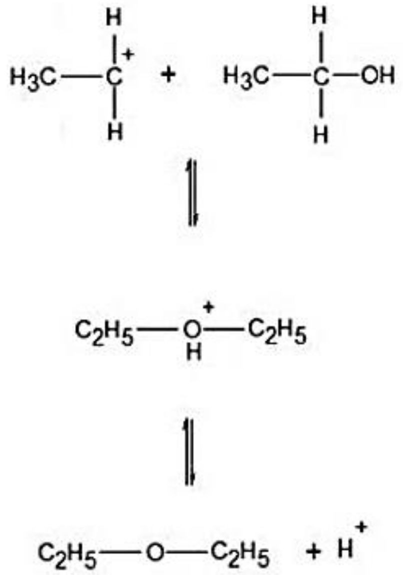


Figure 2.3 The SN_1 reaction of ethanol dehydration to DEE.

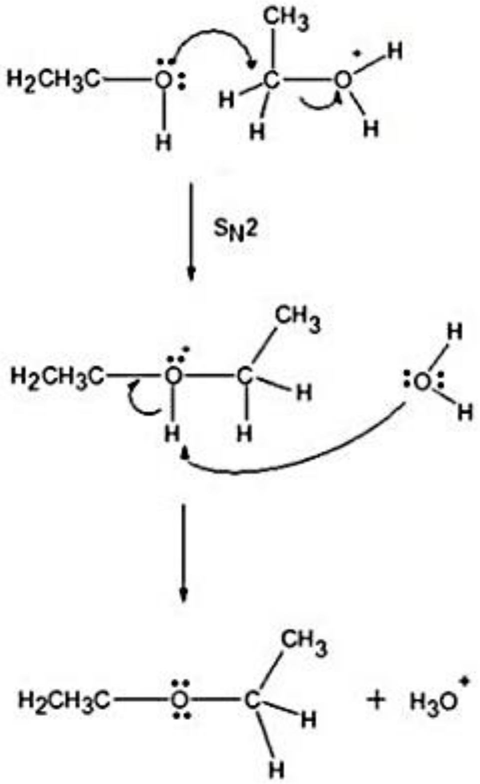


Figure 2.4 The SN_2 reaction of ethanol dehydration to DEE [14].

To make ethanol dehydration more friendly industry, researchers have investigated catalysts to increase ethylene selectivity and ethanol conversion at lower reaction temperature. Many catalysts are researched such as alumina and transition metal oxides, silicoaluminophosphates (SAPO), HZSM-5 zeolite catalyst, and heteropolyacid catalysts.

2.2 Aluminum oxide (Al_2O_3)

2.2.1 Properties of aluminum oxide

The Al atom has 3 valence electrons. Aluminium is a transition element that produces salts with both acids and bases. It is a reducing agent, reacting very strongly with oxygen to form alumina, for which the enthalpy of formation is very high. Alumina catalysts are used in the most of the current industrial reactors of ethylene production with many applications due to its high thermal stability, various physical and chemical properties. It has the amorphous structure and the crystal structure. A general formula is "Al_2O_3", the surface area is 0.5 to 600 m^2/g. These properties and the acidity of alumina depend on the method of synthesis, purity, water desorption and heat treatment.

Alumina can be industrially synthesized; gibbsite, boehmite and bayerite. There are eight transition of alumina such as beta phase (β-Al_2O_3), gamma phase (γ-Al_2O_3), chi phase (χ-Al_2O_3), eta phase (η-Al_2O_3), delta phase (δ-Al_2O_3), kappa phase (κ-Al_2O_3), theta phase (θ-Al_2O_3) and alpha phase (α-Al_2O_3). Each phase has unique crystal structure and properties. For example, gamma alumina has high porosity and surface area. The most stable phase at all temperatures is alpha alumina, which is not porous as shown in **Figure 2.5-2.6**. Octehedral Al ions are black, tetrahedral are grey. **Figure 2.7-2.8** displayed the crystal structure of gamma and kappa alumina, respectively.

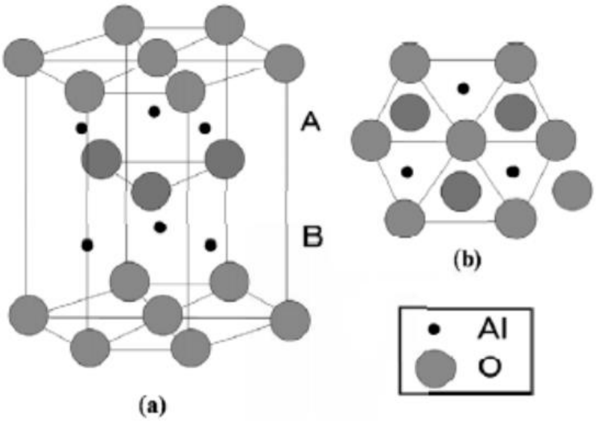


Figure 2.5 (a) Alpha phase and (b) top view of alpha-alumina structure [15].

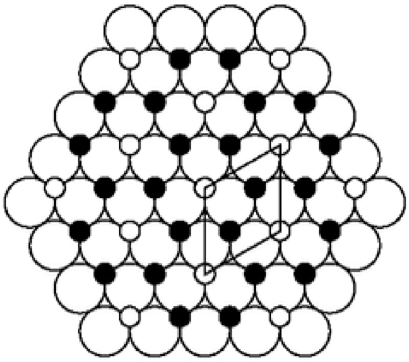


Figure 2.6 The first layer in the alpha alumina structure.

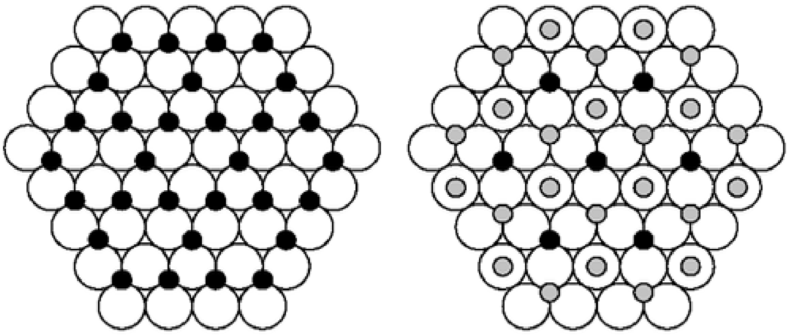


Figure 2.7 The first two layers in the gamma alumina structure.

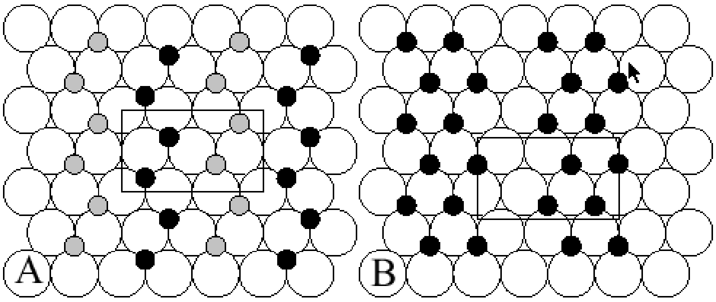


Figure 2.8 The first two layers in the kappa alumina structure.

The formula reactants of aluminum oxide (hydroxides) are shown as below.

- Gibbsite or Hydrargillite : gamma- Al$(OH)_3$
- Bayerite : alpha- Al$(OH)_3$
- Nordstrandite : beta- Al$(OH)_3$
- Boehmite : gamma- Al(OOH)
- Diaspore : alpha- Al(OOH)
- Corundum (alpha-Al_2O_3)

The transition of aluminas is obtained by the thermal decomposition of aluminium hydroxides or oxyhydroxides except alpha alumina. Each initial structure leads to phase formation with a different temperature. The phase of alumina depends on calcined temperatures of reactant (gibbsite, boehmite, and etc.) [16]. For example, gibbsite is calcined at 280°C to 650°C to obtain chi phase, while calcination at 750°C to 1150°C to obtain the kappa phase. Boehmite is obtained by calcination at 480°C to 780°C to obtain the gamma phase, while the calcination at 780°C to 920°C obtain the delta phase. Hydroxide structure goes through at least two transition structures when the temperature rises before reaching the alpha alumina structure. Typically, a very disorganized structure occurs at low temperature through water loss but structure at least one high temperature is better organized. The main properties of transition aluminas are their very particular texture, surface area, activity and thermal stability. Phase transformation of alumina is shown in **Figure 2.9**. The physical characteristics of alumina transition are summarized in the **Table 2.1**.

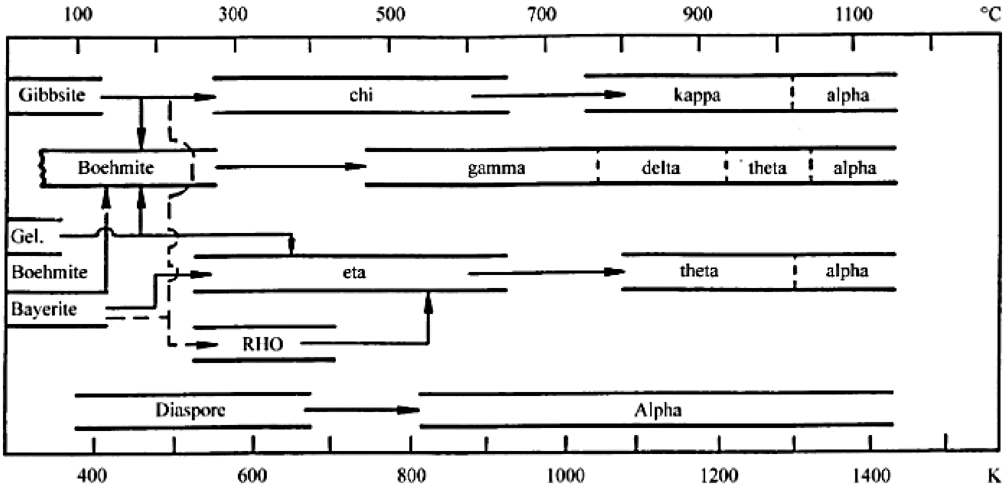
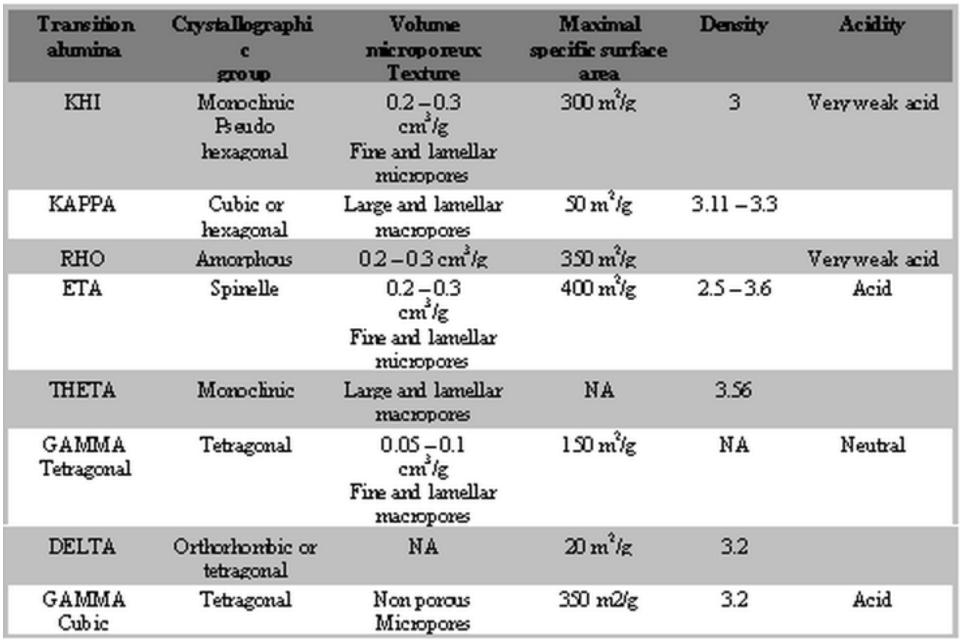


Figure 2.9 The phase transformation of aluminum hydroxide with various temperature [17].

Table 2.1 The physical characteristics of alumina transition.



Transition alumina	Crystallographic group	Volume microporeux Texture	Maximal specific surface area	Density	Acidity
KHI	Monoclinic Pseudo hexagonal	0.2 – 0.3 cm^3/g Fine and lamellar micropores	300 m^2/g	3	Very weak acid
KAPPA	Cubic or hexagonal	Large and lamellar macropores	50 m^2/g	3.11 – 3.3	
RHO	Amorphous	0.2 – 0.3 cm^3/g	350 m^2/g		Very weak acid
ETA	Spinelle	0.2 – 0.3 cm^3/g Fine and lamellar micropores	400 m^2/g	2.5 – 3.6	Acid
THETA	Monoclinic	Large and lamellar macropores	NA	3.56	
GAMMA Tetragonal	Tetragonal	0.05 – 0.1 cm^3/g Fine and lamellar macropores	150 m^2/g	NA	Neutral
DELTA	Orthorhombic or tetragonal	NA	20 m^2/g	3.2	
GAMMA Cubic	Tetragonal	Non porous Micropores	350 m2/g	3.2	Acid

On the surface of a transition alumina, There are both the Al and O atoms. These are respectively acid and basic Lewis centres. The hydroxides will have an acidic or basic Brønsted behavior depending on how they are linked in the network and in the ambient media. When water molecules in aluminum oxide are eliminated by calcination, it forms Lewis acid site and basic site as shown in **Figure 2.10** [18]. On the other hand, water molecules are added as pretreated catalyst, it transforms from Lewis acid site to weak Brønsted acid sites as shown in **Figure 2.11** [18].

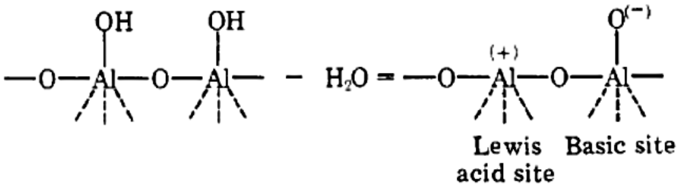


Figure 2.10 Lewis acid site and basic site formed on alumina

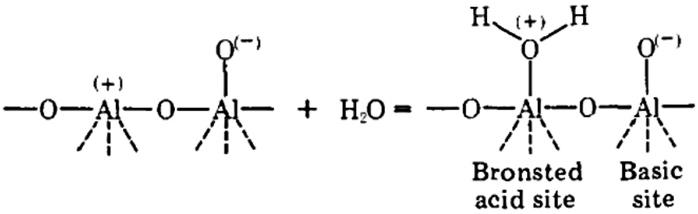


Figure 2.11 Brønsted acid sites formed on alumina

2.2.2 Synthesis of aluminum oxide: the solvothermal method

The synthesis of aluminum oxide has many techniques such as calcination, precipitation, sol-gel, hydrothermal and solvothermal method [19-21], which each technique use different solvent. Usually, the calcination method is used to synthesize alumina with suitable reactants but this method have to proceed at high temperature affecting to loss in the surface area and changes in surface properties [22]. So it is difficult to control particle size. The precipitation method is simple for synthesis of alumina but the particle will not aggregate homogenous that leads to low active dispersion [23, 24]. In addition, the sol-gel method used metal alkoxide as precursors for produce aluminum oxide [25, 26]. Unfortunately, this method is long gelation periods and alkoxide have high cost.

