

การสังเคราะห์ไดเมทิลอีเทอร์จากปฏิกิริยาการขจัดน้ำจากเมทานอลโดยใช้ตัวเร่งปฏิกิริยา
 γ - Al_2O_3 และ γ - χ - Al_2O_3

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SYNTHESIS OF DIMETHYLETHER (DME) FROM DEHYDRATION OF
METHANOL USING γ - Al_2O_3 AND γ - χ - Al_2O_3 CATALYSTS

Miss Jutharat Khom-in

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จุฬารัตน์ ขอมอินทร์: การสังเคราะห์ไดเมทิลอีเทอร์จากปฏิกิริยาการขจัดน้ำจากเมทานอล โดยใช้ตัวเร่งปฏิกิริยา γ - Al_2O_3 และ γ - χ - Al_2O_3 (SYNTHESIS OF DIMETHYL ETHER (DME) FROM DEHYDRATION OF METHANOL USING γ - Al_2O_3 AND γ - χ - Al_2O_3 CATALYSTS) อ. ที่ปรึกษา: ศ.ดร. ปิยะสาร ประเสริฐธรรม, 106 หน้า

ศึกษาปฏิกิริยาการขจัดน้ำจากเมทานอลเกิดเป็นไดเมทิลอีเทอร์ด้วยแกมมาอะลูมินา ไคอะลูมินาและเฟสผสมระหว่างแกมมากับไคที่อัตราส่วนต่างๆกัน โดยมีขนาดอนุภาคระดับนาโน ลักษณะของตัวเร่งปฏิกิริยานำไปวิเคราะห์ด้วยการกระเจิงรังสีเอ็กซ์ การดูดซับทางกายภาพด้วยไนโตรเจน การส่องกราดด้วยกล้องจุลทรรศน์อิเล็กตรอน การคายแอมโมเนียด้วยการเพิ่มอุณหภูมิแบบตั้งโปรแกรม และการไทเทรตโดยการแลกเปลี่ยนไอออน ผลของการคายแอมโมเนียด้วยการเพิ่มอุณหภูมิแบบตั้งโปรแกรม และการไทเทรตโดยการแลกเปลี่ยนไอออน ในส่วนแรกพบว่าแกมมาอะลูมินาที่สังเคราะห์ขึ้นโดยวิธีโซลโวลูมอลมีความเป็นกรดมากกว่าแกมมาอะลูมินาทางการค้า และจากการศึกษาปฏิกิริยาพบว่าตัวเร่งปฏิกิริยาแกมมาอะลูมินาที่สังเคราะห์ขึ้นโดยวิธีโซลโวลูมอล ให้อัตราผลได้ของไดเมทิลอีเทอร์มากกว่า ในส่วนที่สองพบว่าอะลูมินาเฟสผสมที่อัตราส่วนไค 20% ที่สังเคราะห์โดยวิธีโซลโวลูมอล เพิ่มความเป็นกรดที่พื้นผิวของอะลูมินา และจากการศึกษาปฏิกิริยาพบว่าตัวเร่งปฏิกิริยาอะลูมินาเฟสผสมที่มีไค 20% ที่สังเคราะห์โดยวิธีโซลโวลูมอล ให้อัตราผลได้ของไดเมทิลอีเทอร์สูงสุดและมีความเสถียรในการสังเคราะห์ไดเมทิลอีเทอร์ และในที่สุดพบว่า อะลูมินาเฟสผสมที่อัตราส่วนไค 20% ที่สังเคราะห์โดยวิธีโซลโวลูมอลมีความเป็นกรดมากกว่าอะลูมินาเฟสผสมที่อัตราส่วนไค 20% ที่สังเคราะห์โดยวิธีการผสมทางกายภาพและจากการศึกษาปฏิกิริยาพบว่าตัวเร่งปฏิกิริยาอะลูมินาเฟสผสมที่อัตราส่วนไค 20% ที่สังเคราะห์โดยวิธีโซลโวลูมอลให้อัตราผลได้ของไดเมทิลอีเทอร์มากกว่า ดังนั้นตัวเร่งปฏิกิริยาที่เหมาะสม คือ ตัวเร่งปฏิกิริยาอะลูมินาเฟสผสมระหว่างแกมมากับไคที่อัตราส่วนไค 20% โดยสังเคราะห์จากวิธีโซลโวลูมอล

