Final Report

Liquid-phase dehydration of ethanol using alumina-based acid catalysts

By

Asst. Prof. Sasiradee Jantasee

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Rajamangala University of Technology Thanyaburi

Project Granted by the Thailand Research Fund

บทคัดย่อ

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ชื่อโครงการ: ปฏิกิริยาการขจัดน้ำของเอทานอลในสถานะของเหลวโดยใช้ตัวเร่งปฏิกิริยาฐานอะลูมินา

ชื่อนักวิจัย และสถาบัน: ผศ.ดร.ศศิรดี จันทสี
ภาควิชาวิศวกรรมเคมีและวัสดุ คณะวิศวกรรมศาสตร์
มหาวิทยาลัยเทคโนโลยีราชมงคลธัญบุรี

อีเมล์: sasiradee.j@en.rmutt.ac.th

ระยะเวลาโครงการ: 1 พฤษภาคม 2561 – 30 เมษายน 2563

บทคัดย่อ:

ปฏิกิริยาดีไฮเดรชันแบบใช้ตัวเร่งของเอทานอลในสถานะของเหลวบนตัวเร่งปฏิกิริยาแกมมาอะลูมินา (G), ไคอะลูมินา (C) และอะลูมินาเฟสผสมในอัตราส่วนโดยน้ำหนักของแกมมา-ไคที่แตกต่างกัน จากการศึกษาพบว่าตัวเร่งปฏิกิริยา 25G:75C มีค่าคอนเวอร์ชันของเอทานอลที่สูงที่สุดเท่ากับ 37.12% แต่อย่างไรก็ตามผลได้ของผลิตภัณฑ์ไดเอทิลอีเทอร์ที่สูงที่สุดเกิดจากตัวเร่งปฏิกิริยาไคอะลูมินา เนื่องจากตัวเร่งปฏิกิริยานี้มีปริมาณตำแหน่งว่องไวชนิดกรดกลางถึงกรดแก่สูงที่สุด การเพิ่มขึ้นของปริมาณเฟสแกมมาในตัวเร่งปฏิกิริยาอะลูมินาเฟสผสมส่งผลให้มีการลดลงของผลได้ของไดเอทิลอีเทอร์ แต่ช่วยเพิ่มผลได้ของอะซีตัลดีไฮด์ ตัวเร่งปฏิกิริยาแกมมาอะลูมินาและตัวเร่งปฏิกิริยาแกมมา-ไคอะลูมินาเฟสผสมที่อัตราส่วน 75G:25C ให้ผลิตภัณฑ์เฉพาะอะซีตัลดีไฮด์เท่านั้น นอกจากนี้ได้ศึกษาผลของตัวทำละลายต่อการเร่งปฏิกิริยาของตัวเร่งปฏิกิริยาแกมมาอะลูมินาเกรดการค้า การเติมโทลูอีนหรือเฮปเทนลงไปในปฏิกิริยาเอทานอลดีไฮเดรชันส่งผลให้มีการเพิ่มขึ้นของเอทานอลคอนเวอร์ชัน ซึ่งน่าจะเป็นผลมาจากค่าคงที่ไดอิเล็กทริกของโทลูอีนและเฮปเทนสามารถกระตุ้นการเกิดประจุที่เป็นตำแหน่งที่ว่องไวต่อการเร่งปฏิกิริยาได้

คำหลัก : เอทานอลดีไฮเดรชัน, สถานะของเหลว, อะลูมินา, แกมมา, ไค

Abstract

Project Code : MRG6180166

Project Title : Liquid-phase dehydration of ethanol using alumina-based acid catalysts

Investigator : Asst. Prof. Sasiradee Jantasee, D.Eng
Chemical and Materials Engineering, Faculty of Engineering
Rajamangala University of Technology Thanyaburi

E-mail Address : sasiradee.j@en.rmutt.ac.th

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Abstract:

The catalytic dehydration of ethanol in liquid phase over the gamma-alumina (G), chi-alumina (C), and different weight ratio of gamma-chi-mixed phase alumina catalysts were investigated. It was found that the 25G-75C catalyst had the highest ethanol conversion of 37.12%. However, the highest diethyl ether yield occurred from the chi-alumina catalyst because it had the highest amount of moderate to strong acid site. The increasing of a gamma-phase content in the mixed phase alumina catalysts resulted in the decreasing of diethyl ether yield but it can enhance the acetaldehyde yield. The gamma alumina catalyst and the gamma-chi-alumina catalyst at the ratio of 75G:25C produced only acetaldehyde. Moreover, the solvent effect on the catalytic activity of commercial gamma-alumina was also studied. The addition of the toluene or heptane in the ethanol dehydration resulted in the increasing of ethanol conversion. It is assumed that the dielectric constant of the toluene and heptane can alter the electronic effects of catalytic active site formation.

Keywords: Ethanol dehydration, Liquid phase, Alumina, gamma, chi

1. Executive summary

1.1 Introduction to the research problem

Biomass utilization has been receiving high attention due to concerns about the reducing of petroleum feedstocks and greenhouse gases emission. Many chemicals production processes shift toward biomass-derived feedstocks in place of fossil resource in order to reduce carbon dioxide emissions [1,2]. Considerable developments have been reported in the use of ethanol as alternative motor vehicle fuels, fuel additives [3] or as a feedstock to produce hydrogen [4, 5] since it can be produced from agricultural raw materials such as sugar cane, starch, and lignocellulosic materials [6]. In the last decade, there is also growing interest in converting ethanol to value-added chemicals [7-9]. It can be used as a renewable feedstock for both the production of primary chemicals, such as ethylene, propylene, diethyl ether and 1,3-butadiene, as well as the production of oxygenated chemicals, such as 1-butanol, ethyl acetate, acetic acid, acetaldehyde and ketone [10-12]. This is because the process for converting ethanol to these chemicals is quite simple, non-corrosive, less toxic, and green technology. It always requires only ethanol as a feedstock [11].

Catalytic ethanol dehydration over solid acid catalysts such as alumina and zeolite can produce ethylene and diethyl ether depending on the reaction temperature [13]. This process occurs at lower reaction temperature than thermal cracking bringing about the reduction of energy cost of production. The production of ethylene from dehydration reaction has been applied at the industrial level using alumina as the catalysts [14]. Moreover, Fan et al. [10] reported that bioethanol can produce ethylene at the industrial level. The properties of catalysts and the reaction condition have an important effect on the pathway mechanism to produce the desire products. Many researchers have investigated several catalysts to increase desired products yield and decrease reaction temperature in order to make ethanol dehydration more industry-friendly [8-11,16].

Alumina-based catalyst is very interesting catalyst for the ethanol dehydration due to its high surface area, high thermal stability, fine particle size wide chemical and physical properties and inhibit side reaction [17]. The catalytic ethanol dehydration occurs via solid acid catalysts, where the acidity and acid strength are the key factor to impact the catalytic activity. The acid strength and concentration of alumina are low when calcined below 300°C, while calcination at 500°C decreases Bronsted acid site. The calcination temperature above 600^0C results in adjacent hydroxyl group form into water molecule [50]. Khom-in et al. [17] investigated activities of mixed γ- (gamma) and χ- (chi) phase alumina supports in dehydration reaction. They discovered that mixed γ- and χ-phase Al_2O_3 supports have higher activities towards dehydration reaction compared to single γ-Al_2O_3 or χ-Al_2O_3 supports.