Solvothermal synthesis is a method of producing chemical compounds. It is very similar to the hydrothermal method. Both synthesis are conducted in a closed system using autoclaves. The reactions temperature is higher than the boiling point of the intermediary in liquid or supercritical media as shown in **Figure 2.12.** The only difference being that the precursor solution is usually not aqueous ("hydro-" means water as solvent but "solvo-" means any kind of solvent such as alcohols, glycols, organic compound and so on). The solvothermal method is a synthesis of inorganic compounds from organic compounds at temperatures range between 200 to 300°C under autogenous pressure of the organics. Using the solvothermal method gains the benefits of both the sol-gel [27] and hydrothermal routes [28]. It can precisely control particle size, shape distribution, and crystallinity of metal oxide nanoparticles or nanostructures. Therefore, the product synthesized via solvothermal method can be considered to prepare highly dispersed catalysts. These characteristics can be changed by experimental parameters, reaction temperature, reaction time, solvent type, surfactant type, and precursor type.

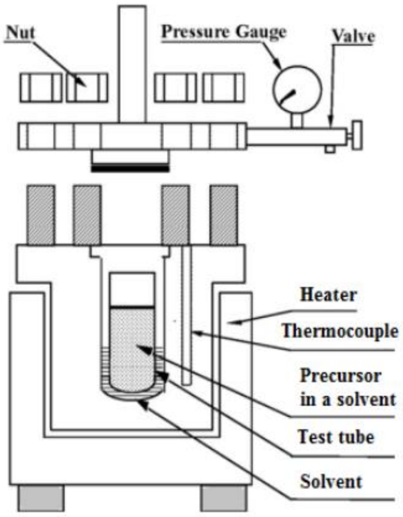


Figure 2.12 Autoclave reactor for solvothermal method [29].

2.3 Boron and Boron Oxide

Boron is a chemical element. The symbol is “B”. It has atomic number 5. The structure of boron several exist. For instant, amorphous boron is a brown powder, and crystalline boron is black. It is extremely hard about 9.5 on the Mohs scale and a poor conductor at room temperature. Boron is used in fiber, polymers and ceramics industry, dopant for semiconductors, and boron-containing reagents are used as intermediates in the synthesis of organic fine chemicals. Boron is similar to carbon in its capability to form stable covalently bonded molecular networks. The oxidation rate of boron depends upon the crystallinity, particle size, purity and temperature. Boron does not react with air at room temperature, but at higher temperatures it is burnt to form boron trioxide :

$$4B + 3O_2 \longrightarrow 2B_2O_3$$

Boron trioxide is one of the oxides of boron. It is white, glassy solid. The formula form is B_2O_3. It is always found as the amorphous form. However, it can be crystallized after extensive annealing. It is known as one of the most difficult compounds to crystallize. The crystalline form shown in **Figure 2.13**. Boron trioxide is produced by heating boric acid above ~300°C. Boric acid will initially decompose into water steam and metaboric acid (HBO_2) at around 170°C, and heating above 300°C will produce more steam and boron trioxide. The reactions are :

$$H_3BO_3 \longrightarrow HBO_2 + H_2O$$

$$2HBO_2 \longrightarrow B_2O_3 + H_2O$$

The applications of boron oxide is (1) fluxing agent for glass and enamels (2) starting material for synthesizing other boron compounds such as boron carbide (3) an additive used in glass fibres (optical fibres) (4) using in the production of borosilicate glass (5) The inert capping layer in the LEC process for the production of gallium arsenide single crystal (6) an acid catalyst in organic synthesis.

In an acid catalyst in organic synthesis, T.Curtin et al. (1991) [9] study an acidity of boria on alumina. The catalysts are prepared with a uniform distribution of boria. They found that addition of boria into alumina possess non-selective strongly acid sites as a result of the formation bond between boria and alumina. The boria give intermediate Bronsted acid strength.

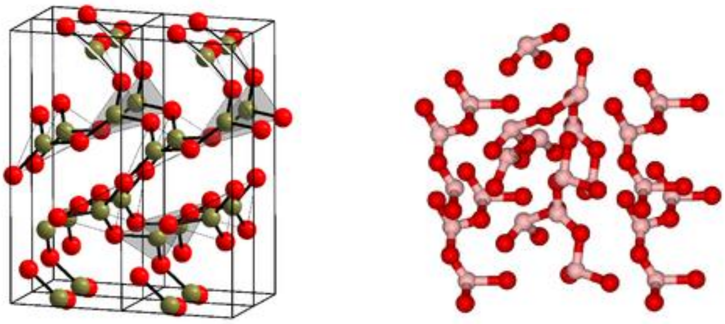


Figure 2.13 The crystalline structure of boron trioxide

2.4 Deactivation of catalyst

Catalysts are used a range of applications for long time. By definition, a catalyst is not consumed in the reaction. The active site of catalyst can continuously react when it desorb substances and products from the surface. However, the performance or the activity of the catalyst was reduced by the period, the catalyst has deactivated cause decrease in the yield of product. There are many processes that catalysts deactivate; coke formation, poisoning, sintering and etc. But alumina catalyst does not occur poisoning and sintering deactivation. Coke formation is deactivation in alumina catalyst which the surface is covered with deposited carbon. The active sites of the catalyst will be cover by carbonaceous residues which it will block the reactants to attach with the catalyst. Coke formation can be illustrated in **Figure 2.14**.

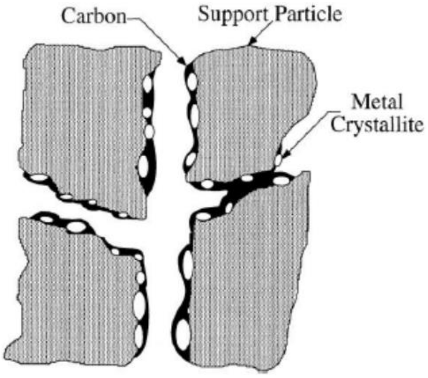


Figure 2.14 Coke formation on surface catalyst [30].

For catalytic bioethanol dehydration to form ethylene, the main cause of coke formation is due to the decomposition of ethylene to form carbon compound as shown in Equations 3 and 4.

$$C_2H_4 \leftrightarrow 2C + 2H_2 \qquad (3)$$

$$C_2H_4 \leftrightarrow C + CH_4 \qquad (4)$$

There are the two type of reaction that possibly occur coke on catalyst in bioethanol dehydration reaction. The behavior of coke deposition is important to the kinetic study and reactor design.

2.5 Literature reviews

2.5.1 Catalysts in ethanol dehydration reaction

The CO_2 emission is a crucial problem in the chemical industry. Therefore, using ethanol instead of petroleum to produce ethylene is the reduction of CO_2 emission. Ethanol utilize from biomass fermentation. It is well known that the catalyst in the ethanol dehydration is solid acid catalysts such as phosphoric acid, metal oxide, heteropolyacid and zeolites. In 1930, the dehydration of ethanol is used phosphoric acid. Later, Pan (1986) [31] studied clay and coke supports loaded phosphate. Pearson et al. (1981) [32] studied parameters for reaction such as reaction temperature, ethanol concentration, space velocity, and life span of catalyst. The phosphoric acid catalyst give high ethylene yield but the catalysts were rapid deactivated by coke formation on surface of catalyst.

Takahara et al. (2005) [10] studied effect of H-mordenites, silica–alumina and zeolites catalysts on ethanol dehydration. H-mordenites were the most active for the dehydration. The catalysts have both the Brønsted and Lewis acid sites. They found that the Brønsted acid sites are active sites for the dehydration of ethanol into ethylene. So the catalysts which have more Brønsted acid sites obtianed better activity during the dehydration process.

Varisli et al. (2006) [33] investigated different heteropolyacid catalysts for dehydration reaction in a temperature range of 140–250°C, which is tungstophosphoricacid (TPA), silicotungsticacid (STA) and molybdophosphoricacid (MPA). It found that heteropolyacid catalyst TPA obtained highly ethylene yields over 0.75 at 250 °C while at lower temperatures the main product is DEE. This is considered higher activity than the conventional solid acid at lower temperatures. However, STA obtained the highest activity in ethanol dehydration explained by the higher number of Keggin protons. It is higher stability than TPA at over temperature 200°C. Besides, reporting of the $Ag_3PW_{12}O_{40}$ heteropolyacid catalysts by Mactachowski et al. (2012) [34]. It found that the humidity had effect on the catalytic activity. The selectivity of ethylene decreased with increasing the humidity, while Ethanol conversion increased completely.

Zhang et al. (2008) [35] reported the activity and stability of γ-Al_2O_3, HZSM-5 (Si/Al = 25), silicoaluminophosphate (SAPO-34) and Ni-substituted SAPO-34 (NiAPSO-34) catalysts. Conversion of ethanol and selectivity to ethylene decreased in the order HZSM-5 > NiAPSO-34 > SAPO-34 > γ-Al_2O_3. For the stability of catalyst, NiAPSO-34 and SAPO-34 were better than other catalysts. NiAPSO-34 sample obtained higher both weak and strong acid sites and possessed more weak acid sites. NiAPSO-34 was the suitable catalyst in the dehydration of ethanol, comprehensively.

2.5.2 Modify gamma-Al_2O_3

In the ethanol dehydration to ethylene, has been used as a catalyst. It required the high reaction temperature of 450 °C to produce ethylene by giving the relatively low ethylene yield of 80%. Thus, γ-alumina catalysts are modified to reduce the reaction temperature and increase ethylene yield to make it more economically efficient. Zhang et al. (2008) [35] studied gamma alumina catalysts in ethanol dehydration. It found that it obtained the maximum ethylene selectivity to 90.1% at 475°C. Chen et al. (2007) [36] found that when γ-alumina catalysts are promoted by titanium oxide, the TiO_2/γ-Al_2O_3 catalyst can increase ethylene selectivity up to 99.4% at 500°C. It can convert ethanol to ethylene nearly 100% at 460°C.

Khom-in et al. (2008) [19] investigated dehydration of methanol to dimethyl ether (DME) by using nanocrystalline Al_2O_3 catalysts with mixed γ- and χ-crystalline phases. The γ-Al_2O_3 catalyst containing 20 wt% of χ-phase shown the highest yield (86%) with good stability for DME synthesis. The NH3-TPD and ion-exchange titration comfirm that the existence of 20 wt% χ-phase in γ-Al_2O_3 increased significantly both the density and the strength of surface acidity of alumina.

El-Hakam et al. (2008) [37] investigated properties of aluminium borates-alumina (ABA). It is prepared by co-precipitation in the range temperature 840-900°C, then calcined at high temperature 600, 800, 1100°C. the catalysts are used in the cracking of ethylbenzene and isopropanol dehydration reactions. They found that the acidity on catalyst suface increased with boron content increased, leading to better activity of reaction.

Saih et al. (2009) [38] reported catalytic activity of CoMo catalysts supported on boron-modified alumina for the hydrodesulphurization. A characterization of B_2O_3–Al_2O_3 support showed that boric acid reacts with surface Al–OH groups to form a boria over-layer, probably via Al–O–B bridges. Leading to the formation of B–OH groups on surface. These Al–O–B bridges have the stabilization of an over-layer of boron species on the surface of alumina. They found that boron contents below 5wt% correspond to a monolayer dispersion of boria on alumina. In monolayer dispersion range, HDS activity significant increase with increasing the boron content due to boria will make the distribution of Co and Mo better.

Xiu et al. (2011) [39] studied mesoporous boria–alumina composite with high specific surface area and pore volume. The composite has been prepared through an evaporation-induced self-assembly (EISA) process. NH_3-TPD detected both strong Lewis and Brønsted acid sites. NMR and FT-IR show the B–O–Al bonds in the composite. In the reaction of methanol dehydration to dimethyl ether (DME), it demonstrated high conversion of methanol (85%) and good selectivity (100%) of DME.

Erkfeldt et al. (2012) [40] studied In_2O_3, Ga_2O_3, and B_2O_3 supported on γ-alumina by impregnation for lean NO_x reduction with DME as reducing agent. At low temperatures The In_2O_3/Al_2O_3 catalysts gave the highest NO_x conversion. In the other hand, The Ga_2O_3/Al_2O_3 and B_2O_3/Al_2O_3 catalysts gave the highest NO_x conversion at higher temperatures. The acid-base properties of γ-Al_2O_3 are investigated by Petre et al. (2002) [41]. The addition of B_2O_3 on alumina leads to increase of the number of acid sites, while Ga_2O_3 and In_2O_3 additives decrease the acidity of alumina. The basicity can be verify by using SO_2 as a probe molecule. It found that the number of surface basic sites on alumina strongly decreased by the addition of boron oxide, while it was slightly affected by the addition of gallium oxide and decreased by the addition of indium oxide.

CHAPTER III

EXPERIMENTAL

This chapter explains the procedures, including the catalyst preparation, the experimental for ethanol dehydration reaction and the characterization of catalyst.

3.1 Catalyst preparation

The alumina catalyst was prepared by the solvolthermal method and it was modified with boron by impregnation method.

3.1.1 The chemicals in the catalysts preparation

- Aluminum isopropoxide : AIP (98%) $[(CH_3)_2CHO]_3Al$ (Aldrich)
- Toluene (99%) $C_6H_5CH_3$ (Merck)
- 1-Butanol (99%) $C_4H_{10}O$ (Merck)
- Methanol CH_3OH (Merck)
- Ultra high purity nitrogen gas (99.99%) (TIG)
- Boric acid H_3BO_3 (99.5%)

3.1.2 Synthesis of mixed phase alumina catalysts

Al_2O_3 catalysts with various gamma/chi phase compositions were prepared by solvothermal method. Approximately aluminum isopropoxide (AIP) 25 g was suspended in a mixed solution of toluene (50 ml) and 1-butanol (50 ml) for mixed γ- and χ-crystalline phase. The γ-crystalline phase use toluene solvent. The χ-crystalline phase use 1-butanol solvent. The autoclave was purged completely by nitrogen then heating up to $300^{\circ}C$ at a rate $2.5^{\circ}C/min$ and holding for 2 h. After the system was cooled down, the resulting powders were washed with methanol several times using centrifugation then dried in air. The powders were calcined at 600°C by air flow 95 cm^3/min with a heating rate of 10°C/min and holding at that temperature for 6 h.