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JUTHARAT KHOM-IN: SYNTHESIS OF DIMETHYLETHER (DME) FROM DEHYDRATION OF METHANOL USING γ - Al₂O₃ AND γ - χ - Al₂O₃ CATALYSTS. THESIS ADVISOR: PROF. PIYASAN PRASERTHDAM, Dr.Ing., 106 pp.

Dehydration of methanol to dimethyl ether (DME) was investigated over nanocrystalline γ -Al₂O₃, χ -Al₂O₃ and mixed γ - and χ -crystalline phases with various ratios. The catalysts were characterized by X-ray diffraction (XRD), N₂ physisorption, NH₃-temperature programmed desorption (NH₃-TPD), and ion-exchange titration. Firstly, It was found that the NH₃-TPD results revealed that γ -Al₂O₃ with synthesized by solvothermal method had higher acidity than commercial exhibited the higher yield. Secondly, the NH₃-TPD and ion-exchange titration results revealed that the existence of 20 wt% χ -phase in γ -Al₂O₃ with synthesized by solvothermal method increased significantly both the density and the strength of surface acidity of alumina. γ -Al₂O₃ catalyst containing 20 wt% of χ -phase with synthesized by solvothermal method exhibited the highest yield (86%) with good stability for DME synthesis. Lastly, It was found that the NH₃-TPD and ion-exchange titration results revealed that 20 wt% χ -phase in γ -Al₂O₃ with synthesized by solvothermal method had higher acidity than 20 wt% χ -phase in γ -Al₂O₃ with synthesized by physical mixture method exhibited the higher yield. Therefore, the appropriate catalyst was 20 wt% χ -phase in γ -Al₂O₃ catalyst with synthesized by solvothermal method.

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CHAPTER I

INTRODUCTION

Dimethyl ether (DME) is a potential alternative fuel for future diesel engine operation because of its lower NO_x emission, near-zero smoke amounts, and lesser engine noise compared to conventional diesel oil [Fei et al. 2006, Xia et al. 2006, and Yaripour et al. 2005]. It can also be used to replace chlorofluorocarbons (CFCs) which destroy ozone layer of the atmosphere and used as an aerosol propellant, aided by its liquefaction property, such as hair spray and shaving cream [Jiang et al. 2004, Jun et al. 2002, Kim et al. 2006, Vishwanathan et al. 2004, Xia et al. 2006, and Xu et al. 1997].

Dimethyl ether can be produced by methanol dehydration over a solid acid catalyst or direct synthesis from syngas over a bifunctional catalyst [Fei et al. 2006, Fu et al. 2005, and Xia et al. 2006]. Methanol dehydration to dimethyl ether is a potential process and more favorable in views of thermodynamics and economy [Jiang et al. 2004 and Yaripour et al. 2005]. Such reaction occurs in different pathways on different type of solid-acid catalysts such as $\gamma\text{-Al}_2\text{O}_3$, HZSM-5, HY zeolite, silica-alumina, phosphorus-alumina, fluorinated alumina, etc. [Duarte de Farias et al. 2004, Fei et al. 2006, Fu et al. 2005, Jiang et al. 2004, Jun et al. 2002, Kim et al. 2006, Vishwanathan et al. 2004, Xia et al. 2006, Xu et al. 1997, and Yaripour et al. 2005].

Al_2O_3 is used as a common catalyst because of its fine particle size, high surface area, surface catalytic activity, excellent thermal stability, high mechanical resistance, and wide range of chemical, physical, and catalytic properties [Meephoka et al. 2008, Mekasuwandumrong et al. 2003, and Pansanga et al. 2008]. Among the various crystalline phases of Al_2O_3 , $\gamma\text{-Al}_2\text{O}_3$ has received much attention due to less generation of by product [Kim et al. 2006 and Xia et al. 2006]. In order improve the acidity of $\gamma\text{-Al}_2\text{O}_3$, addition of some dopants such as borate, silica, phosphorous, and fluorine has been studied [Duarte de Farias et al. 2004, Fu et al. 2005, Xia et al. 2006, Xu et al. 1997, and Yaripour et al. 2005].