There are very few researches dealing with alcohol dehydration in condensed phases using heterogeneous catalysts. The liquid-phase dehydration of ethanol is carried out at lower temperature than the gas-phase ethanol dehydration. Thus, it is more suitable for diethyl ether production than ethylene production because dehydration of ethanol to diethyl ether is exothermic. On the other hand, dehydration of ethanol to ethylene favored at moderate to high temperature because it is endothermic reaction. So, it is suitable for the gas-phase ethanol dehydration. There is report revealed that dehydration of linear alcohols to dialkyl ether performed in the liquid-phase of pure alcohols over solid acid catalysts shown ether selectivity and yields higher than 90% at temperature lower than in the gas-phase reaction [18]. It does not require the process to volatilize the liquid reactant resulting in the reduction of energy cost compared to the gas-phase reaction. In addition, the products with low boiling points such as diethyl ether or the gas-phase products formed in the liquid-phase ethanol dehydration can be easily separated from the reaction system.

This proposed research aims to develop the alumina-based solid acid catalysts for liquid-phase dehydration of ethanol that should have similar or higher ethanol conversion and yield of diethyl ether comparing to the results from gas-phase dehydration of ethanol. Since the ethanol dehydration in liquid phase performs at low temperature causing low ethanol conversion and diethyl ether yield, the chemical promoters are added into catalysts to improve the catalytic activity for diethyl ether production.

1.2 Literature review

1.2.1 Ethanol [3,5]

The chemical compound ethanol is also known as ethyl alcohol or grain alcohol with the chemical formula C_2H_5OH. The other names of ethanol are alcohol, ethyl alcohol and drinking alcohol. Pure ethanol is a flammable, easily soluble in water and good solvent. Ethanol can lose a proton from the hydroxyl group and very weak acid, weaker than water. The ethanol properties are shown in Table 1.

Table 1. Properties of ethanol.

Properties	Specification
Appearance	Colorless liquid
Molar mass	46.07 g/mol
Density	0.7893 g/cm^3 at 20 °C
Melting point	-114.5 °C
Boiling point	78.5 °C

Ethanol can be produced by the fermentation of renewable sources such as sugarcane, molasses and cassava roots. The ethanol compound is widely used as a chemical solvent, either for scientific chemical testing or in synthesis of other organic compounds and is an important chemical for producing many kinds of manufacturing industries. At present, Thailand has produced ethanol to be blended with gasoline called "gasohol" because the government has a policy to support the use of biofuels to replace fossil fuels such as the government to use money from the fuel fund for subsidy of gasohol E20 and gasohol E85 (20% and 85% ethanol mixtures, respectively). Several agricultural products such as sugarcane, starch, molasses, cassava, corn, lignocelluloses etc. can be used as raw materials for the production of bio-ethanol. The production process depends on raw materials used and fermentation process is usually applied. However, many countries such as Brazil and Thailand mostly use ethanol to blend with gasoline with highly ratio to be used as fuel for vehicles that causes of corrosion in engine. [4] Because ethanol blends with gasoline affect different engines in each model. There are 2 main issues: 1) Ethanol is a substance that has good moisture absorption properties. In the production, must avoid having to mix water because the amount of water that is mixed affects the poor mix of gasoline, causing it to not be able to use this fuel. 2) Fuel compatibility, especially with older cars found that corrosion and other damage in the fuel system cause damage to the engine.

However, Thailand Integrated Energy Blueprint or TIEB 2015 is under the Energy Efficiency Plan (EEP 2015) targets 1.2 million electric plug-in hybrid and electric vehicle batteries (BEV) by 2036. One of the policies to drive the plan such as electric vehicles (EV) that are promoted by the BOI, will receive excise tax reduction from 2% to 0% since 1 January 2020 until 31 December 2022, totaling 3 years to promote vehicle that are environmentally friendly faster.

In addition to ethanol blending in gasoline, ethanol is a substance that has economic value and can be converted into many valuable substances such as diethyl ether, ethylene, etc.

1.2.2 Ethanol dehydration

Ethanol consists of hydroxyl group in molecule. It can be dehydrated by using solid acid catalysts. In the catalytic dehydration of ethanol to form ethylene, an acid catalyst first protonates the hydroxyl group, which leaves as a water molecule. The conjugate base of the catalyst then deprotonates the methyl group, and the hydrocarbon rearranges into ethylene or diethyl ether. In addition to the main product of ethylene and the main byproduct of ether, the reaction of ethanol dehydration may also generate small number of byproducts such as acetaldehyde, hydrocarbons (methane, ethane, propylene) and etc. The reaction is endothermic, and because of this, the optimal reaction temperature is fairly high, ranging from 180 °C to 500 °C. Maintaining the reaction temperature constitutes much of the energy cost in industrial application of the reaction, since competing reactions into diethyl ether or acetaldehyde are favored outside of the temperature range and so decrease ethylene yield [10,19]. Among the secondary intermediates potentially obtainable by converting ethanol, ethylene and diethyl ether (DEE) can be obtained by catalytic dehydration using a solid acid catalyst upon reactions as follows [20];

$$C_2H_5OH \longrightarrow C_2H_4 + H_2O \qquad (1)$$

$$2C_2H_5OH \longrightarrow C_2H_5OC_2H_5 + H_2O \qquad (2)$$

$$C_2H_5OH \longrightarrow C_2H_4O + H_2 \qquad (3)$$

The first reaction (1) has already been applied at the industrial level in the 1960s using alumina as the catalysts [21]. The second reaction (2) occurs on the same catalysts under low temperature (below 240 °C) at moderate ethanol conversion, allowing very high selectivity and significant yields (>70%). In addition, acetaldehyde can be obtained by dehydrogenation of ethanol as seen in the third reaction (3).

The simplified reaction mechanism of ethanol catalytic conversion over mixed oxides is presented in Figure 1. Ethylene is formed by catalytic dehydration of ethanol which requires one ethanol molecule to generate carbocation during the reaction. First, the proton from acid catalyst protonates the hydroxyl group of ethanol molecule to remove the water molecule. Then, the conjugate base of the catalyst then deprotonates the methyl group, and the hydrocarbon rearranges into ethylene [10]. This reaction requires strong acid site or Brønsted acid site, and redox reaction leading to dehydrogenation rather than dehydration [22-24]. This is an easy reaction occurring typically in very mild conditions and the rate limiting step of the reaction is thus water desorption to regenerate the active site.

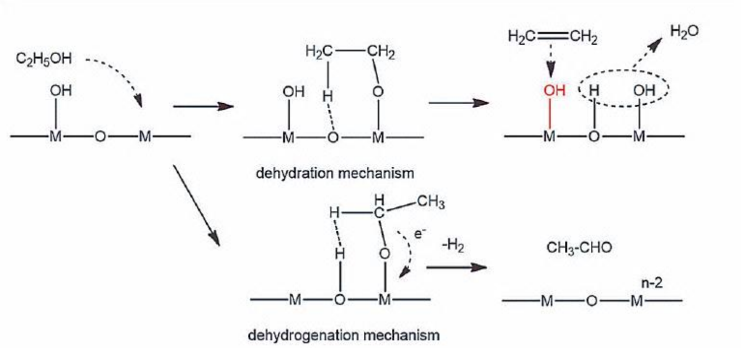


Figure 1. Simplified reaction mechanism of ethanol conversion over mixed oxide catalysts [25].