3.1.3 Preparation of boron modified mixed phase alumina catalysts

The B/Al_2O_3 catalyst was prepared by incipient wetness impregnation technique with boric acid (H_3BO_3). The boron loading was fixed at 2 wt% on dry basis. First, boric acid was dissolved in deionized water. Then, the solution was added dropwise into Al_2O_3 support. The obtained catalyst was dried in oven at 110°C overnight and calcined in air at 500°C for 4h, respectively.

The mixed phase alumina is denoted as M-Al, whereas gamma alumina and chi alumina are denoted as G-Al and C-Al, respectively. The boron modified alumina catalysts were identified by B-M-Al, B-G-Al and B-C-Al.

3.2 Catalyst characterization

3.2.1 X-ray diffraction (XRD)

X-ray diffraction (XRD) patterns were determined by the SIEMENS D5000 X-ray diffractometer and Cu Kα radiation with a Ni filter in the 2θ range of 20° to 80° with a resolution of 0.02°. The crystallite size was calculated from Scherrer equation by using γ-alumina as external standard.

3.2.2 Nitrogen physisorption (BET)

The BET surface area, pore volume and pore diameter of catalysts were determined by Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. The sample was thermally treated at 150°C for 1h before characterization.

3.2.3 Temperature programmed desorption (NH_3-TPD)

The acidity of catalysts was investigated by temperature programmed desorption of ammonia (NH_3-TPD) by using Micromeritics chemisorp 2750 Pulse

Chemisorption System. The sample was pretreated at 500°C under helium flow before saturating with 15%NH_3/He. Then, the sample was desorbed under helium gas flow about 30 min and heated from 40°C to 800°C at heating rate 10°C/min. The amount of ammonia was measured via TCD signal, which is a function of temperature.

3.2.4 Scanning electron microscopy (SEM/EDX)

Morphologies of the catalysts were observed on JEOL JSM-35 CF model scanning electron microscope. An energy dispersive X-ray analyser (EDX) is also used to provide elemental identification and quantitative compositional information.

3.2.5 Transmission electron microscopy (TEM)

The morphology and crystallite size of all catalysts were observed by using JEOL-JEM 20°CX transmission electron microscope operated at 100 kV. The average crystallite size was measured by SemAfore program version 5.00.

3.2.6 Fourier transform infrared spectroscopy (FTIR)

FTIR spectrometer was used for characterization of the functional groups of B/Al_2O_3 catalyst. So, the structures of B/Al_2O_3 catalyst were confirmed by FTIR. Infrared spectra were recorded with Nicolet 6700 FTIR spectrometer and range of scanning from 400 to 4,000 cm^{-1} with scanning times of 64.

3.2.7 Thermogravimetric analysis (TGA)

Thermal stability or thermal decomposition of the catalyst was determined by TGA. A Diamond TG/DTA thermogravimetric/differential thermal analyzer was used in this research with 2-5 mg of catalyst sample. The catalysts are analyzed in temperature range of 50-800°C with a heating rate of 10°C/min and 400 ml/min of nitrogen purge. The weight changing of sample can be observed.

3.2.8 X-ray photoelectron spectroscopy (XPS)

Surface analysis of samples was determined by XPS. It showed the presence of boron. An AMICUS spectrometer was used with Mg K_α X-ray radiation. For a typical analysis, the source was operated at voltage of 15 kV and current of 12 mA. The pressure in the analysis chamber was less than 10^{-5} Pa.

3.3 Reaction study in dehydration of ethanol

In this research, the ethanol dehydration reaction was studied in gas phase at atmospheric pressure. All catalysts is investigated by using the reaction apparatus as shown in **Figure 3.1**.

3.3.1 Chemicals and reagents

- High purity grade hydrogen (99.99%) (TIG)
- Ultra high purity nitrogen gas (99.99%) (TIG)
- Ultra high purity argon gas (99.99%) (TIG)
- Absolute ethanol (Merck)

3.3.2 Instruments and apparatus

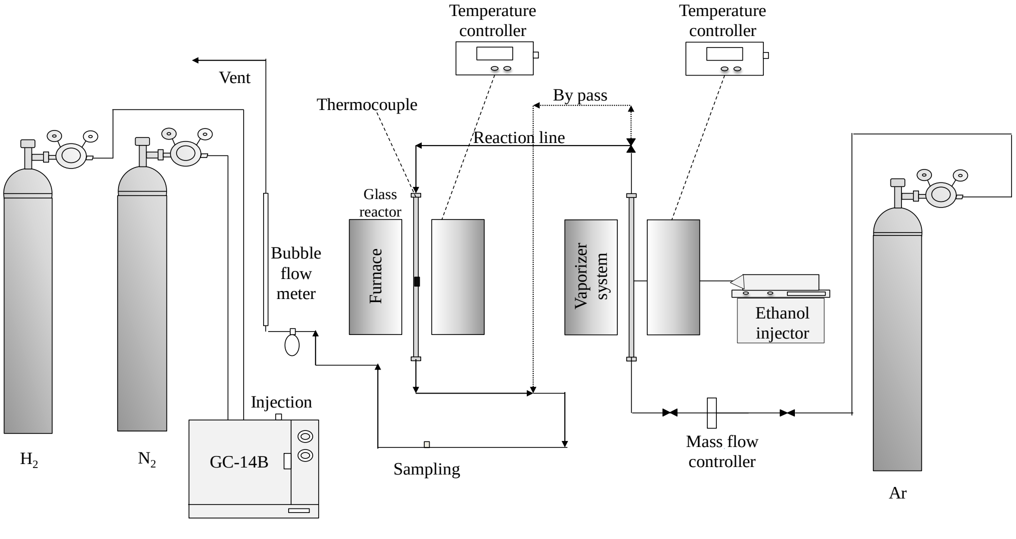


Figure 3.1 Ethanol dehydration system.

From **Figure 3.1**, the ethanol dehydration system for catalytic tests consists of:

(a) Reactor : The reactor tube is made from glass tube which is borosilicate type with an inside diameter of 0.7 mm.

(b) Syringe pump : The syringe pump is used for injection ethanol into vaporizer to generate vapor.

(c) Vaporizer : The vaporizer is equipment to vaporize ethanol from liquid phase to vapor phase. It is operated at temperature of 120°C at atmospheric pressure. This temperature is higher than the boiling point of ethanol, thus ethanol can be vaporized.

(d) Furnace and heating tape : The furnace is heated to the catalyst packed reactor tube. The temperature of the furnace is controlled by temperature controller. For heating tape, it wrap on the line at outlet of reactor. The heating tape is used to prevent the condensation of water.

(e) Temperature controller :

- At furnace, the temperature of furnace is set at any temperatures in range between 200°C to 400°C.
- At vaporizer, the temperature is set at 120°C.

(f) Gas controlling system : Argon is a carrier gas, which is used to carry ethanol vapor into the furnace and reactor. The flow rate of carrier gas is adjusted by mass flow controller.

(g) Sampling : The sample is collected at sampling to analyze by GC.

(h) Gas chromatography (GC) : A Gas chromatography is used for investigating ethanol conversion and product selectivity. It equipped (Shimadzu GC-14B) with flame ionization detector (FID) with DB-5 capillary column. The operating condition for gas chromatography is reported;

- Detector: FID
- Capillary column: DB-5
- Carrier gas: Nitrogen (99.99vol.%) and Hydrogen (99.99vol.%)
- Column temperature
    - Initial: 40°C
    - Final: 40°C
- Injector temperature: 150°C
- Detector temperature: 150°C
- Time analysis: 7 min
- Analyzed gas: ethanol, ethylene, diethyl ether, acetaldehyde

From above system, the absolute ethanol was fed into the reactor by using a syringe pump. Ethanol liquid was vaporized into ethanol gas by vaporizer and passed through the reaction line to reactor. When ethanol gas feed contact with active sites of alumina catalysts, the product of ethanol dehydration reaction are produced. All feed and reaction products were collected at sampling, and then they were injected to analyze by gas chromatography.

3.3.3 Ethanol dehydration reaction procedure

The dehydration of ethanol was performed in a fixed-bed continuous flow reactor with 0.7 mm inside diameter. In the experiment, 0.01 g of a packed quartz wool and 0.05 g of catalyst were loaded into the reactor. The catalyst was pretreated with argon (50 ml/min) at 200°C for 1 hour under atmospheric pressure. This reaction was kept under gas flow. The reaction temperature was controlled and measured by thermocouple which located in the catalyst bed. The reaction was carried out in the temperature range from 200°C to 400°C. The products were analyzed by a Shimadzu GC14B gas chromatograph with FID using capillary column (DB-5).

CHAPTER IV

RESULTS AND DISCUSSION

This chapter describes the characteristic and catalytic activity of alumina and boron modified alumina catalysts in ethanol dehydration reaction. This research studies effect of various phase alumina catalysts and effect of boron modified various phase alumina catalysts on ethanol dehydration. This chapter divided into 2 parts. First, the catalytic performance of all catalysts in ethanol dehydration reaction was investigated with temperature-program between 200°C to 400°C. Second, the stability of catalysts in ethanol dehydration reaction was studied within time on stream around 72 hrs.

4.1 The catalytic performance of all catalysts in ethanol dehydration.

4.1.1 Catalyst Characterization

The catalyst characteristics were investigated by X-ray diffraction (XRD), N_2 physisorption (BET), scanning electron microscopy (SEM/EDX), transmission electron microscopy (TEM), NH_3-tempearture programmed desorption (NH_3-TPD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA).

4.1.1.1 Physical properties

4.1.1.1.1 Nitrogen physisorption

Nitrogen physisorption technique is popularly used for the determination of the surface area, pore size distribution and N_2 adsorption–desorption isotherms of various porous materials. The surface area and pore size distribution can be analyzed how the addition of boron into the pores of alumina would affect porosity. The physical properties of alumina catalysts and boron modified alumina catalysts are summarized in **Table 4.1**. We investigated the properties using N_2 adsorption measurements at -196°C. The BET surface area, pore volume and pore size were obtained. The mixed-phase alumina exhibited the highest surface area compared with gamma and chi alumina. That means chi phase improves the properties of gamma alumina catalyst better. The surface area of solid catalyst increases and the rate of reaction would increase. The BET surface area and pore volume of gamma phase, chi phase and mixed phase alumina decreased with doped boron. This indicated that pores of Al_2O_3 substrate was plugged by boron species. The average pore size diameter of G-Al, B-G-Al, C-Al and B-C-Al remained constant at around 11 nm, while M-Al and B-M-Al gave average pore size diameter about 7.1 nm. The pore size diameter of mixed-phase alumina catalyst was lower than pure phase alumina. This corresponded with BET surface area that the smaller porous provide higher surface area. The M-Al and B-M-Al would be good catalysts for the ethanol dehydration reaction.

Table 4.1 BET surface area, pore volume, pore size diameter of the catalysts.

Sample	BET surface area S_{BET} (m^2/g)	Pore volume P_v (cm^3/g)	Pore size diameter P_d (nm)
G-Al	178	0.7	11.1
B-G-Al	151	0.6	11.8
C-Al	149	0.6	11.1
B-C-Al	132	0.4	10.1
M-Al	178	0.5	7.3
B-M-Al	173	0.5	6.9

The nitrogen isotherm identified the physisorption mechanism of all catalysts indicating that the catalyst is monolayer-multilayer adsorption, or micropore filling. The N_2 adsorption–desorption isotherms of the catalysts are shown in **Figure 4.1**. According to the IUPAC classification of physisorption isotherms, the isotherms of catalysts are corresponded to type IV isotherms. It can be indicated as the characteristic of mesoporous structure. The type IV isotherms appear characteristic of H1 or H2 hysteresis loops. From **Figure 4.1**, the hysteresis loop was H1 loop, indicating that the pore structure is in a narrow range of uniform (cylindrical-like) mesopore structure. A change of the hysteresis loop affected the pore structure in these materials [42]. The hysteresis loop of alumina did not differ in comparison with the boron modified alumina. This means that boron modification did not change the characteristic of pore.

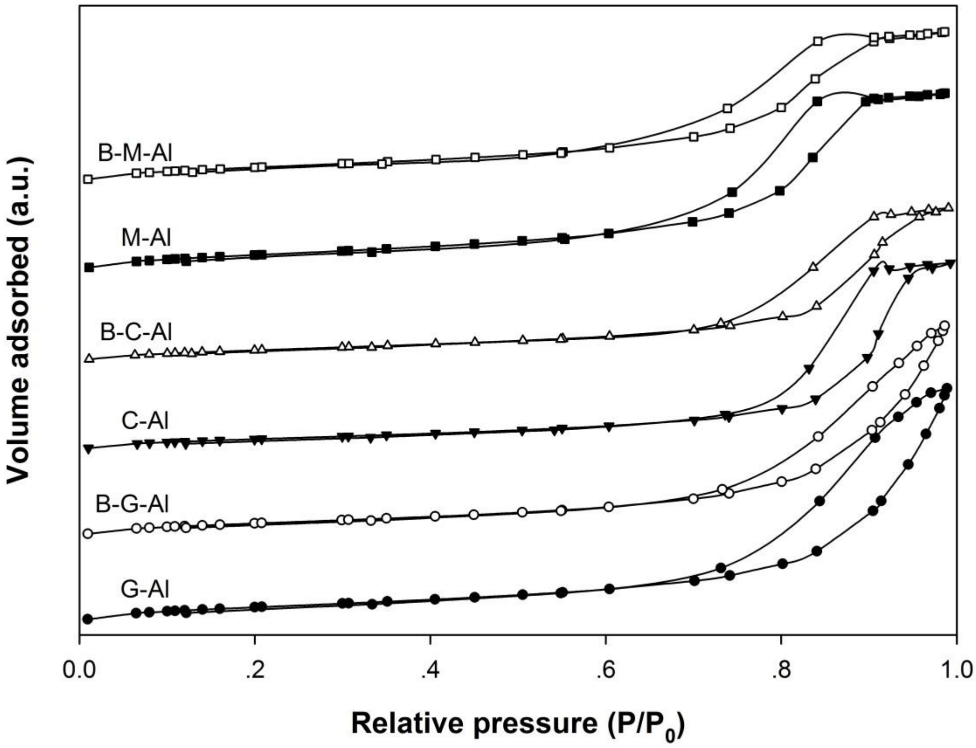


Figure 4.1 The N_2 adsorption–desorption isotherms of alumina and boron modified alumina catalyst with 2wt% boron loading.