χ -Al₂O₃ is one of the metastable polymorphs of transition alumina [Mekasuwandumrong et al. 2008] with relatively high acidity compared to γ -Al₂O₃. It can be prepared directly by solvothermal method using appropriate solvent. The advantages of the solvothermal method are given products with uniform morphology, well-controlled chemical composition, narrow particle size distribution, controlled crystal structures, and controlled grain sizes and morphologies can be controlled by process conditions such as solute concentration, reaction temperature, reaction time and the type of solvent [Pansanga et al. 2008].

This research studied dehydration of methanol to dimethyl ether by compared commercial γ -Al₂O₃ with synthetic γ -Al₂O₃ via solvothermal method. Nanocrystalline γ -Al₂O₃, χ -Al₂O₃, and mixed γ - and χ - crystalline phase Al₂O₃ with various χ/γ ratios were prepared by the solvothermal method evaluated in this reaction. The catalysts were also characterized by X-ray diffraction (XRD), N₂ physisorption, Transmission electron microscopy (TEM), NH₃-temperature programmed desorption (NH₃-TPD) and ion-exchange titration.

The objectives of this research are listed as following:

1. To compare between commercial γ - Al₂O₃ and synthetic γ - Al₂O₃.
2. To investigate nanocrystalline γ -Al₂O₃, χ -Al₂O₃, and mixed γ - and χ - crystalline phase Al₂O₃ with various χ/γ ratios via solvothermal method.
3. To compare between solvothermal method and physical mixture method of the best catalyst of all catalysts.
4. To study the effect of chemical and physical properties of all Al₂O₃ catalysts in methanol dehydration to dimethyl ether (DME). Effect of acidity on activity is subjected.
 - Crystallite size and phase identification are performed by X-ray diffraction (XRD).
 - Surface area is measured by Brunauer-Emmett-Teller (BET) method.
 - Pore distribution is measured by Barret-Joyner-Halenda (BJH) method.

- Morphology is illustrated by using a Transmission Electron Microscopy (TEM).
- Amount of acidity is determined by Ammonia Temperature-Programmed Desorption (NH₃-TPD) and Titration method involving ion exchange.

The present thesis is arranged as follows:

Chapter II reviews the literature.

Chapter III explains the basic theory about dimethyl ether (DME), synthesis of dimethyl ether (DME) and Al₂O₃ catalysts.

Chapter IV shows experimental systems and procedures for the preparation of Al₂O₃ catalysts by solvothermal technique and physical method.

Chapter V presents the experimental results and discussion.

In the last chapter, Chapter VI gives the overall conclusions of this research and recommendations for this work.

CHAPTER II

LITERATURE REVIEWS

2.1 Catalysts for methanol dehydration

There are several studies of solid-acid catalysts and modified γ - Al_2O_3 catalysts. Many researchers have been found better knowledge about high acidity in methanol dehydration to dimethyl ether. These reports are very useful and will use to develop works for the future.

Since 1997, Xu et al. [Xu et al. 1997] studied the catalytic conversion of methanol to dimethyl ether (DME) over a series of solid-acid catalysts, such as γ - Al_2O_3 , H-ZSM-5, amorphous silica-alumina, as well as titania modified zirconia. They were found that all the catalysts are active and selective for DME formation.

In 2002, Jun et al. [Jun et al. 2002] studied the conversion of methanol to dimethyl ether (DME) over γ - Al_2O_3 and modified γ - Al_2O_3 with SiO_2 , ZrO_2 , and B_2O_3 which were synthesized by impregnation method. They were found that the order of the activity at 5 wt% loaded of all catalyst was SiO_2/γ - $\text{Al}_2\text{O}_3 > \text{ZrO}_2/\gamma$ - $\text{Al}_2\text{O}_3 \approx \gamma$ - $\text{Al}_2\text{O}_3 > \text{B}_2\text{O}_3/\gamma$ - Al_2O_3 because SiO_2/γ - Al_2O_3 had the highest acidity and became rather hydrophobic resulting in the decrease of sorption capacity of water. Then, vary wt% loading of SiO_2/γ - Al_2O_3 was examined and found that the γ - Al_2O_3 modified with 1 wt% silica was more active and less deactivated by water.