Most research performed the ethanol dehydration under gas-solid reaction using a packed-bed reactor [4,11,13]. However, gas-phase reaction for ethanol dehydration are performed at temperature higher than 473 K, and it requires the step for producing ethanol saturated vapor leading to high energy consumption [11,13]. Less abundant in the research are investigated in alcohol dehydration in condensed phases using heterogeneous catalysts. Ethanol is liquid phase, so liquid-phase reactions is more practical. Liquid-phase dehydration of alcohol can be achieved yield higher than 90% at temperature lower than gas-phase dehydration [20]. The liquid-phase dehydration of 1-pentanol to di-*n*-pentyl ether were studied experimentally over a commercial gel-type ion-exchange resin with 4% of cross-linking. Selectivity to ether higher than 96% were obtained at all the temperature range 120−150 °C [26]. The selective liquid-phase dehydration of 1-indanol to indene was successfully carried out over HMOR (dealuminated mordenite) and HZSM-5 zeolites, reaching indene yields higher than 90% at 363 K [27]. Moreover, the products with low boiling points such as diethyl ether or the gas-phase products formed in the liquid phase ethanol dehydration can be separated from the reaction system.

1.2.3 Catalyst for dehydration of alcohols

The most heterogeneous catalysts are solids that react with substrates in a liquid or gaseous reaction mixture. Diverse mechanisms for reactions on surfaces are well known, depending on how the adsorption step takes place. Many industrial catalysts are metals and the simple single crystals provide an introduction to the more atomic metal structures used in industrial catalysts. In general, the most crucial factor influencing the catalytic activities for dehydration of ethanol to ethylene appears to be the acidity. Many researchers have investigated to improve and develop the catalyst for many years. Over solid acid catalysts, reaction temperature and contact time play an important role in favoring one or the other dehydration reaction [21].

Alumina (Al_2O_3) is one of the most important chemical compounds used in a variety of applications. Because of its high attrition resistance, high chemical resistance, high thermal resistance and high dielectric strength, alumina is widely used in temperature or electrical resistance applications and also served as catalyst support for many industries [36]. Alumina has a white solid appearance, a molar mass of 101.96 g mol^{-1}, a density of 3.95-4.10 g cm^{-3} and insoluble in water, diethyl ether and ethanol. Alumina also has melting and boiling points of 2072°C and 2977°C, respectively.

Each metastable crystalline structure of alumina (η-, γ-, δ-, θ-, β-, κ-, χ, and α-alumina) depends on the calcination condition of the precursor hydroxide through the thermal dehydration reaction. The precursor includes gibbsite, boehmite, bayerite, nordstrandite and diaspore [37]. The phase transform of precursors into transition alumina is shown in Figure 2.

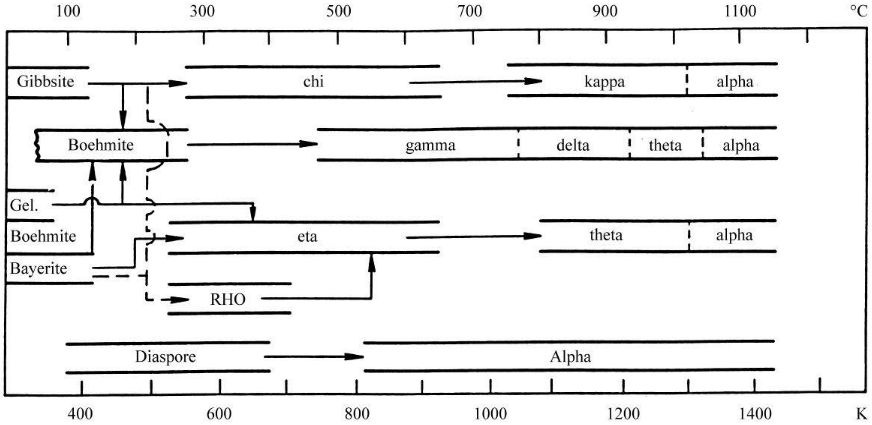


Figure 2. The sequence of aluminum hydroxide transformation [28].

Alumina has acid and basic sites on its surface. The acidity and basicity of alumina depend on the water treatment of alumina as depicted in Figure 3. When treated the alumina with the sufficient quantity of water, Al^{3+} ion in alumina converted Lewis acid sites into Brønsted acid sites, while the basic sites are determined from the O^{2-} anion [29].

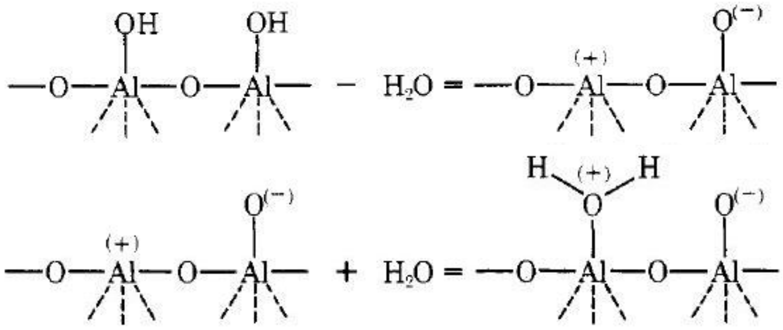


Figure 3. The effect of water addition on alumina acidity [29].

Alumina can be prepared by using various methods such as precipitation, sol-gel and solvothermal techniques [30]. Because of long synthesis time and complexity of precipitation and sol-gel techniques, the synthesis by solvothermal method was picked up as an interesting technique.

The solvothermal synthesis is a method for preparing various materials under high pressure. Solvothermal technique gains the advantage from sol-gel route in controlling of size, shape distribution and crystallinity of particle [17,19]. These characteristics can be modified, by changing experimental conditions (precursor type, solvent type, reaction temperature and reaction time). Because the operation must be carried in closed system with high pressure condition; therefore, stainless steel autoclave is usually used as the reactor.

Phung, T.K. et al. (2014) [31] investigated commercial transition alumina (γ-, δ-, θ-Al_2O_3 and different impurities Na^+, Cl^-) and of their catalytic activity in the dehydration of ethanol. The study found that Total conversion of ethanol with >99% selectivity to ethylene is achieved at 350 °C over the purer Al_2O_3 catalyst (θ-Al_2O_3 with Na < 0.002 wt%). The slightly lower activity on surface area basis of silica-alumina than alumina attributed to the lower density of Lewis acid sites and the absence of significant basicity.

Inmanee, T. et al. (2017) [32] investigated effect of calcination temperature and Mo modification on nanocrystalline (γ- χ)- Al_2O_3 catalysts for catalytic ethanol dehydration. It was found that increasing of calcination temperature resulted in decreased acidity, while the Mo modification on the mixed phase alumina catalyst yielded increased acidity, especially in medium to strong acids. The mixed phase alumina catalyst calcined at 600 °C exhibits the complete ethanol conversion having ethylene yield of 98.8% (at 350 °C) and the Mo-modified catalysts promoted dehydrogenation reaction to acetaldehyde.