The pore size distribution of alumina and boron modified alumina catalyst are shown in **Figure 4.2**. All catalysts exhibit the unimodal pore size distribution. The pore structure is divided into three types by pore size diameter; micropores (<2 nm), mesopores (2-50 nm) and macropores (>50 nm) [43]. In this research, the pore size is in the range of 2 to 50 nm. It indicated that all catalysts have mesoporous structure. From pore size distribution, peak of the gamma alumina catalyst is the broadest peak. This means that the pore size has wide range. The chi phase gave narrower peaks. The peak of mixed phase alumina catalyst was the narrowest pore size distribution, indicating that catalyst has a similar pore size. When the pore is uniformly distributed, it results in improved activity of reaction. So, the mixed phase alumina catalysts are probably the best catalyst.

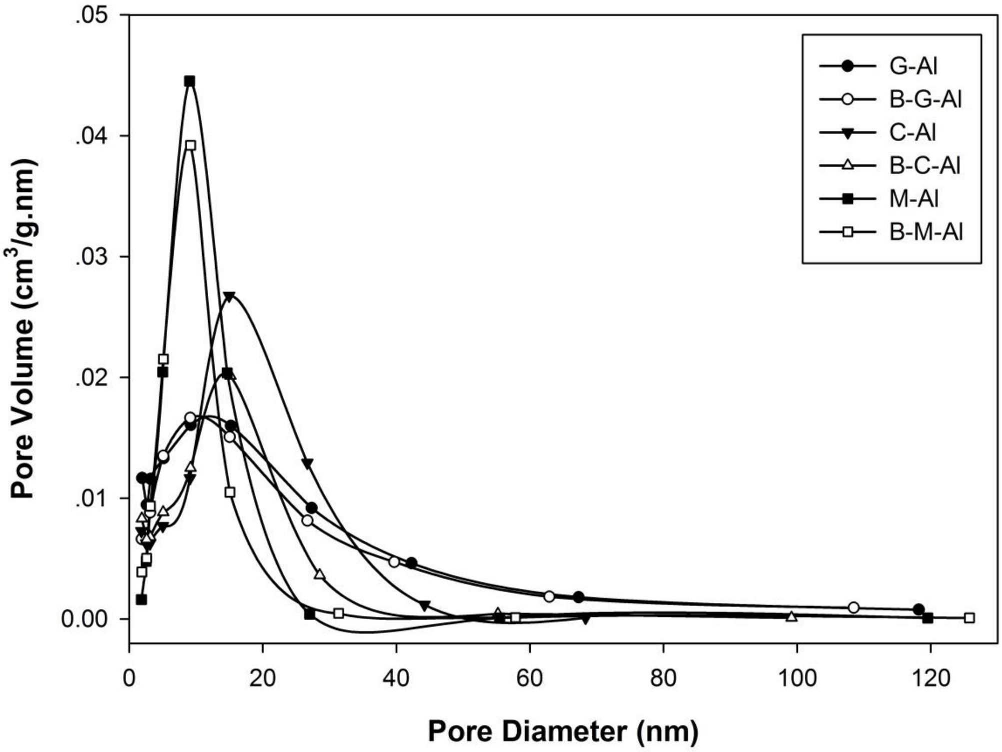
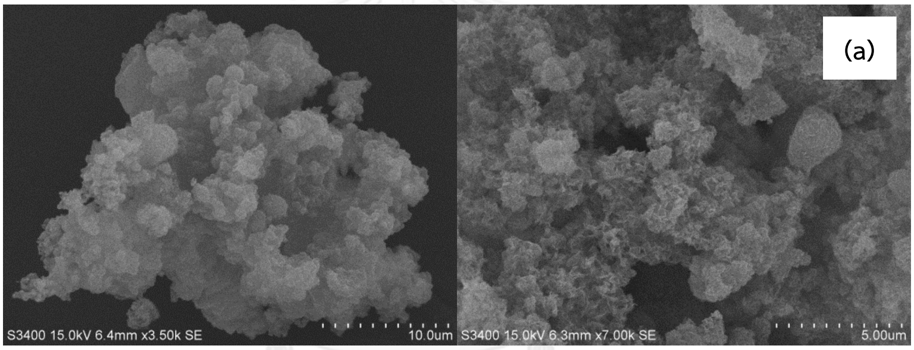
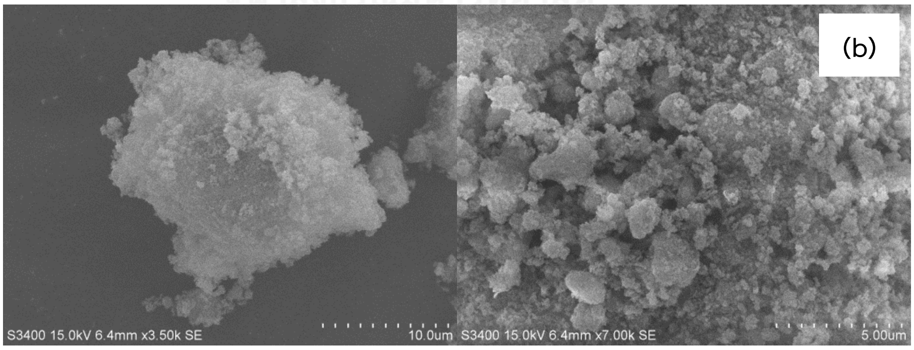


Figure 4.2 Pore size distribution of alumina and boron modified alumina catalyst with 2wt% boron loading.

4.1.1.1.2 Scanning electron microscopy (SEM)

The SEM technique is also widely used to identify phases of catalyst based on qualitative chemical analysis and crystalline structure. Morphologies of mixed phase alumina catalysts and boron modified mixed phase alumina catalysts by SEM technique are shown in **Figure 4.3**. As can be seen from **Figure 4.3**, the structure of gamma phase alumina catalyst was a porous structure, whereas chi phase exhibited smoother surface with irregular shape. The mixed phase gamma-chi alumina catalyst gave the smoothest structure. When modifying catalysts with boron, it was found that the modification of boron into alumina catalyst did not affect the catalyst morphologies. All catalysts show similar former morphological features.





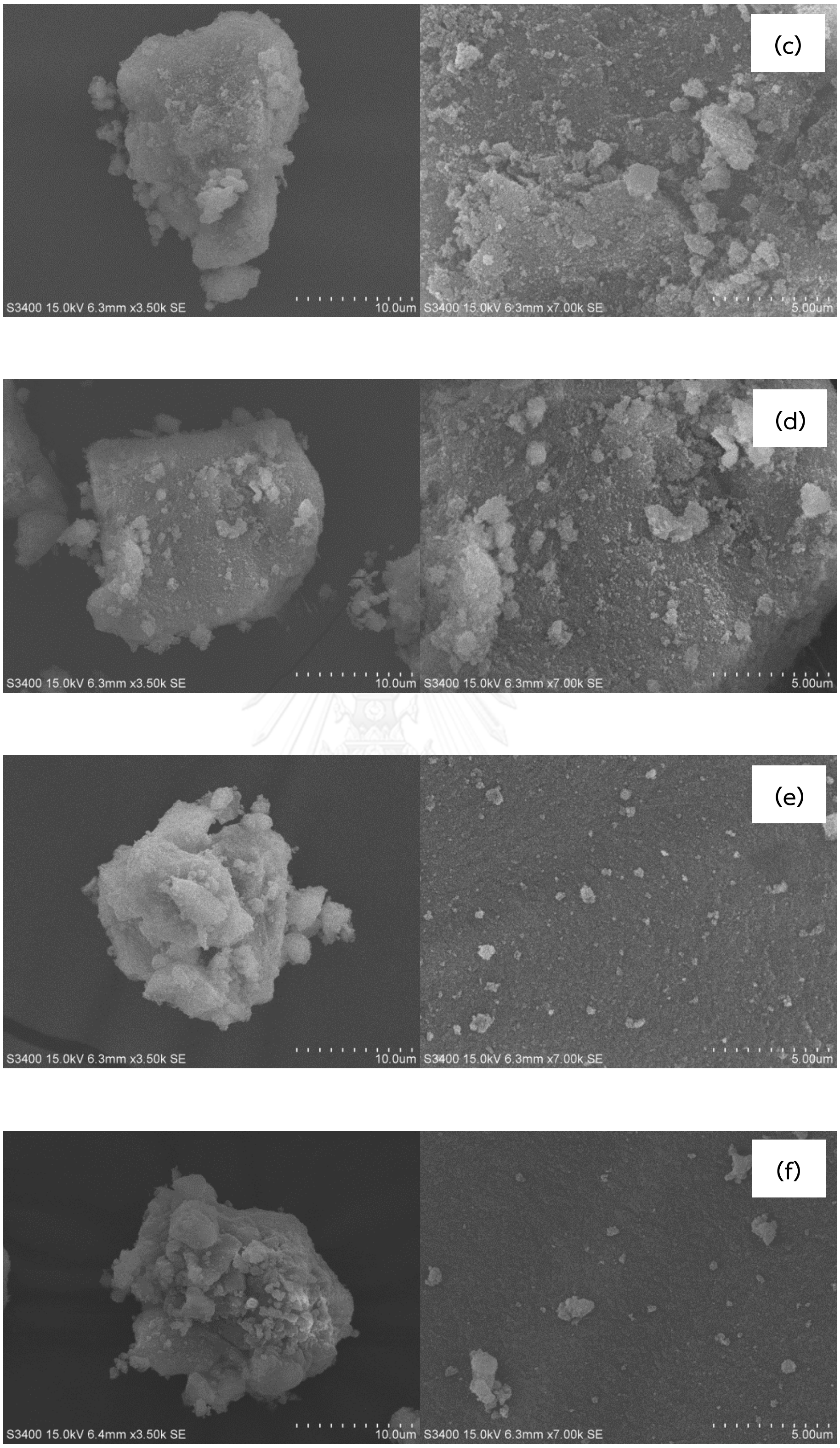
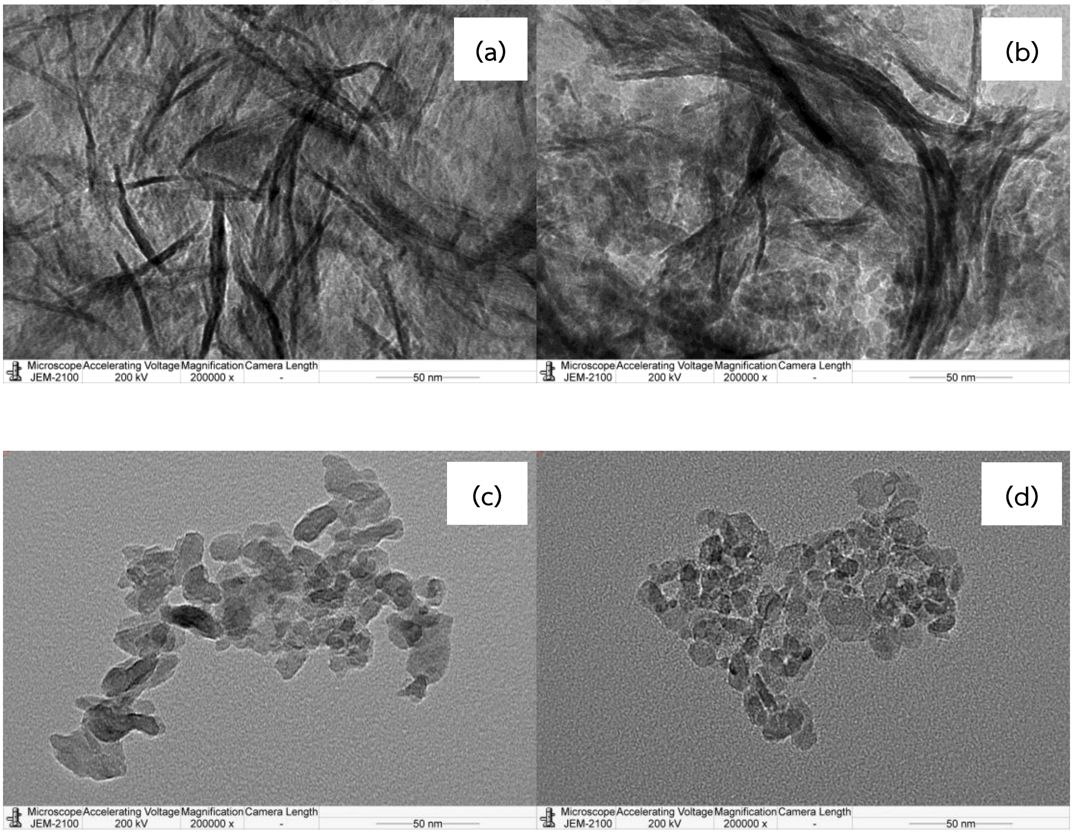


Figure 4.3 SEM micrograph of the catalysts : (a) G-Al, (b) B-G-Al, (c) C-Al, (d) B-C-Al, (e) M-Al, (f) B-M-Al.

4.1.1.1.3 transmission electron microscopy (TEM)

From nitrogen physisorption, it can provide quantitative measurement of pores size distributions. The features of the pore geometry are determined by the morphologies of alumina phase crystallites. Transition phases of alumina can be examined with the transmission electron microscopy (TEM). Previous results, phase transformation of alumina affects morphologies of catalysts. The morphology and distribution of various phase Al_2O_3 and boron particles on Al_2O_3 catalysts were investigated in **Figure 4.4**. The typical TEM micrographs of gamma phase alumina catalysts revealed the wrinkled sheets-like structure, while morphologies of chi phase alumina catalysts were spherical particles. The mixed structure between wrinkled sheets of gamma phase and spherical particles of chi phase were also observed. In the **Figure 4.4 (b), (d)** and **(f)**, the darker spots on the catalyst may represent a concentration of boron, while the lighter areas indicate the alumina catalyst. It was found that the main structure of alumina catalysts was maintained after impregnation and calcination.



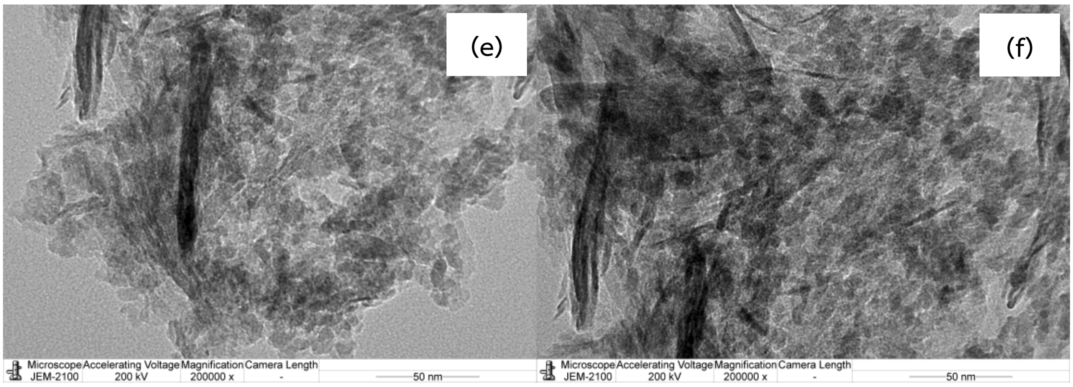


Figure 4.4 TEM micrograph of the catalysts : (a) G-Al, (b) B-G-Al, (c) C-Al, (d) B-C-Al, (e) M-Al, (f) B-M-Al.