In 2004, Duarte de Farias et al. [Duarte de Farias et al. 2004] evaluated $\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3$ catalysts which were synthesized by co-precipitation and impregnation methods applying two calcinations temperatures and boron loadings in methanol dehydration. Catalysts were analyzed by IR spectroscopy of pyridine and CO_2 adsorption. Results showed that boron addition to alumina causes a decrease of the number of basic and Lewis acid sites on alumina surface. It could also be observed an enhancement in acid strength of Lewis sites for impregnated samples. These results showed that boron did not have any promoting effect in methanol dehydration.

Next, Jiang et al. [Jiang et al. 2004] investigated methanol dehydration to dimethyl ether (DME) over ZSM-5 zeolites. Although the catalytic activity was decreased with an increase in silica/alumina ratio, the DME selectivity increased. H-ZSM-5 and NaH-ZSM-5 zeolites were more active for conversion of methanol to DME. Na⁺ ion-exchanged H-ZSM-5 (NaH-ZSM-5) showed higher DME selectivity than H-ZSM-5 due to eliminating of strong acid sites.

Then Vishwanathan et al. [Vishwanathan et al. 2004] studied a series of TiO₂-ZrO₂ mixed oxides with varying molar ratio of TiO₂ to ZrO₂ which were prepared by the co-precipitation method. The catalytic activities were investigated for the vapor phase dehydration of methanol to dimethyl ether (DME) in a fixed-bed reactor under atmospheric pressure. The acid-base properties and CH₃OH conversion activity are increasing with TiO₂ content and an optimum value is achieved for a molar ratio of Ti/Zr in the vicinity of 1/1. At lower reaction temperature (<300 °C), the selectivity for DME is nearly 100%. TiO₂-ZrO₂ catalysts show high stability against water during dehydration reaction.

And they [Vishwanathan et al. 2004] investigated a series of Na-modified H-ZSM-5 catalysts, with Na content varying from 0 to 80 mol%, which were prepared by an impregnation method tested for the dehydration of crude methanol (i.e. pure/anhydrous methanol containing 20 mol% of H₂O) in a fixed-bed micro-reactor under normal atmospheric pressure. Though the unmodified H-ZSM-5 catalyst was more active and stable in the presence of water, the Na-modified H-ZSM-5 catalysts showed the optimum activity (C_{MeOH} > 80%) and 100% selectivity for DME in a wide range of temperatures: 230–340 °C. The catalysts were tested for the time-on-stream (TOS) and remained least sensitive towards water for a total reaction period of 65 h. The superior performance of Na-modified H-ZSM-5 catalyst is attributed mainly to the elimination of strong surface acid-sites by partial substitution of Na in H-ZSM-5, resulting in the prevention of coke and/or hydrocarbon formation.

In 2005, Fu et al. [Fu et al. 2005] studied the nature, strength and number of surface acid sites of H-ZSM-5, steam de-aluminated H-Y zeolite (SDY), γ -Al₂O₃ and Ti(SO₄)₂/ γ -Al₂O₃ catalysts for the dehydration of methanol to dimethyl ether (DME). The H-ZSM-5 and SDY possessed strong Brønsted acidity and exhibited high activity

for the conversion of methanol to DME at relatively low temperatures. The coke was serious over the two zeolite catalysts at 553 K. The dehydration of methanol to DME on γ - Al_2O_3 was found to be low at the temperatures below 573 K though the DME selectivity is high. The modification of the γ - Al_2O_3 by $\text{Ti}(\text{SO}_4)_2$ greatly enhanced the surface Brønsted acidity and also the reaction activity for the dehydration of methanol to DME. In addition, no detectable hydrocarbon by-products and coke were formed on the $\text{Ti}(\text{SO}_4)_2/\gamma$ - Al_2O_3 catalyst in the temperature range of 513–593 K. Thus, the Brønsted acid sites with suitable strength may be responsible for the effective conversion of methanol to DME with high stability.