Janlamool, J. et al. (2017) [33] reported catalytic ethanol dehydration to ethylene over nanocrystalline γ- and χ- Al_2O_3 catalysts. They were found that the high acid density apparently results in high catalytic activity, especially for the equally mixed 50 wt% of both γ- and χ- phase alumina (G50C50). The appearance of metastable χ- alumina structure exhibited better catalytic activity and ethylene yield than γ- alumina. The G50C50 catalyst exhibits the ethylene yield (80%) at the lowest reaction temperature ca. 250 °C while the G70C30 catalyst presences the diethyl ether yield (23%) at 200 °C.

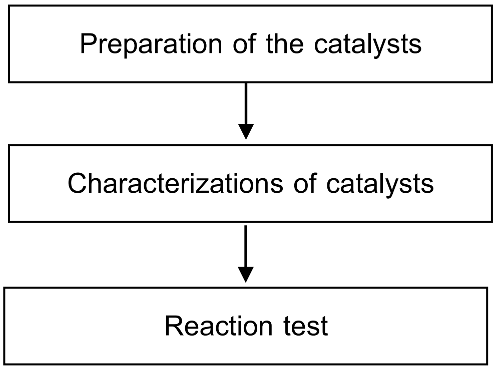
Khom-in, J. et al. (2008) [17] reported dehydration of methanol to dimethyl ether over nanocrystalline Al_2O_3 with mixed γ- and χ- crystalline phases. The γ- Al_2O_3, χ- Al_2O_3 and various mixed phase γ- and χ- Al_2O_3 concluded 0, 10, 20, 50, 80 and 90% χ- phase which all catalysts synthesized by solvothermal method. It was found that the 20 wt% χ- Al_2O_3 catalyst exhibited the highest yield for synthesis of dimethyl ether (86%) for dehydration of methanol reaction because it showed much higher density and strength of surface acidity.

Vanoye, L. et al. (2011) [18] investigated solvent effects in liquid-phase dehydration of ethanol to diethyl ether over heterogeneous sulfonic-acid catalysts that carried out in a stirred batch reactor. The composition of this liquid phase depends on bulk solvent properties. This study suggests that solvent effect should be consider in the modelling of etherification and could explain the discrepancy observed between models and experimental data obtained during liquid-phase formation to ether.

1.3 Objectives

This research was aimed to develop the alumina-based catalysts for the liquid-phase dehydration of ethanol in order to produce high-value chemicals at low or moderate temperature with high selectivity.

1.4 Methodology



1.4.1 Preparation of the catalysts

1.4.1.1 Synthesis of χ-alumina by solvothermal

Chi alumina was prepared via the solvothermal method following the procedure described by Janlamool et al. [43]. Firstly, aluminium isopropoxide was dissolved in 100 ml with toluene solvent in a test tube and 30 ml of toluene in the gap between the test tube and autoclave wall as a chi phase of alumina. The autoclave was heated up to 300 °C for 2 hours. Then, it was cooled down to room temperature. The powder was collected, washed many times with methanol, and separated by centrifugation. It was dried at room temperature. The synthesized chi alumina powder was calcined at 600 °C .

1.4.1.2 Preparation of mixed-phase alumina catalysts

The synthesized χ-Al_2O_3 was mixed with the commercial γ-Al_2O_3 catalysts using a physical mixed method as reported by Ngamposri et al. [44]. First, 1 g of mixed alumina with the weight ratio of 25:75 and 75:25 of the χ-Al_2O_3 and γ-Al_2O_3 was stirred in 20 ml of toluene by equipped with magnetic stirrer at room temperature for 30 minutes. The mixture was separated and washed with toluene. After that, it was dried under vacuum at room temperature, and was calcined at 600 °C for 6 hours in air to obtain the desired composition of γ-χ mixed-phase alumina catalysts.

1.4.2 Catalysts characterizations

N_2 physisorption (N_2 adsorption at -196 °C in a Micromeritics ASPS 2020) was performed to determine surface areas, pore size, pore volume and adsorption isotherm of the different alumina catalysts.

X-ray diffraction (XRD) using Bruker D8 Advance X-ray diffractometer with Cu-K_α radiation (λ = 1.54056 Å) with Ni filter in the range 2θ range of 20-80 degrees was performed to determine the phase composition of the different mixed phase alumina catalysts.

TEM (JEOL mode JEM 2100) was used to determine the morphology of all catalysts.

Temperature-programmed desorption of ammonia (NH_3-TPD) was used to investigate the total surface acidity of all catalysts using a Micromeritics Chemisorp 2750. In this experiment, 0.10 g of alumina was pretreated with helium flow 25 mL/min at 500 °C for 1 h (heating rate of 10 °C /min), and then the catalyst was adsorbed NH_3 at 30 °C for 1 h. Finally, the physisorbed NH_3 was desorbed under a He flow with heat temperature to 500 °C for 1 h. The amount of ammonia in effluent was measured via the thermal conductivity detector (TCD).

1.4.3 Reaction test

Catalytic dehydration of ethanol in liquid phase was carried out in batch stainless-steel autoclave as seen in Figure 4. The liquid phase reaction testing system is shown in Figure 9. First, 25 ml of ethanol and 1 g of catalyst were entered into the reactor. The autoclave was purged with nitrogen, after that it was pressurized to 20 bars with nitrogen at room temperature. Then, it was heated up to 200°C and pressurized up to 42 bar. The reaction was held for 2 hours. The reactor was cooled down to room temperature. All products and the remained reactant were analyzed by the Shimadzu GC8A gas chromatograph with flame ionization detector (FID) using capillary column (DB-5). The operating condition is also shown above.

Figure 4. The reaction system for liquid-phase dehydration of ethanol.

1.4.4 Analysis of data

The catalytic performance in ethanol dehydration reaction can be determined from ethanol conversion, product selectivity and product yield as shown below;

Ethanol conversion

$$\text{Ethanol conversion (\%)} = \frac{(\text{mole of ethanol feed}\times\text{initial volume})-(\text{mole of ethanol in product}\times\text{finally volume})}{(\text{mole of ethanol feed}\times\text{initial volume})}\times 100$$

Product Selectivity

$$\text{Product selectivity (\%)} = \frac{\text{mole of each product}}{\text{Total moles of product}}\times 100$$

Product yield

Product yield (%) = Ethanol conversion × Selectivity of each product

1.5 Schedule for the entire project

Activity	1st Year		2nd Year	
	1st half	2nd half	1st half	2nd half
(a) Literature reviews	■			
(b) Preparation of the catalysts	■			
(c) Characterizations of catalysts	■			
(d) Liquid-phase dehydration of ethanol test with and without solvent	■	■	■	■
(e) Data analysis		■		■
(f) Report writing		■		■
(g) Submission of international publication			■	

2. Results and discussion

2.1 Catalyst characterization

X-ray diffraction technique was used to determine the phase composition of the different mixed phase alumina catalysts. The XRD patterns of whole catalysts at diffraction angle (2θ) from 20° to 80° are shown in Figure 5. The characteristic of the gamma-alumina was located within the diffraction peak at 32°, 37°, 39°, 45°, 61° and 66°. Furthermore, the characteristic diffraction peak of the chi-alumina especially occurred at 43°. For all the γ-χ mixed phase alumina catalysts, they displayed both characteristic peaks of gamma and chi alumina. The peak intensity at 43° increased with increasing the ratio of chi alumina.