4.1.1.2 Chemical properties

4.1.1.2.1 X-ray diffraction (XRD)

X-ray diffraction technique is a tool used for identifying the crystal structure of catalysts including the size, shape and internal stress of small crystalline regions since the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. As the result, it is able to identify the phase of alumina catalyst and the boron modified alumina catalyst. The XRD patterns of alumina catalyst prepared by the solvothermal method of AIP in toluene and 1-butanol and those of boron modified alumina catalyst are shown in **Figure 4.5**. The characteristic peaks of γ-phase crystalline alumina was found at 32°, 37°, 39°, 45°, 61° and 67°. When toluene was added in 1-butanol, the major XRD peak at 43° occurred indicating the presence of χ-phase crystalline of alumina [19, 21, 44, 45]. The intensity of χ-Al_2O_3 peaks became stronger with increasing amount of toluene content.

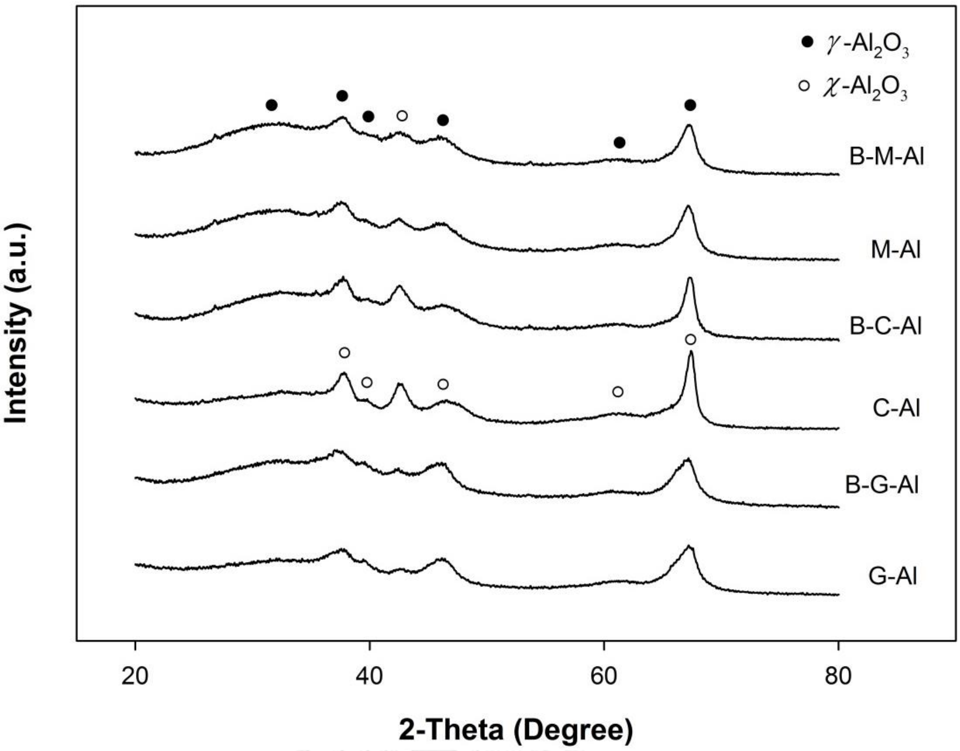


Figure 4.5 XRD patterns of alumina and boron modified alumina catalyst.

For the XRD patterns of boron modified mixed-phase alumina catalyst, the XRD peak of boron did not appear, revealing that the dispersion of boron on the alumina surface was well. Previous research showed that boron loading on alumina between 1 and 5 wt% had a monolayer dispersion [38]. In this work, alumina was modified with 2 wt% of boron, thus, it indicates that the boron species is well dispersed on the alumina surface as monolayer. In addition, the amount of boron can be identified by ICP (not shown here), it was around 1.4-1.6 wt%.

The average crystallite size of all catalysts is calculated using the Scherrer equation of X-ray diffraction technique as shown in **Table 4.2**. The crystallite sizes were found to be in the range of 5.1–10.9 nm. It can be seen that the crystallite size of γ-phase alumina is lower, while surface area is higher which according to previous research [46]. The crystallite size of alumina catalysts tended to decrease with adding of boron. The crystallite size was corresponding to BET surface area showing that the smaller crystallite size exhibits higher surface area.

Table 4.2 Crystallize size of the catalysts.

Sample	crystallite size(nm) (XRD of Al_2O_3)
G-Al	5.1
B-G-Al	5.2
C-Al	10.9
B-C-Al	9.8
M-Al	7.0
B-M-Al	6.8

4.1.1.2.2 Fourier transform infrared (FTIR)

Fourier transform infrared spectroscopy is technique which is an easy way to identify the presence of certain functional groups in a molecule of catalyst. Also, one can use to find interaction between alumina and boron by the unique collection of absorption bands. The FTIR spectra of alumina catalysts and boron modified alumina catalysts are shown in **Figure 4.6**. As can be seen, all of catalyst display the important broad absorption band around 800 cm^{-1} and another band in the range of 1500–1200 cm^{-1}. The absorption bands around 650 and 800cm^{-1} can be attributed to the presence of AlO_6 octahedron and AlO_4 tetrahedron, respectively. The FTIR results clearly show IR band of boron in the range 1500-1200 cm^{-1} with adding boron content, which implies as the asymmetric stretching of the B – O band of triangle [BO_3] units [47]. The peak at 1022 cm^{-1} was attributed to the BO_4 asymmetric stretching [39]. The absorption bands between 1500 and 1200 cm^{-1} may be represent to the formation of crystalline aluminum borate [37]. This confirmed that it was present.

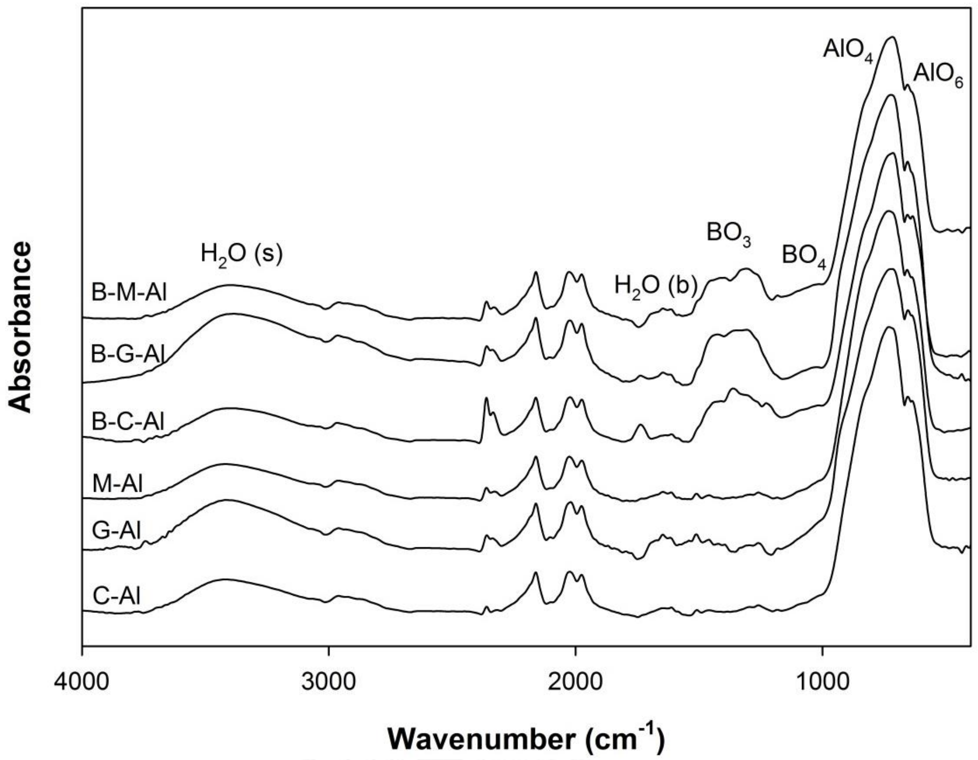


Figure 4.6 FTIR spectra of B_2O_3-Al_2O_3 supports in the hydroxyl stretching region.

4.1.1.2.3 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface quantitative spectroscopic technique. It can measure the element composition, chemical state and electronic state of the elements which exist within a material. The XPS technique is used to investigate the emitted electron kinetic energy. The electron binding energy of each element is measured. Boron species and the relative quantity of each element on the surface of alumina catalysts are shown in **Table 4.3**. The atomic concentration of boron on alumina surface is displayed by B/Al ratio. The B/Al ratio is in the range of 2.1-2.5 %atomic concentration. The catalysts were investigated in the B 1s, Al 2p, O 1s for binding energy regions. The Al 2p and O 1s peaks were detected at the binding energy between 74.1 to 75.8 eV and 532.1 to 533.5 eV, respectively. From the **Table 4.3**, it can be found that the binding energy values of B 1s for all boron modified alumina catalyst samples was around 193 eV.

These binding energies are very similar to those characteristic of B_2O_3 according to Saih et al [38]. Thus, we can assume that boron species on the alumina surface are present in a chemical environment similar to that corresponding to B_2O_3.

Table 4.3 XPS analysis of boron modified alumina catalyst

Sample	Binding Energy (eV)			Atomic Conc %	
	B 1s	O 1s	Al 2p	Al/O	B/Al
B-G-Al	192.0	532.1	74.1	0.29	0.21
B-C-Al	194.3	533.5	75.8	0.31	0.24
B-M-Al	192.6	532.4	74.6	0.29	0.25

4.1.1.2.4 Temperature programmed desorption (NH_3-TPD)

Temperature-programmed desorption (TPD) technique is widely used for characterizing the acid sites on oxide surfaces. Studying the quantity and strength of the acid sites on alumina, is essential to understanding and predicting the performance of a catalyst. NH_3-TPD is the method of observing ammonia desorbed molecules from a surface of catalyst when the surface temperature is increased. The acid properties of all catalysts are observed by temperature programmed desorption of ammonia. The NH_3-TPD profiles of the catalysts are shown in **Figure 4.7**. The results of NH_3-TPD are divided into two ranges, weak to moderate acid sites (<250°C) and strong acid sites (250-500°C). Deconvolution of NH_3-TPD curve provided the amount of acid sites with Gaussian curve fitting method. As can be seen in NH_3-TPD profile, there is the weak to moderate acid sites more than strong acid sites agreement with **Table 4.4**. The acidity of catalyst was investigated to compare with alumina catalyst as shown in **Table 4.4**. This table shows the amount of weak to moderate, strong and total acidity. It is demonstrated that γ-phase alumina catalyst exhibits the highest total amount of acid sites with undoped boron, followed by χ-phase and γ-χ mixed phase alumina. These results are corresponded in a decrease total surface acidity of catalyst from 497 to 435 μmol/g cat. as shown in **Table 4.4**. According to Khom-in et al. [19], the existence of χ-phase in γ-Al_2O_3 increased significantly surface acidity of alumina. In this research, when γ-phase alumina is adjusted with χ-phase alumina, resulting to improve weak/strong ratio of catalyst acidity. That means the amount of weak acid sites of the mixed phase alumina has increased. In addition, the strong acid site leads to occur undesirable by-products and significant coking [48]. From the foregoing, acidity is divided into weak to moderate and strong acid sites. Since the catalytic activity of solid acid catalysts for ethanol dehydration depends on both the number and strength of acid sites. When boron is added onto alumina catalyst, weak to moderate acid sites, strong acid sites and total acidity increased. The weak acid site significantly enhanced. This investigation is in agreement with the NH_3-TPD profile, where the peak of weak to moderate and strong acid site became broader and shifted to lower temperature. The weak/strong acid site ratio of B-M-Al was the highest, followed by B-G-Al and B-C-Al. The Brønsted or Lewis adsorption sites cannot be concluded from the NH_3-TPD results. It has been implied that the peak at lower temperature may be attributed to Brønsted acid sites whereas in case of Lewis acid sites it is in reverse order [18, 49]. It is possible that activity of ethanol dehydration is better when the weak acid site increases. This concludes that boron addition has an effect on the acidity of the alumina catalysts. Chen et al. [36] reported that the weak to moderate acid site enhanced resulting in a higher ethylene selectivity in ethanol dehydration reaction. El-Hakam et al. [37] found that the acidity on catalyst surface increased with boron content increased, leading to better activity of reaction. The weak/strong acid site ratio was found to be in the order: B-M-Al > B-G-Al > M-Al > C-Al ≈ B-C-Al > G-Al. However, it is clearly shown that acidity of γ-Al_2O_3 catalyst was improved when it contained an appropriate amount of χ-phase Al_2O_3 and the amount of boron content.

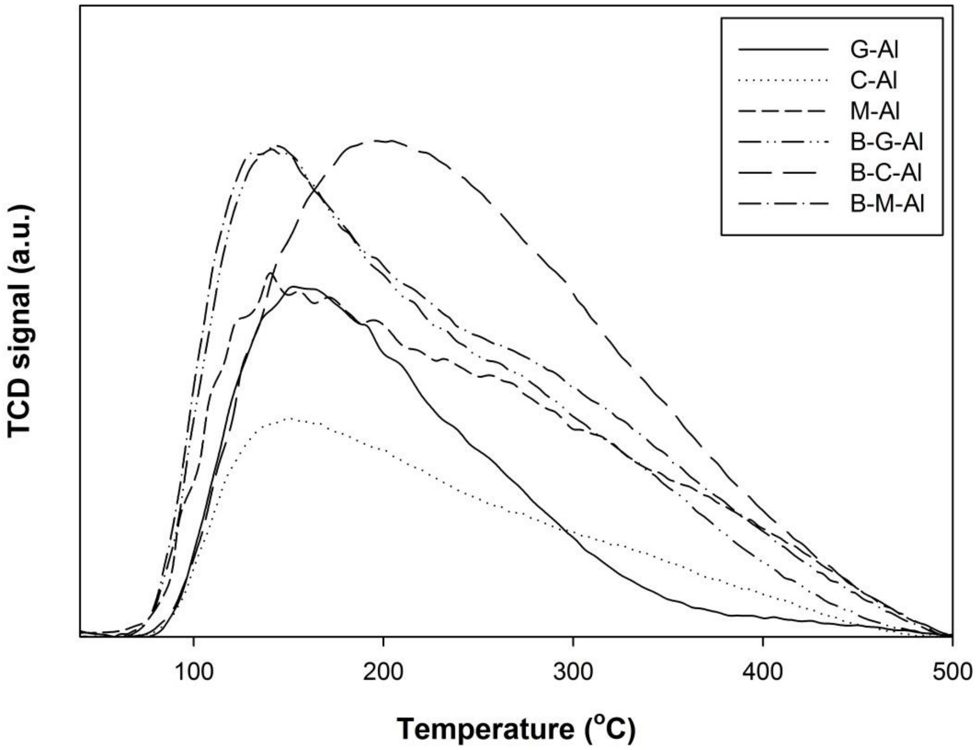


Figure 4.7 NH_3-TPD profiles of the alumina catalysts and boron modified alumina catalysts.