Next, Yaripour et al. [Yaripour et al. 2005] studied a series of solid-acid catalysts with different components contents which were prepared by co-precipitation (sol–gel) method comprised γ - Al_2O_3 and modified γ - Al_2O_3 with silica. Dehydration of methanol to dimethyl ether (DME) on solid-acid catalysts was studied in a fixed-bed flow reactor at a temperature of 300 °C under atmospheric pressure and a GHSV of 15,600 h^{-1} . According to the experimental results, the pure γ - Al_2O_3 catalyst shown a good catalytic activity, but this sample undergoes a fairly rapid and irreversible deactivation. Silica-modified catalysts have shown better performance compared to the untreated γ - Al_2O_3 . It was found that surface areas and surface acidity increase with increasing in the silica loading at aluminosilicate catalysts.

And they [Yaripour et al. 2005] investigated silica–titania and modified γ - Al_2O_3 with phosphorus which were prepared by co-precipitation (sol–gel) method studied in dehydration of methanol to dimethyl ether (DME). Silica–titania catalysts exhibited low activity for DME synthesis. Phosphorus-modified catalysts showed better performance compared to the untreated γ - Al_2O_3 . It was found that surface areas increased with increasing in the molar ratio of aluminum-to-phosphorus at aluminum phosphate catalysts. Also, it was observed that the surface acidity of aluminum phosphate catalysts decreased with increasing in the molar ratio of Al/P at aluminum phosphate catalysts. The sample of non-stoichiometric aluminum phosphate (molar ratio of Al/P = 2) exhibited the best conversion without any by-product.

Then in 2006, Fei et al. [Fei et al. 2006] examined synthesis of dimethyl ether (DME) via methanol dehydration over HY zeolite and over Fe-, Co-, Ni-, Cr-, or Zr-modified HY zeolite. Zr- and Ni-modified HY zeolite exhibited higher activity and stability for methanol dehydration, while Fe-, Co-, and Cr-modified HY zeolite deactivated quickly due to carbon deposition.

Next, Kim et al. [Kim et al. 2006] studied the effect of γ - Al_2O_3 as a binder on the catalytic performance of Na-modified ZSM-5 which was investigated by using the dehydration of methanol to dimethyl ether (DME). Though the addition of γ - Al_2O_3 lowered the activity of NaHZSM-5, it broadened the operative temperature range (OTR), thereby resulting in more stable catalysts. The ZSM-5 containing 70% of γ - Al_2O_3 was found to be an efficient catalyst, exhibiting quite high activity as well as wide OTR. This beneficial effect is ascribed to the adequate dilution of the strong acid sites of ZSM-5 in the γ - Al_2O_3 matrix.

Then, Xia et al. [Xia et al. 2006] studied fluorination by NH_4F solution which was used to modify the acidity of alumina. It was disclosed that both surface area and acidity of alumina were enhanced by the treatment with 0.1 mol/l NH_4F solution, while modification with more concentrated NH_4F solutions leads to the decrease in surface area of alumina and thereby weakens its acidity. The catalytic properties of these alumina samples were subsequently investigated in the production of DME. Sample treated by 0.1 mol/l NH_4F solution, performed best in methanol dehydration because of its strongest acidity.

From the literature described above, it can be concluded that the acidity of catalyst plays an important role on the catalytic activity for methanol dehydration. The higher acidity is, the higher the activity is however hydrocarbons are detected due to the strong acid sites. Therefore, DME formation is related to sites with weak and medium acidity or mild acidity.

2.2 Characterization and analysis

There are several studies of catalysts characterization and analysis of the reactant product. These reports are very useful and guideline for this work.