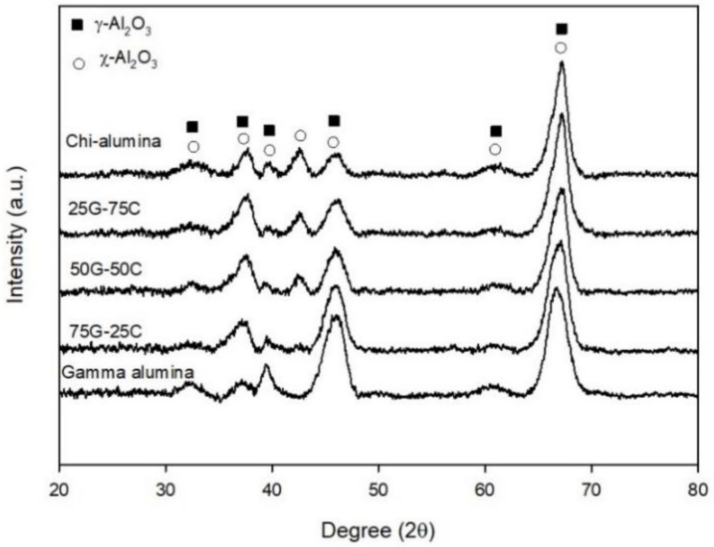


Figure 5. XRD pattern of the alumina-based catalysts.

The N_2 physisorption was performed to determine surface areas, pore size, pore volume and adsorption isotherm of the different alumina catalysts. The surface area, pore volume and pore diameter of all catalysts are shown in Table 2. Comparing between chi alumina and gamma alumina catalysts, the gamma alumina catalyst has higher surface area and pore volume, but the chi alumina catalyst has larger pore size diameter. The BET surface area and pore volume of alumina increased from 161.35 to 217.23 m^2/g and 0.50 to 0.68 cm^3/g, respectively when the content of gamma phase was increased. However, the average pore size diameter of mixed phase γ-χ alumina catalysts were around 9 nm.

Table 2. BET surface area, pore volume and pore diameter of the mixed-phase alumina catalysts

Catalysts	**BET surface area**[a] **A_{BET} (m^2/g)**	**pore volume**[b] **Vp (cm^3/g)**	**pore size diameter**[c] **D_{BJH} (nm)**
Chi alumina	161.35	0.50	8.06
25G-75C	160.54	0.58	9.42
50G-50C	157.63	0.60	9.66
75G-25C	188.94	0.66	9.30
Gamma alumina	217.23	0.68	7.39

[a] Determined from BET method

[b,c] Determined from BJH desorption method

In addition, the nitrogen adsorption-desorption isotherms of all studied catalysts are presented in Figure 6. It indicates that all catalysts exhibit the identical shape of type IV isotherms, referring to mesoporous structure as described by the IUPAC. The alumina-based catalysts also displayed the characteristics of a hysteresis loop obtained a range of high relative pressure (0.7-0.95), associating with capillary condensation of N_2 taking place in the presence of mesopores.

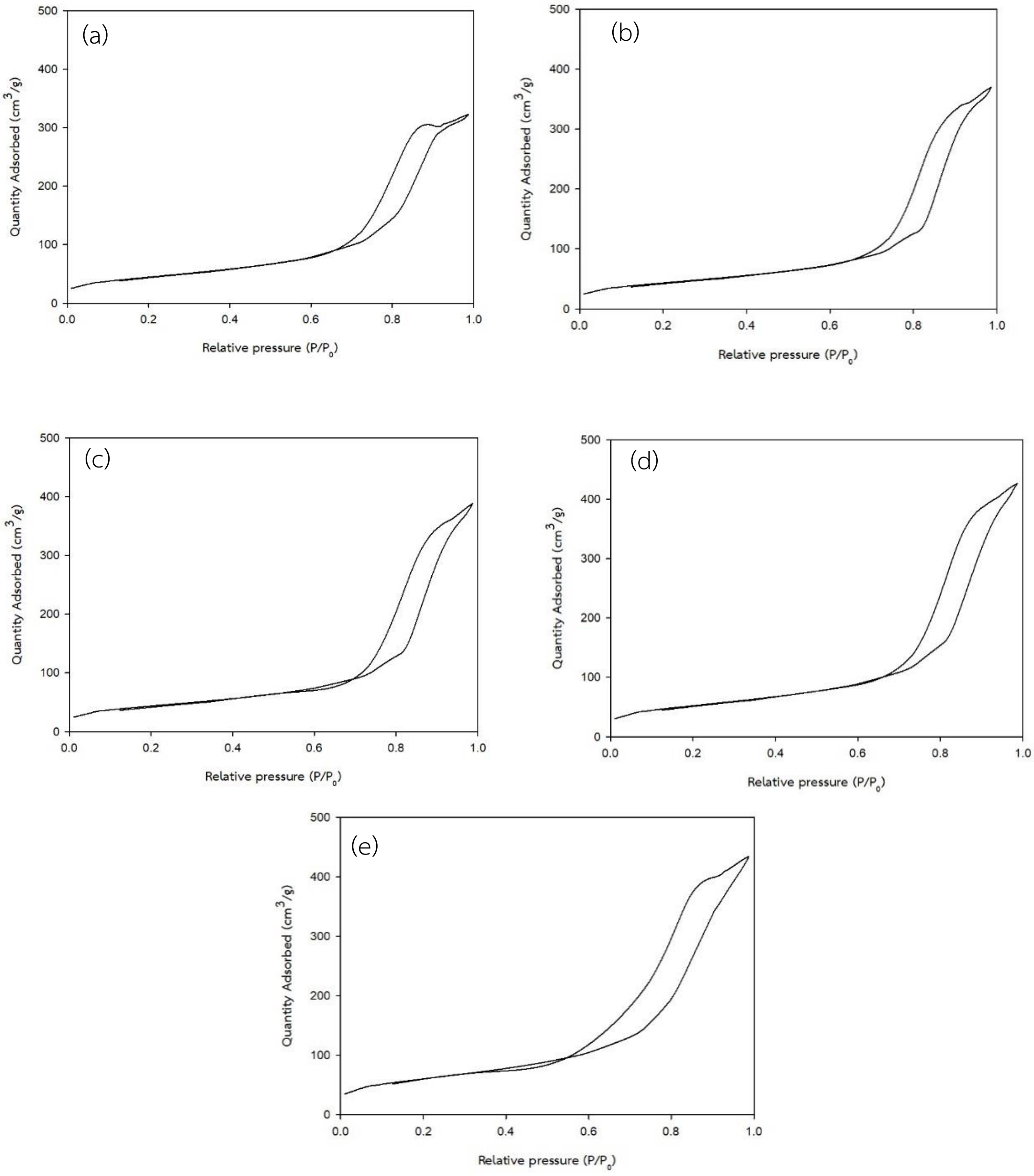


Figure 6. The N_2 adsorption-desorption isotherms of all catalysts (a) Chi alumina (b) 25G-75C (c) 50G-50C (d) 75G-25C and (e) Gamma alumina.

Transmission electron microscopy (TEM)

The identification of alumina phases presents and shape and size distribution of alumina-based catalysts were observed by transmission electron microscopy as shown in Figure 7.