Table 4.4 The amount of acidity of alumina and boron modified alumina catalyst

Sample	NH_3 desorption (μmol NH_3/g cat.)		Total amount of acid sites (μmol g^{-1})	Weak/Strong acid site ratio
	weak	strong		
G-Al	317	180	497	1.8
B-G-Al	463	195	658	2.4
C-Al	295	153	448	1.9
B-C-Al	506	270	776	1.9
M-Al	304	131	435	2.3
B-M-Al	486	149	635	3.3

4.1.2 Catalytic performance

To evaluate the catalytic activity and product selectivity of the alumina catalysts, the ethanol dehydration was investigated at 200°C to 400°C. In the ethanol dehydration, each product is produced at the different temperature. It consisted of almost exclusively ethylene and diethyl ether. Ethylene is produced at higher temperature, while diethylether favors lower temperature due to its exothermic reaction. Besides, the acidity property of catalyst is an important factor which influenced on the conversion of ethanol and product selectivity. To examine the effect of reaction temperature on the catalytic performance of their catalysts, the ethanol conversion was tested with temperature program over various catalysts was shown in **Figure 4.8**. Comparison the different phases of alumina catalyst at 400°C, the mixed phase alumina gave the highest conversion because its surface area is the highest. It is known already that the catalyst has a high surface area exhibits great activity. In addition, the acidity of the catalyst is suitable for ethylene production. The ethanol conversion was found to be in the order: B-M-Al > M-Al > C-Al > B-G-Al ≈ B-C-Al > G-Al. It follows the weak/strong acid site ratio in the order: B-M-Al > B-G-Al > M-Al > C-Al ≈ B-C-Al > G-Al. Because of the weak over the strong results in the conversion of ethanol dehydration increased as well. Boron modified mixed phase alumina catalyst gave a complete conversion at temperature 400°C due to the addition of boron on alumina leads to increase of the number of acid sites (weak to moderate acid sites more than strong acid sites) which is good for ethanol dehydration. This is consistent with previous research that the boron oxide gave the medium Brønsted acid strength [9], which favors for the ethanol dehydration reaction [10]. Therefore, the mixed phase alumina catalysts modified with boron (B-M-Al) increases the activity of ethanol dehydration.

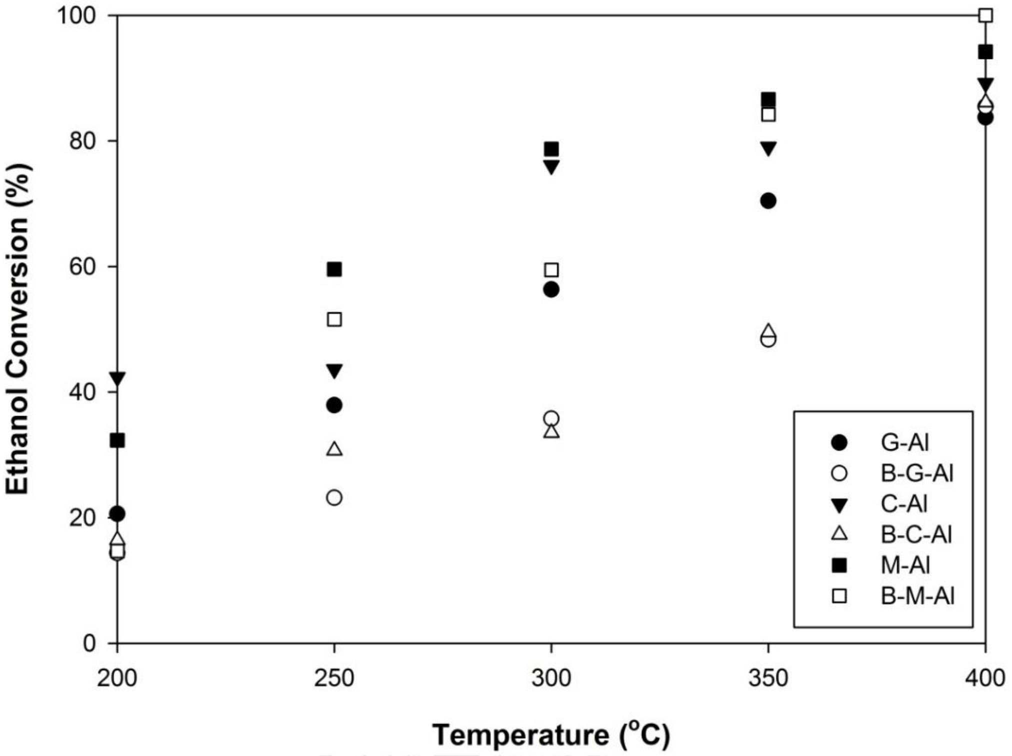


Figure 4.8 Ethanol conversion profiles in ethanol dehydration of various alumina catalysts.

Ethylene, diethylether and acetaldehyde selectivity of various alumina catalysts for the dehydration of ethanol is shown in **Figures 4.9** to **4.11**, respectively. When the reaction temperature was raised, the ethanol conversion and the selectivity to ethylene increased significantly. The selectivity of ethylene at 400°C was in the order of C-Al > M-Al > B-M-Al > B-G-Al > B-C-Al > G-Al as shown in **Figure 4.9**. On the other hand, the selectivity of diethylether obviously decreased with increasing temperature as seen in **Figure 4.10**. It reveals DEE selectivity indicating that mostly all catalysts exhibit high DEE selectivity at reaction temperature between 200 to 250°C because DEE production is exothermic. In addition, acetaldehyde hardly occurs compared with ethylene and diethylether as shown in **Figure 4.11**.

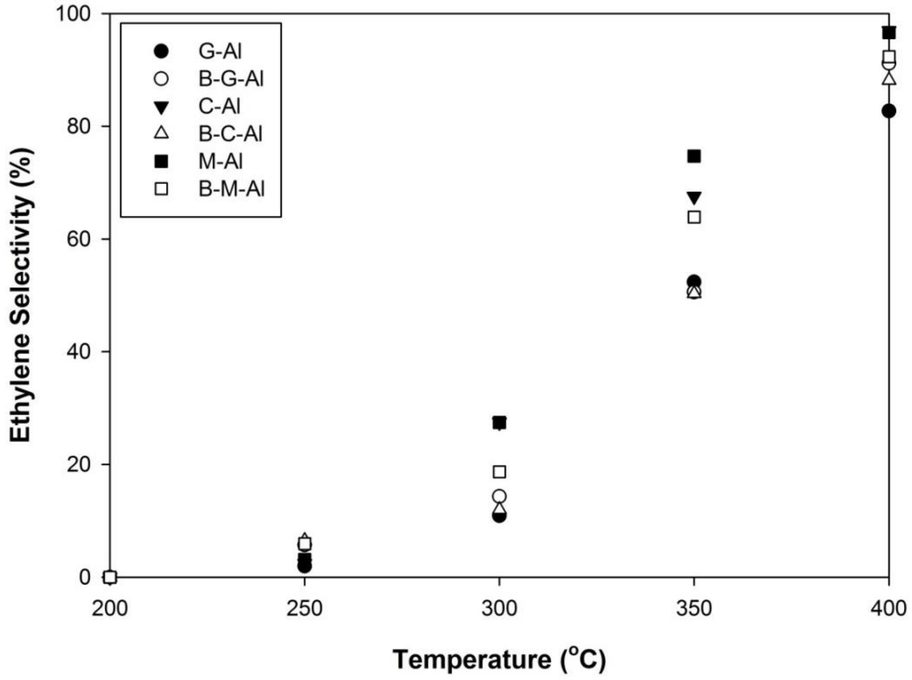


Figure 4.9 The selectivity of ethylene of various alumina catalysts in ethanol dehydration.

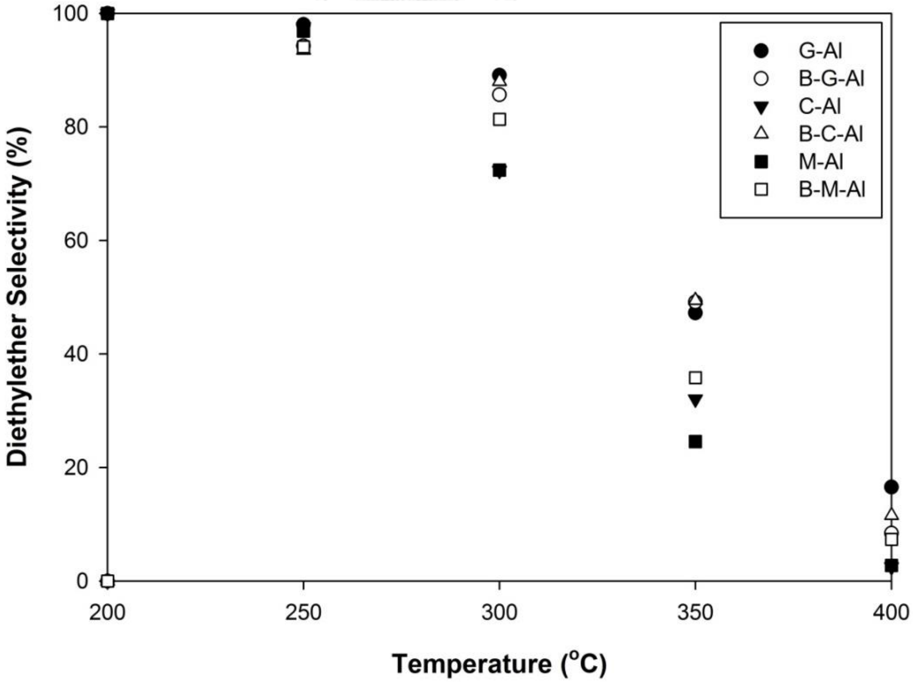


Figure 4.10 The selectivity of diethylether of various alumina catalysts in ethanol dehydration.

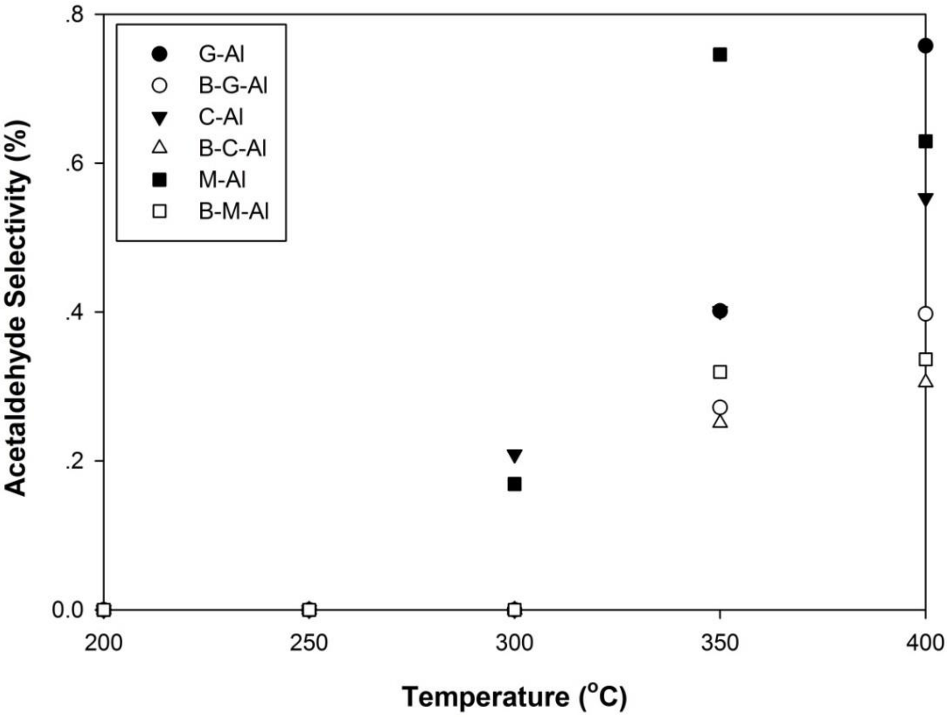


Figure 4.11 The selectivity of acetaldehyde of various alumina catalysts in ethanol dehydration.

4.2 The stability of catalysts in ethanol dehydration reaction

The stability of mixed γ- and χ- phase Al_2O_3 catalyst and boron modified mixed γ- and χ- phase Al_2O_3 catalyst can be determined by running reaction with time on stream. **Figure 4.12** demonstrates the conversion as a function with time on stream at isothermal conditions (400°C) of the catalysts. All catalysts were deactivated because of coke deposition on the acid active sites. When the reaction temperature increases, the coke deposition usually increased. As shown in **Figure 4.12**, both of catalysts slightly deactivated after reaction for 72 hours and yield of ethylene decreased from 96% to 91%. The coke deposition mostly occured in micropores structure [50]. Therefore, the coke deposition in the mesopores cannot block the feed diffusing to the active sites or products diffusing from the active sites resulting to both catalysts still have high activity at 72 h. The boron modified mixed γ- and χ- phase Al_2O_3 catalyst showed the highest initial activity (86%), while mixed

γ- and χ- phase Al_2O_3 catalyst presented initial activity at 53%. It means that boron modified mixed γ- and χ- phase Al_2O_3 catalyst slightly exhibited effective catalytic activity and stability more than mixed γ- and χ- phase Al_2O_3 catalyst, which remained unchanged for 72 h of time on stream. Therefore, the boron modified mixed γ- and χ- phase Al_2O_3 catalyst presents much slightly stability and resistance to coke formation.