Ng [Ng 2002] studied the effects of drying on catalyst activities in methanol dehydration. A feed gas mixture consisting of 10% methanol balanced in helium was introduced into the top bed reactor, which was maintained at the reaction. Gaseous methanol was introduced into the system via an evaporator-condenser system and the methanol containing gas stream was preheated and then trace heated to avoid condensation. At the downstream of the reactor, trace heating was also applied to avoid liquid products condensation. A small fraction of the reactor effluent was piped to a G.C. for on-line analysis. The catalytic activity was calculated based on CH₃OH conversion or CH₃OCH₃ yield. Other compounds in the effluent stream (CO, CO₂, H₂O, CH₃OH and CH₃OCH₃) were analysed on-line with a Shimadzu 14B gas chromatograph with a TCD detector and a Porapak-Q column operating at 110 °C.

[López et al. 2007] The number of catalytically available acid sites was determined by titration, chemisorption, and elemental analysis methods. The titration technique involved an ion-exchange step, in which 0.2 g of catalyst was added to 10 mL of a 3.42 M aqueous solution of NaCl under stirring. After 30 h of ion exchange at 28 °C between the catalyst H⁺ ions and the Na⁺ ions in solution, the liquid was filtered off and titrated with a 0.05 N aqueous NaOH solution. The endpoint for titration was determined using a pH meter (pH 7) and corroborated using pH paper.

CHAPTER III

THEORY

3.1 Dimethyl ether: DME

Dimethyl Ether (DME) is an ether compound having a molecular structure in which one oxygen atom and two methyl groups are bonded. DME is a fuel which is pure and rich in hydrogen as the chemical structure ($\text{CH}_3\text{-O-CH}_3$) shows. DME is a gas looking colourless, smelling etheric at room temperature and under normal pressure, non-toxic, and good safety. DME is non-corrosive to metals, stable under high temperature or high humidity conditions, containing no chlorine fluoride hydrocarbon. It is a substitute for freon. Moreover, it is possible to treat as liquid at normal ambient temperatures as its boiling point is -25°C . In the case of burning DME, there are no emissions of SO_x or particulate and the emissions of NO_x , and CO_2 , which are causes of global warming, are extremely small. [Fujimoto 2004, Garimella et al. 2007, Mii et al. 2005, and Sudo 2002]

DME can be called the "Clean Energy Media in the 21st Century". DME is expected to be regarded as new energy, being available for various purposes such as an LPG alternative and clean fuel for power generation, a substitute to LNG, coal and petroleum, for diesel engines and fuel cells. [Fujimoto 2004].

3.1.1 Advantages of dimethyl ether (DME)

Table 3.1 shows the physical properties and characteristics of DME [Garimella et al. 2007]. The physical properties of DME are very attractive for a substitute of LPG, diesel oil etc. as a clean fuel without NO_x and particulate matter and DME is not corrosive for conventional construction materials [Mii et al. 2005]. On the other hand, DME has lower heating value, lower viscosity, lower lubricity and a tendency of swelling of specific rubber and specific plastics [Mii et al. 2005]. The many useful of dimethyl ether (DME) is shown in Figure 3.1 [Fujimoto 2004].

Table 3.1 Physical Properties and Characteristics of DME [Garimella et al. 2007].

Property	DME	Diesel	Methane (LNG)	Methanol	LPG
Formula	CH ₃ OCH ₃		CH ₄	CH ₃ OH	C ₃ H ₈
Boiling point, deg. C	-25	180-370	-162	65	-42
Liquid density, g/cm ³	0.66	0.84	0.42	0.79	0.49
Cetane Number	55-60	40-55	-	5	5
Explosion limits, %	3.4-18	0.6-6.5	5-15	5.5-26	2.1-9.4
Auto Ignition temperature, deg. C	235	250	650	450	
Heat of evaporation, kJ/kg	460 at -20°C and 410 at +20°C	250	-	1110	