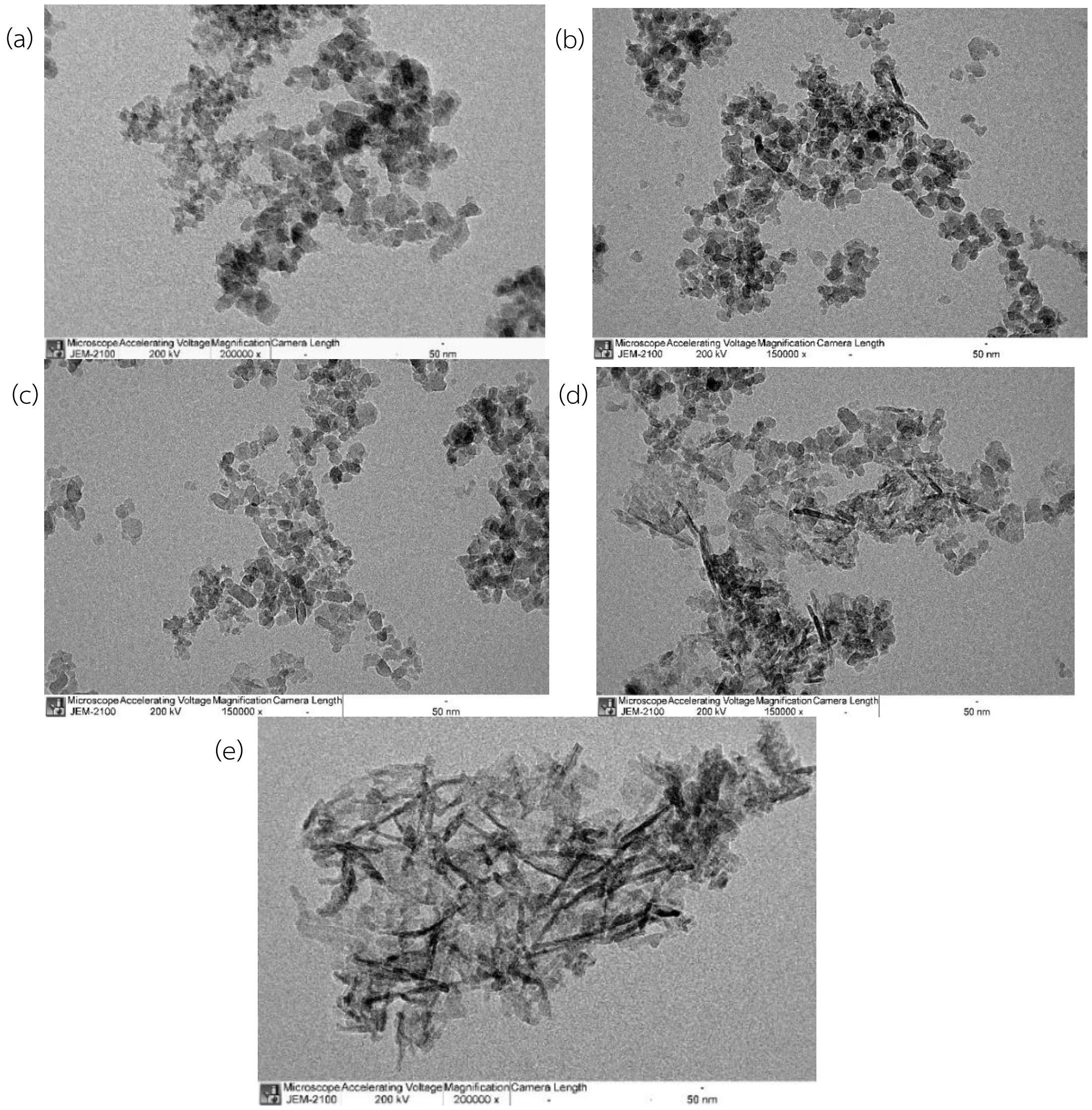


Figure 7. TEM images of all catalysts (a) Chi alumina (b) 25G-75C (c) 50G-50C (d) 75G-25C and (e) Gamma alumina.

The morphologies of the pure chi alumina and gamma alumina are completely different. The chi alumina seems to have a spherical shape while the gamma alumina looks like a rod particle. The mixed structures between the spherical particles of chi alumina and the rod particle of gamma alumina was observed for the mixed phase catalysts (Figure 7b-7d). However, catalyst particles of all catalysts are apparently agglomerated.

The temperature-programmed desorption of ammonia (NH_3-TPD)

Temperature-programmed desorption of ammonia was used to determine the acid strength and surface acidity of catalysts. The acid strength of all catalysts can be determined from the desorption temperature. The peak at temperature below 250°C relates to the weak acid site, while the peaks observed at 250-400°C and above 400°C relate to the acid site with moderate to strong strength, respectively.

From Table 3, it can be observed that the main acid sites of the catalysts, excepting commercial gamma alumina catalyst, were the moderate to strong acid sites. The chi alumina catalyst exhibited the highest moderate to strong acid site of 888.24 μmol NH_3/g. The total acid site of the catalysts was arranged in order from high to low, as follows: Chi alumina > 25G-75C > 50G-50C > 75G-25C > Gamma alumina. Additionally, an increasing of the gamma-alumina percentage resulted in an enhancement of weak acid sites, but the moderate to strong acid site was decreased.

Table 3. NH_3-TPD analysis of all catalysts.

Catalysts	**Acidity (μmol NH_3/g)**		
	Weak	**Moderate to strong**	**Total acid site**
Chi alumina	310.79	888.24	1199.03
25G-75C	257.13	747.28	1004.41
50G-50C	250.94	715.17	966.11
75G-25C	363.57	594.78	958.35
Gamma alumina	559.27	348.16	907.43

2.2 Reaction test

From Table 4, the gamma alumina had the least ethanol conversion (ca.25.58%). The 25G-75C catalyst had the highest ethanol conversion of 37.12%. The chi alumina catalyst gave the higher selectivity of DEE than the 25G-75C and 50G-50C catalysts. However, 100% selectivity of acetaldehyde was occurred from the liquid phase ethanol dehydration using the 75G-25C and gamma alumina catalysts.

The raising of gamma content in the mixed phase alumina catalysts resulted in the diminution of DEE yield. The moderate to strong acid site is selective for the diethyl ether production. The chi alumina catalyst showed the highest diethyl ether selectivity since it had higher amount of moderate to strong acid site. The 75G-25C and gamma alumina catalysts had higher surface area and pore volume. It seems that most active sites of the 75G-25C and gamma alumina catalyst are in the pores. However, the liquid phase dehydration of ethanol did not occur coke formation because low reaction temperature was used as noticed by the color of all catalysts did not change.

Table 4. Results of reaction test.

Catalysts	Conversion (%)	Selectivity (%)		Yield (%)	
		Acetaldehyde	**DEE**	**Acetaldehyde**	**DEE**
Chi alumina	35.57	0.43	99.57	0.15	35.42
25G-75C	37.12	28.16	71.84	10.46	26.66
50G-50C	31.53	16.69	83.31	5.31	26.21
75G-25C	32.14	100	0	32.14	0
Gamma alumina	25.58	100	0	25.58	0

In summary, the high amount of moderate to strong acid site can enhance the catalytic activity and DEE selectivity. Liquid phase ethanol dehydration with the chi alumina catalyst presented almost 100% of DEE selectivity. In contrast, the 75G-25C catalyst produced only the acetaldehyde at the highest acetaldehyde yield.