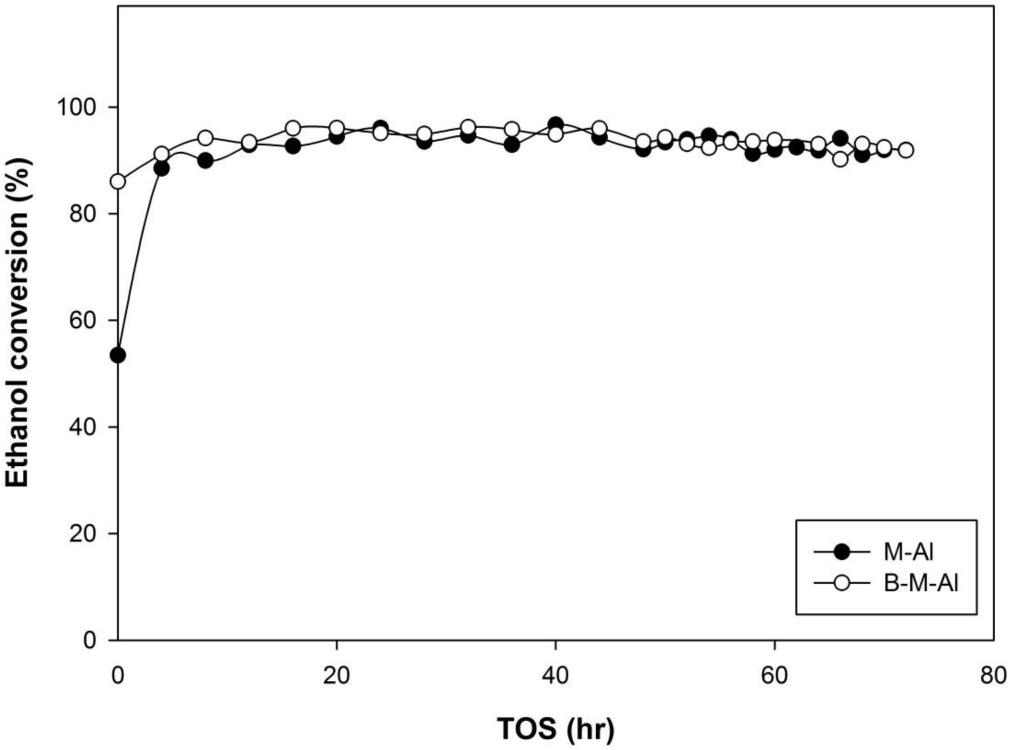


Figure 4.12 Comparison of the stability of M-Al and B-M-Al catalysts.

Figure 4.13 shows the selectivity of M-Al and B-M-Al catalysts with TOS. Although the catalytic activity and stability of B-M-Al is better than ever, but ethylene selectivity of it is worse. However, it was obvious that B-M-Al obtained higher amount of diethylether than M-Al, while acetaldehyde scarcely occurred.

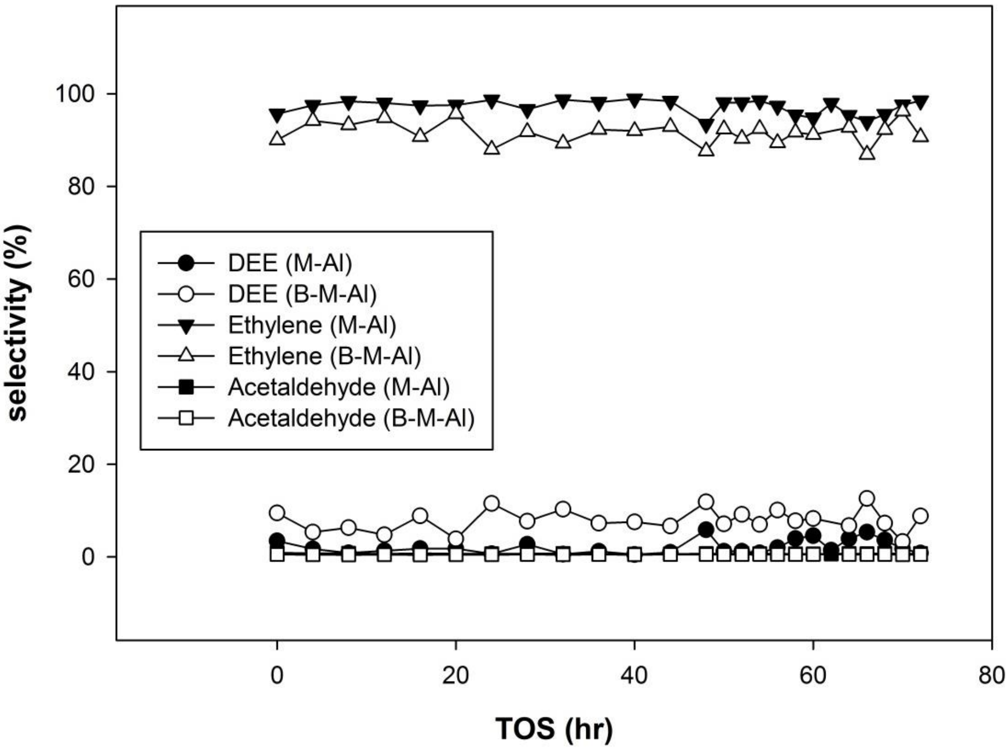


Figure 4.13 Comparison of the selectivity of M-Al and B-M-Al catalysts with TOS.

The TGA analysis is used to investigate the coke deposition. **Figure 4.14** was performed on the spent M-Al and B-M-Al catalyst with reaction time of 72 h compared with the unspent M-Al and B-M-Al catalyst. As seen in Figure 4.14, all of catalysts show the weight loss at the temperature range of 200-700 °C, which is attributed to the coke burning. There is a difference of the amount of weight loss, 3.5 wt.% for the spent M-Al and 3.1 wt.% for the spent B-M-Al, indicating that the coke deposition of the spent B-M-Al is lower than that of the spent M-Al. It indicates that the boron doping can inhibit the formation of the coke deposition, which is concluded that introduction of boron into mixed phase alumina catalyst improved stability of catalysts with decreasing the coke formation.

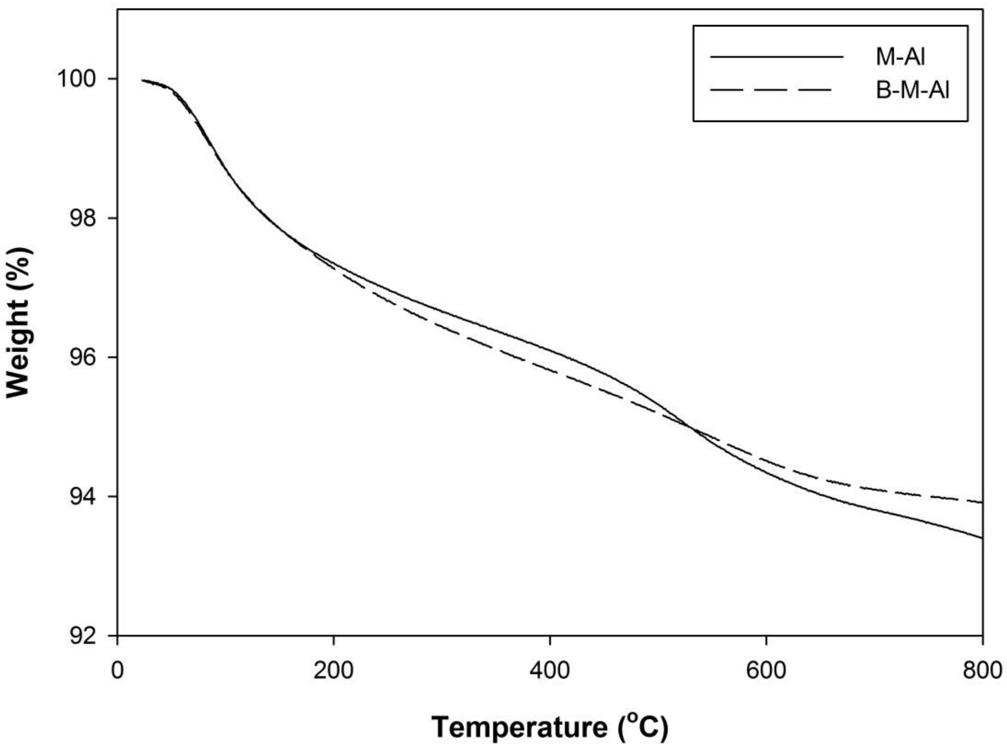


Figure 4.14 TGA profiles of the spent M-Al and B-M-Al catalyst compared with the unspent M-Al and B-M-Al catalyst.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this research, the different phases of alumina catalysts were successfully synthesized by solvothermal method. The mixed γ-χ phase alumina catalyst gave the highest surface area among other pure gamma and chi aluminas. It also had higher acidity, which is preferred for ethanol dehydration reaction. As the result, the mixed γ- and χ- phase Al_2O_3 catalysts exhibited the highest ethanol conversion. Improving alumina catalyst with 2wt% boron makes the good dispersion of boron on the surface of alumina. The addition of boron, amounts of weak acid sites were increased more than strong acid sites, which is good for ethanol dehydration due to this reaction required Brønsted acid site. When boron was introduced into the catalysts, the boron modified mixed γ- and χ- phase Al_2O_3 catalyst gave a complete conversion at temperature 400°C. Therefore, the mixed phase alumina catalysts modified with boron obtained the highest activity of ethanol dehydration. The boron modified mixed γ- and χ- phase Al_2O_3 catalyst presents much stability and resistance to coke formation.

5.2 Recommendations

Since the acidity property significantly affects on catalytic activity of ethanol dehydration. In this research, the acidity of catalyst was only investigated by using NH_3-TPD which divided acid sited into weak and strong acid site in addition total acidity. However, NH_3-TPD technique cannot investigate distinction between Bronsted and Lewis acid site. In order to progressive understand this reaction. Thus, we should be used the pyridine FT-IR to distinguish types of acid sites. ^{27}Al-NMR technique can be used to find the amount of Bronsted acid site. Furthermore, acid strength which corresponded to TOF should be studied by initial enthalpy of ammonia adsorption. In addition, the coke formation should also be measured by temperature-programmed oxidation method with IR detection (TPO-IR) specifically for the analysis of CO_2 released. Also, the regeneration of catalyst should be investigated in ethanol dehydration reaction. For industry applications, we should use bioethanol as reactant.

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APPENDIX

APPANDIX A

CATALYST PREPARATION

Calculation of boron loading

The boron modified mixed phase alumina catalysts were prepared by impregnation method with an aqueous solution of boric acid (H_3BO_3). The catalyst was calculated based on 1 g of catalyst used.

For example of boron modified gamma-chi mixed phase alumina catalyst, the M-Al with modification of 2%wt boron was prepared as follow:

Basis: 1g of catalysts

Reagent: - boric acid 99.5% (H_3BO_3)
Molecular weight = 61.83 g/mol
- boron (B) ,atomic weight = 10.82 g/mol
- gamma-chi mixed phase alumina catalyst

The catalyst composition would be as follow:

Boron = 0.02 g
gamma-chi mixed phase alumina catalyst = 1.00-0.02 g
= 0.98 g

Boric acid (H_3BO_3) is consisted of B 1 atom so weight of B in H_3BO_3 is 10.82 g.

B 10.82 g in H_3BO_3 61.83 g
B 0.02 g in H_3BO_3 61.83x0.02/10.82 = 0.1143 g

The purity of boric acid (H_3BO_3) is 99.5%.

H_3BO_3 99.5 g to H_3BO_3 100 g

H_3BO_3 0.1143 g to H_3BO_3 100x0.1143/99.5 g

= 0.1149 g

So, boric acid was used to 0.1149 g.

APPANDIX B

CALIBRATION CURVE

Calibration curves of reactant and products in ethanol dehydration reaction were used to calculate of composition. The calibration curves of ethanol, ethylene, DEE and acetaldehyde are shown in **Figure B.1-B.4**. The ethanol is reactant. The ethylene is main product while the diethylether and acetaldehyde are byproducts of this reaction. The gas chromatography Shimadzu model 14B and capillary column DB-5 of flame ionization detector (FID) was used to analyze the concentration of these. The GC conditions are presented in **Table B.1**.

Table B.1 Conditions of GC-14B.

Parameters	Condition
Width	5
Slope	100
Drift	0
Min.area	300
T.DBL	1000
Stop time	12 min
Atten	2
Speed	3
Method	Normalization
SPL.WT	100
IS.WT	1

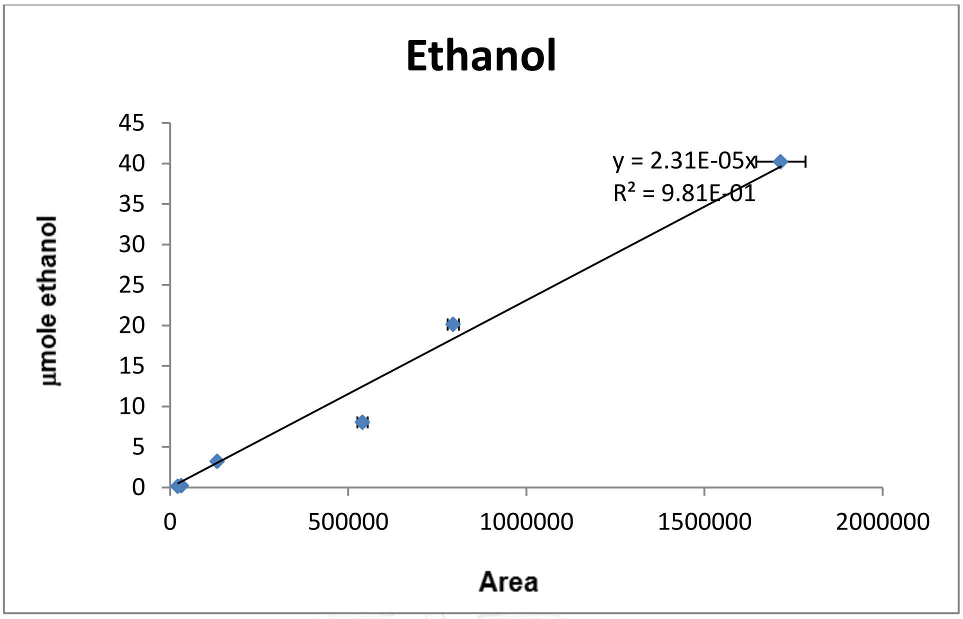


Figure B.1 The calibration curve of ethanol.