2.3 The solvents effect in liquid phase of ethanol dehydration reaction

Three solvents including heptane, toluene and chlorobenzene were used to investigate the solvent effect in the liquid phase ethanol dehydration. The commercial gamma alumina catalyst was selected to use in this part. The considering terms of catalytic activity consist of ethanol conversion and products selectivity as presented in Table 5.

It can be noticed that the reaction of the gamma alumina catalyst with or without solvents can produce only acetaldehyde. The addition of toluene or heptane resulting in an increasing of ethanol conversion. The gamma alumina catalyst with heptane has the highest ethanol conversion of 32.35%. However, the gamma alumina catalyst with chlorobenzene decreased the ethanol conversion to 14.81%. This indicates that too high dielectric constant (ε) of solvent obviously affected to have low activity in liquid phase dehydration of ethanol reaction. It is assumed that different dielectric constant of solvent can alter the electronic effects of active site formation or different in mass transfer in the reaction system.

Table 5. Results of reaction test.

Catalyst	Solvents	Conversion (%)	Acetaldehyde Selectivity (%)
Gamma alumina	-	25.58	100
	Toluene	30.43	100
	Heptane	32.35	100
	Chlorobenzene	14.81	100

3. Conclusion

In this research, characteristics and catalytic performance of various catalysts including chi alumina, mixed phase γ-χ-alumina and gamma alumina catalysts for the liquid phase of ethanol dehydration were investigated. Furthermore, the effect of solvent such as heptane, toluene and chlorobenzene in liquid phase of ethanol dehydration reaction were studied.

The catalytic performance was also investigated in liquid phase ethanol dehydration with reaction temperature at 200 °C for 2 hours and internal pressure up to 42 bars of the alumina-based catalysts. The chi alumina catalyst presented both acetaldehyde and DEE. It had the highest DEE yield of 35.42% while the 75G-25C and gamma alumina catalysts produced only the acetaldehyde. Moreover, the amount of acid site, mass transfer effect and diffusion of reactant are important for liquid phase dehydration of ethanol.

The addition of solvent in the liquid phase ethanol dehydration reaction resulted in an increasing of ethanol conversion because solvent can support the accessibility of reactant to active site on catalysts. Moreover, low dielectric constant of solvent obviously affected to have high activity. The gamma alumina catalyst with heptane has the highest ethanol conversion of 32.35% in liquid phase dehydration of ethanol reaction.

4. Recommendations

4.1 The pyridine-adsorbed IR spectra should be used to investigate types of acidity including Brønsted acid site and Lewis acid site.

4.2 The stability of all catalysts should be investigated for ethanol dehydration reaction in vapor phase.

4.3 Another condition reaction such as residence time, ethanol concentration, etc. at low reaction temperature for vapor and liquid phase ethanol dehydration should be studied.

4.4 The solvent effect with chi alumina and mixed phase γ- χ-alumina catalysts in liquid phase ethanol dehydration should be investigated.

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APPENDIX A

Calibration curve of Reactant and Product

The calibration curve was calculated by injection substance into GC-FID and detected by chromatogram in area of substance versus amount of injection substance. The calibration curve of reactant and product were shown in **Figure A1 - A4**.

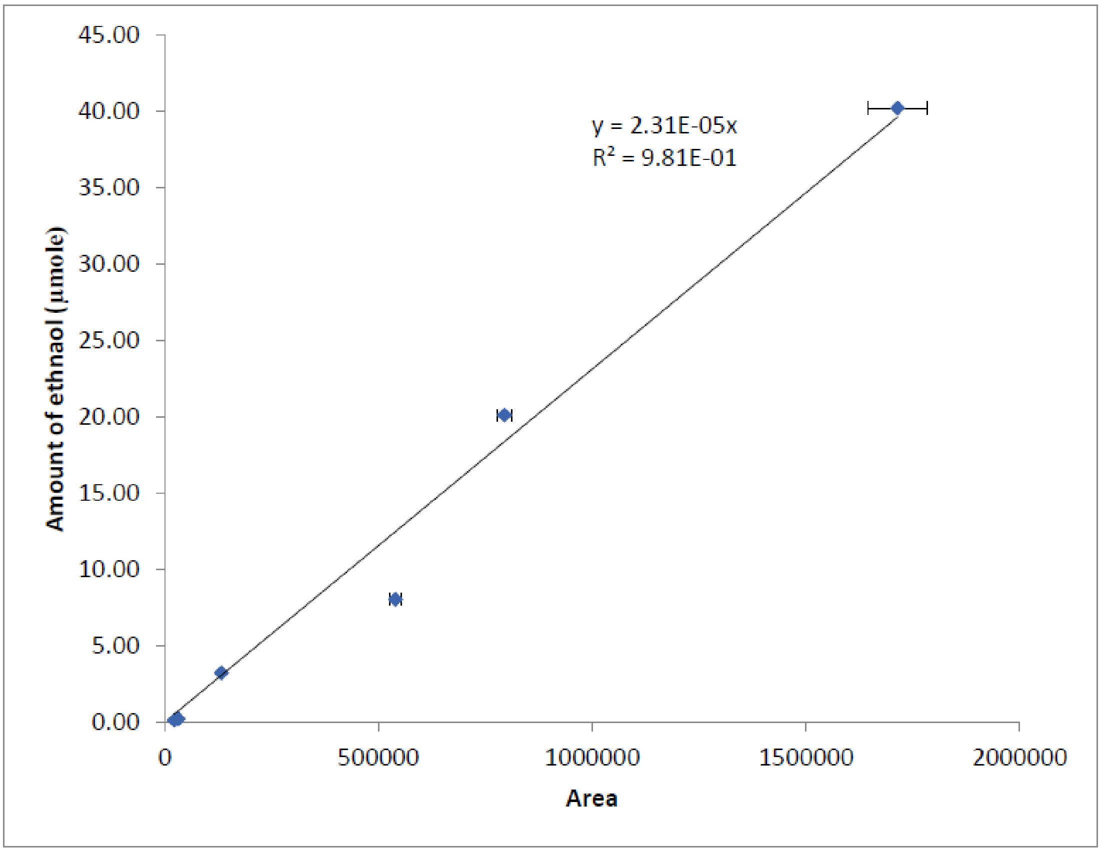

Figure A 1. The calibration curve of ethanol

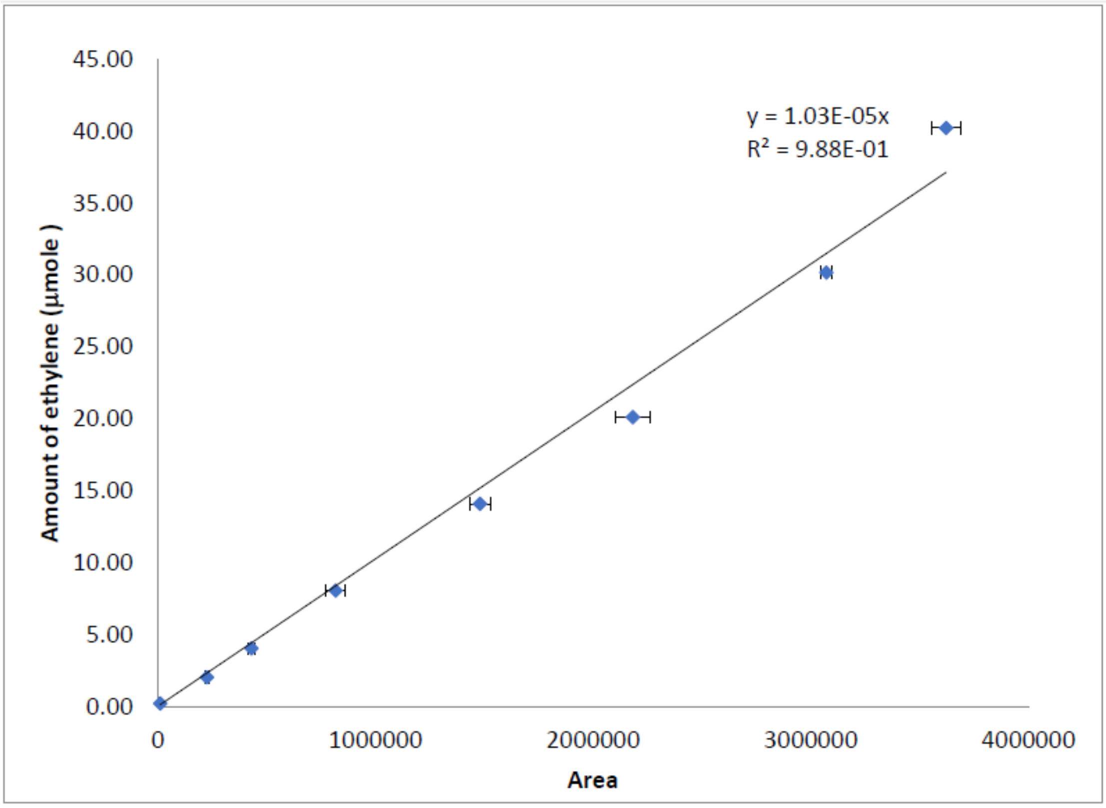

Figure A 2. The calibration curve of ethylene

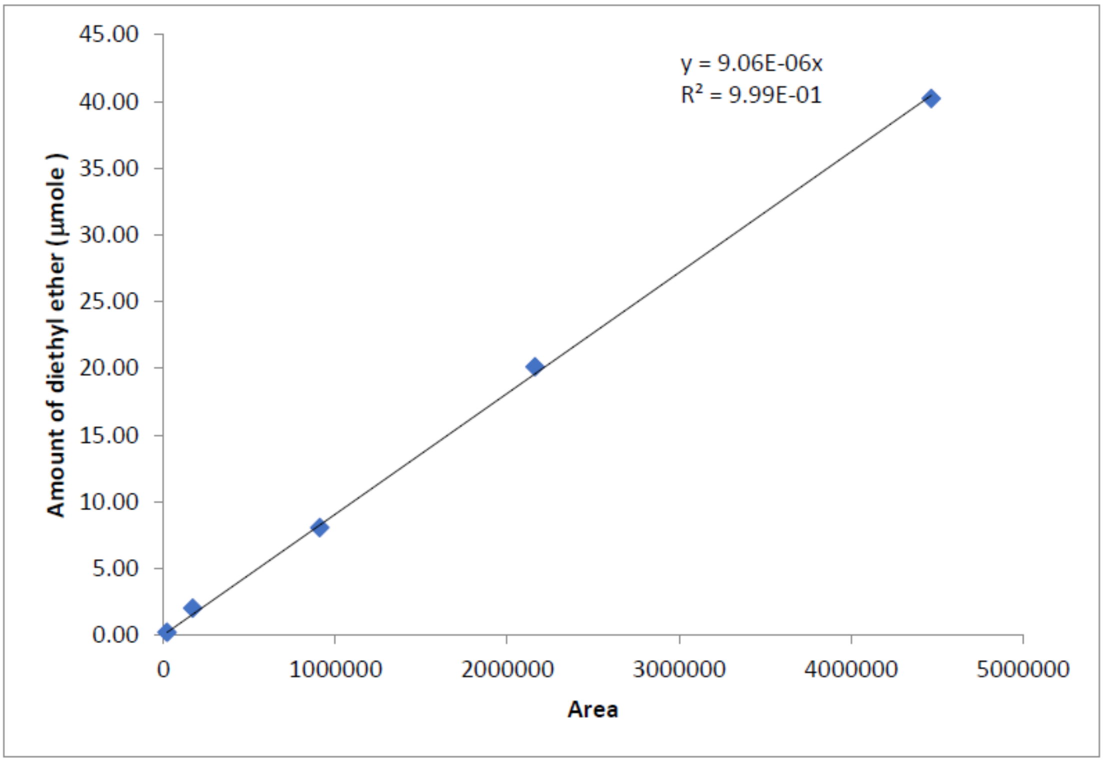

Figure A 3. The calibration curve of diethyl ether

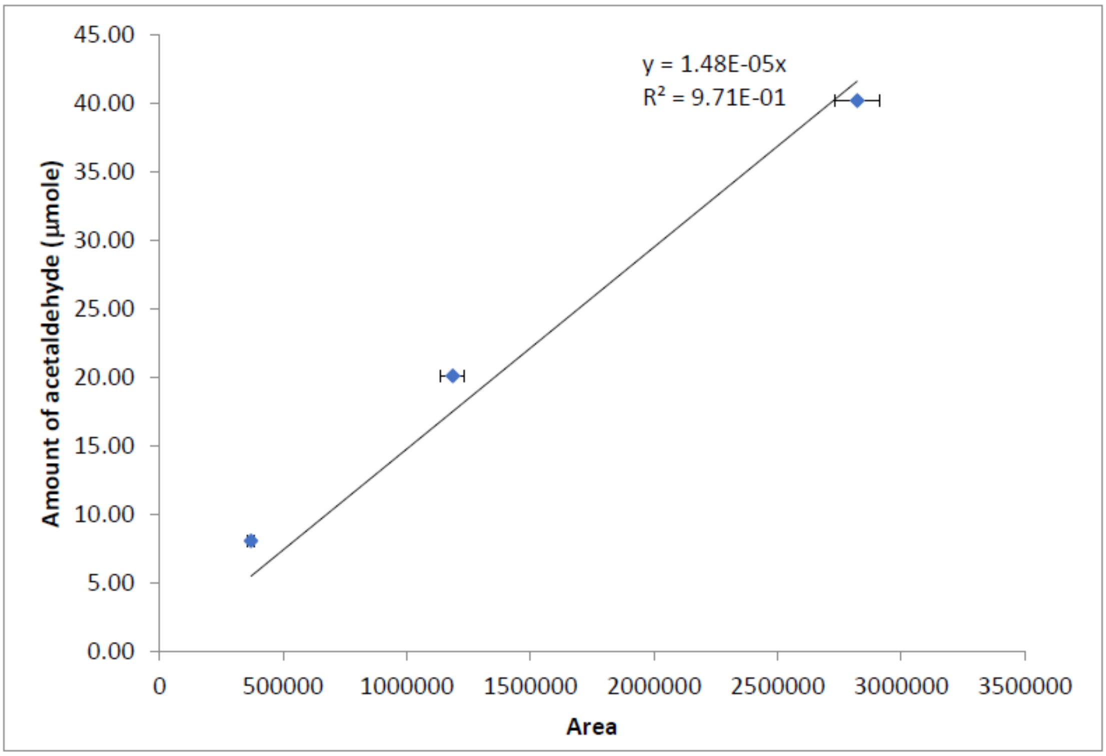

Figure A 4. The calibration curve of acetaldehyde