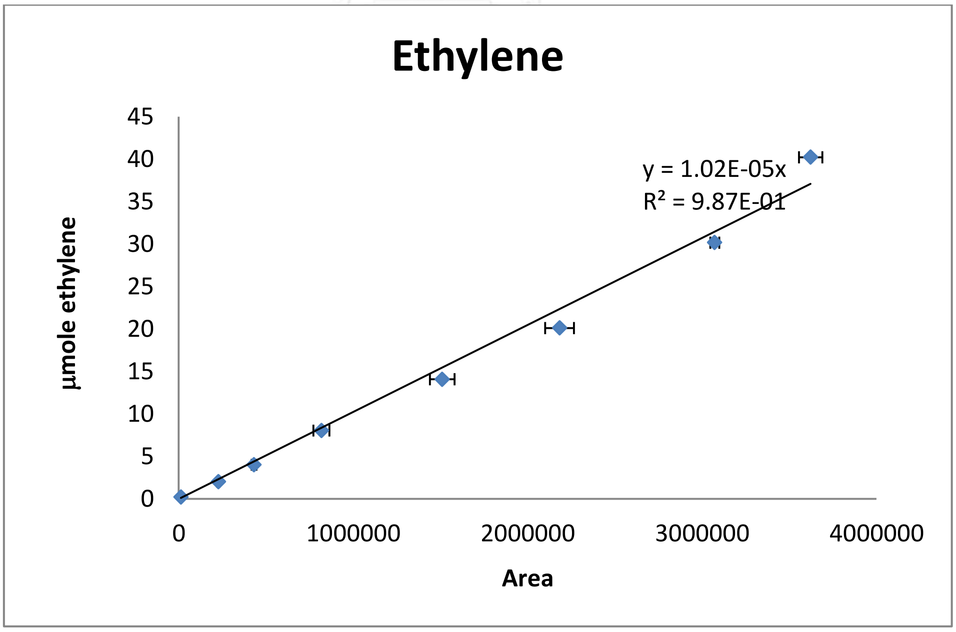


Figure B.2 The calibration curve of ethylene.

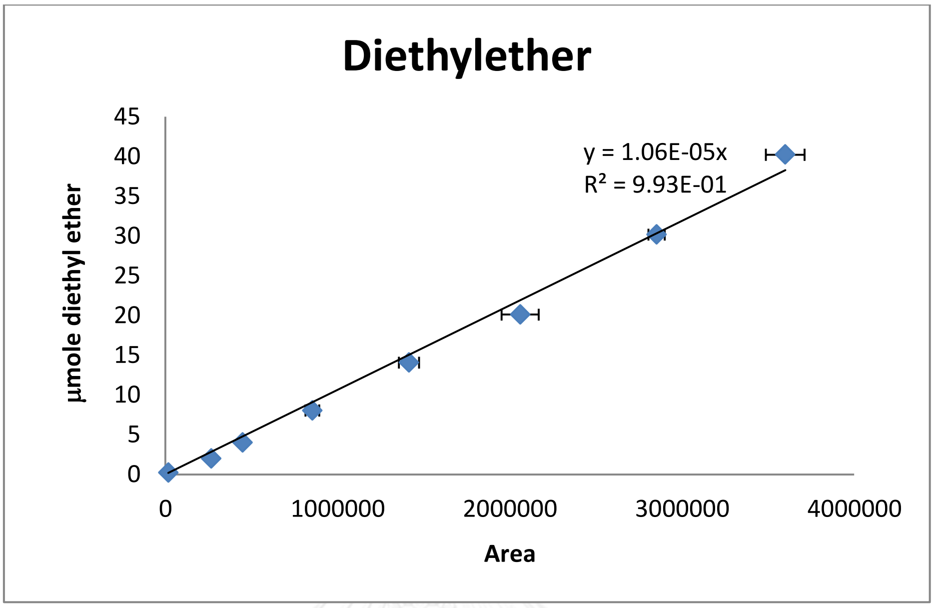


Figure B.3 The calibration curve of DEE.

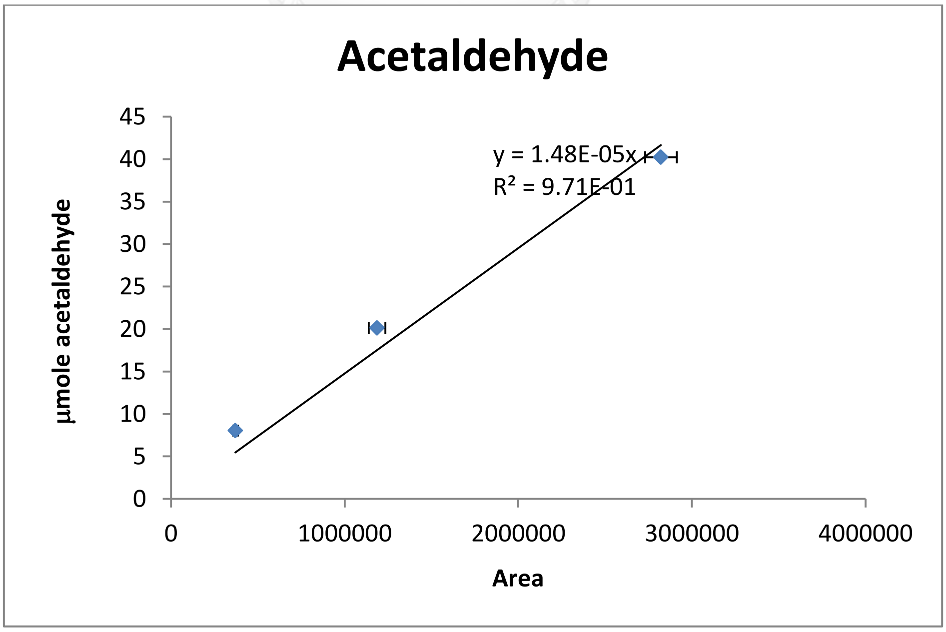


Figure B.4 The calibration curve of acetaldehyde.

APPANDIX C

CONVERSION AND SELECTIVITY

Ethanol conversion

The ethanol conversion is calculated from the mole of ethanol converted relative to ethanol in feed.

$$\text{Ethanol conversion (\%)} = \frac{\text{mole of ethanol}_{\text{in}} - \text{mole of ethanol}_{\text{out}}}{\text{mole of ethanol}_{\text{in}}} \text{ x } 100$$

Product selectivity

The product selectivity calculated from the mole of product (A) formed with respect to mole of ethanol converted.

$$\text{selectivity of A (\%)} = \frac{\text{product of A}}{\text{total product}}$$

Where A is mole of ethylene, diethylether, or acetaldehyde.

Total product is mole of (ethylene + diethylether + acetaldehyde).

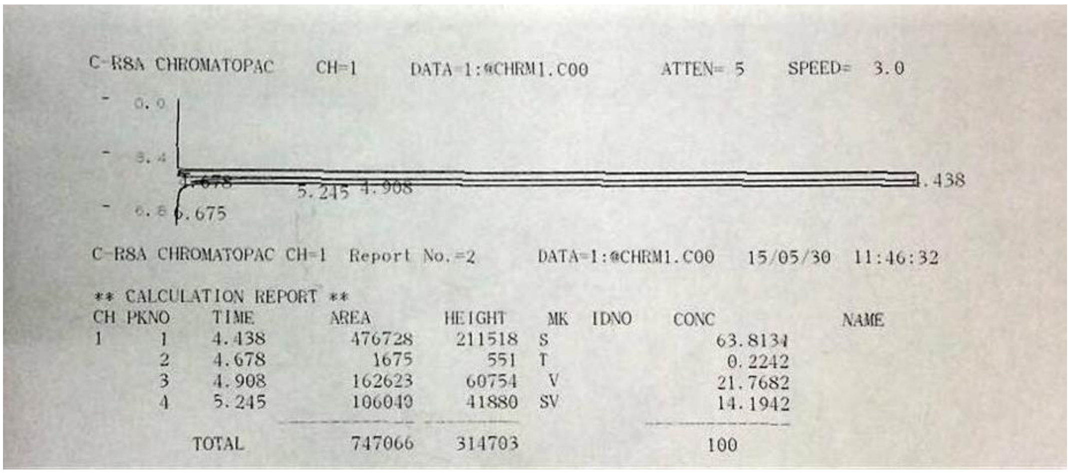
From calibration curve;

Mole of ethanol = $(2.31\text{x}10^{-5})$ x area

Mole of ethylene = $(1.02\text{x}10^{-5})$ x area

Mole of diethylether = $(1.06\text{x}10^{-5})$ x area

Mole of acetaldehyde = $(1.48\text{x}10^{-5})$ x area



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```

```
C-R8A CHROMATOPAC CH=1  Report No.=2       DATA=1:@CHRM1.C00    15/05/30   11:46:32

** CALCULATION REPORT **
CH PKNO     TIME        AREA       HEIGHT    MK  IDNO     CONC              NAME
1     1     4.438       476728     211518  S                63.8134
      2     4.678         1675        551  T                 0.2242
      3     4.908       162623      60754   V               21.7682
      4     5.245       106040      41880  SV               14.1942
                    ------------ ----------            ------------
            TOTAL       747066     314703                  100
```

Figure C.1 The GC result.

From **Figure C.1**, the area of reactant and product can be detected by gas chromatography. The peak at 4.438 minute shown area of ethylene, while peak at 4.678, 4.908 and 5.245 minute represented area of acetaldehyde, ethanol and diethylether, respectively.

$$\text{So,} \qquad \text{mole of ethanol} = (2.31\text{x}10^{-5}) \text{ x } 162623$$

$$= 3.76 \text{ mole}$$

APPANDIX D

CALCULATION OF ACIDITY

Calculation of acidity

The acidity was investigated by NH_3-TPD, it can calculate the amount of weak, strong and total acid site of catalysts from area of NH_3-TPD profile.

$$\text{Acidity of catalysts} = \frac{\text{mole of ammonia desorption}}{\text{weight of catalyst}}$$

To calculate mole of NH_3 desorption from the calibration curve of NH_3 as follow:

NH_3 desorption (mole) = 0.0003 x area under peak of the NH_3-TPD profile

APPANDIX E

CATALYST DEACTIVATION

The coke deposition is investigated by the TGA analysis. It can be observed from weight loss in the range of temperature 200 to 700 °C.

For example, weight loss of boron modified mixed phase alumina catalyst is calculated.

At 200°C, %weight loss = 100-97.2= 2.8

At 700°C, %weight loss = 100-94.1= 5.9

So, %weight loss in the range of temperature 200 to 700 °C is 5.9-2.8 = 3.1%

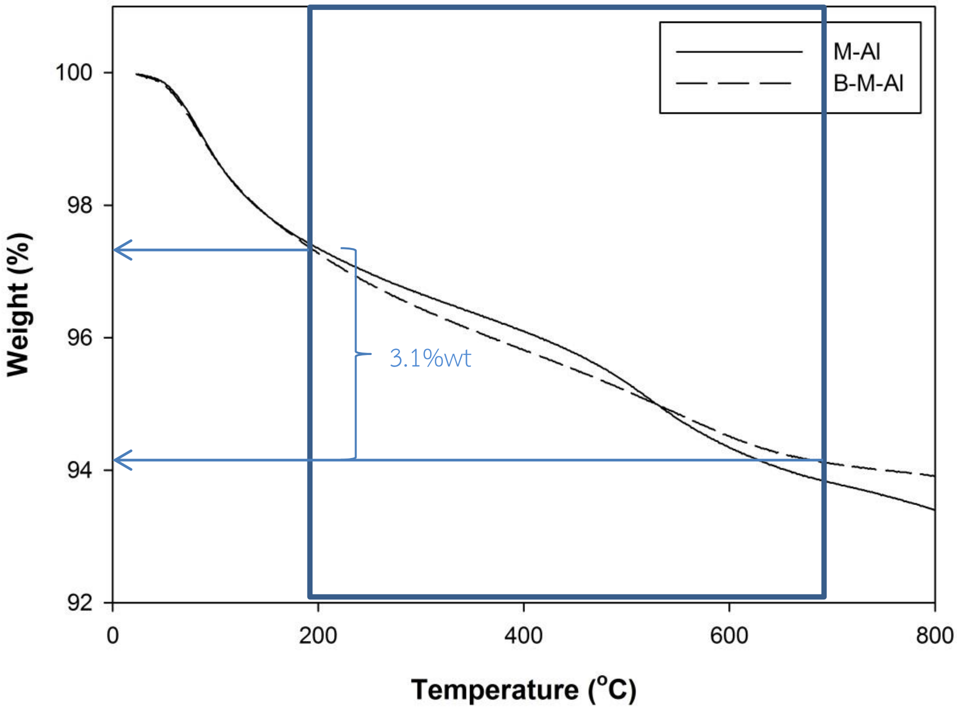

Figure E.1 TGA profiles of the M-Al and B-M-Al catalyst.

APPANDIX F

CALCULATION OF ALUMINA PHASE

Phase of alumina is calculated from XRD area of chi peak at 43°. **Figure F.2** shown the calibration curve of %chi phase of alumina catalyst.

For example, the %chi phase of mixed phase alumina catalyst is calculated from peak area of XRD at 43°. When the area from XRD curve was found, it lead to %chi phase by using calibration curve.

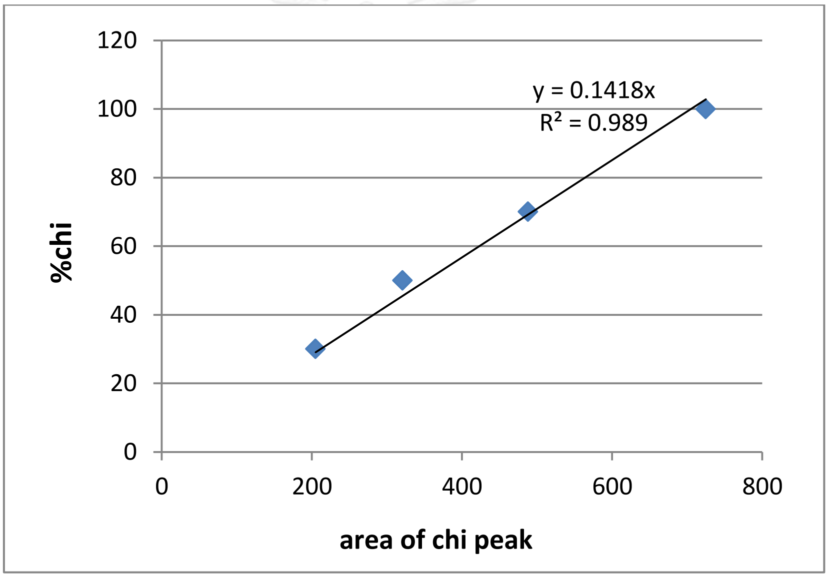

Figure F.1 The calibration curve of XRD chi phase.

APPANDIX G

LIST OF PUBLICATION

Proceeding

Nopparat Boonsinvarothai and Bunjerd jongsomjit, "Synthesis and characterization of boron modified alumina catalyst for ethanol dehydration to ethylene." Proceeding of the 9th Pure and Applied Chemistry International Conference 2015 (PACCON2015), Amari Watergate Hotel Bangkok, Thailand, January 21-23, 2015.

VITA

Miss Nopparat Boonsinvarothai was born on February 21, 1991 in Lampang, Thailand. She graduated the Bachelor’s Degree in Chemical Engineering from the Department of Chemical Technology, Faculty of Science, Chulalongkorn University (CU) in May 2013. She continued the Master of Engineering in Chemical Engineering, Chulalongkorn University (CU) in June 2013.