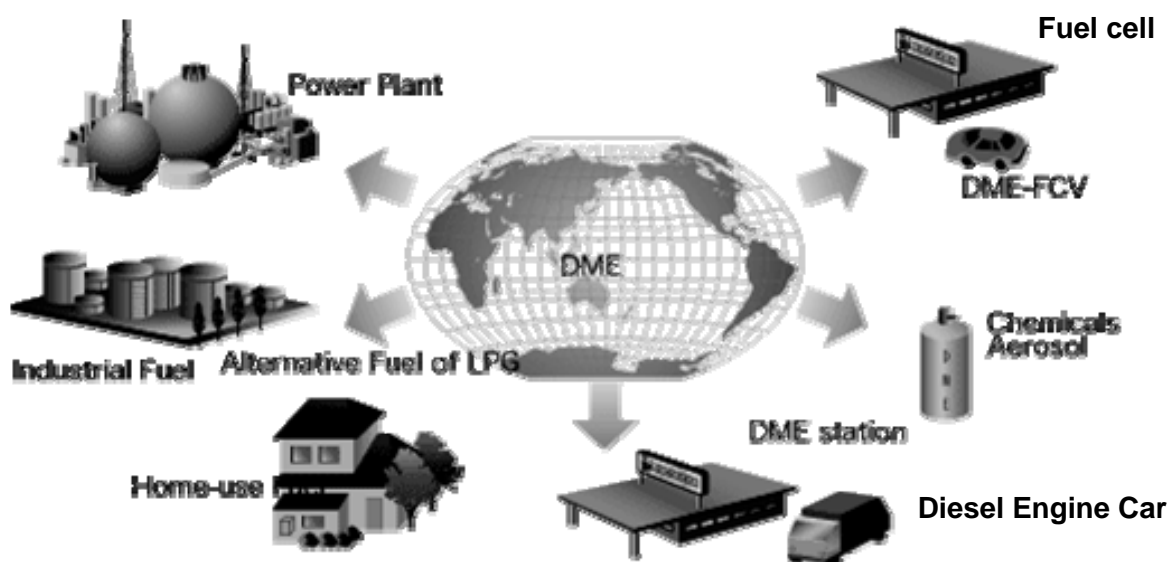


Figure 3.1 DME used as fuel [Fujimoto 2004].

DME is a clean fuel that never generates sulfur oxide and particulate when burned and can reduce environmental adverse effects. DME is a clean energy medium which can be mass produced from natural gas, coal bed methane, the synthetic gas produced by coal gasification and so on. Therefore, DME can be used as a fuel for thermal power generation. [Fujimoto 2004, Mii et al. 2005, and Sudo 2002].

DME cetane number being 55 – 60 is very similar to diesel oil [Fujimoto and Mii et al.]. The greatest advantage of DME when used as an automobile fuel is that its high cetane number makes it applicable to a diesel engine and being an oxygen containing fuel, it prevents a diesel engine from emitting soot and particulate matter to a greater extent than diesel fuel does. [Mauskar 2007 and Sudo 2002]

DME can also be used as an alternative fuel to LPG, because the toxicity to the human body is low and safety is high [Fujimoto 2004 and Mii et al. 2005].

DME is a new fuel as a safe, environmentally benign energy source for fuel cells. Consumption is expected as fuel for fuel cells as it is favorable on the heat balance and the reaction heat of DME reforming is low. [Fujimoto 2004 and Mii et al. 2005].

DME is currently used as a chemical for aerosol propellants in spray cans for the cosmetic industry etc. instead of chlorofluorocarbons [Mii et al. 2005].

DME can be blended up to 20% with LPG and used for household cooking and heating, without any modifications to equipment or used as a replacement [Garimella et al. 2007, Mii et al. 2005 and Sudo 2002].

3.1.2 Storage and the transportation of dimethyl ether (DME)

DME boiling point is below minus 25 °C and close to LPG, which is easily liquefied and stored. It is possible to change existing LPG storage and transportation facilities by only exchanging a few parts, because the boiling point is lower at -25°C and it can be liquefied at a pressure as low as 0.6 Mpa at normal temperatures [Fujimoto 2004].

3.2 Dimethyl ether (DME) production processes

The DME production processes are an indirect synthetic method using the dehydration reaction of methanol and a direct synthetic method of producing DME from synthetic gas made from coal, biomass, natural gas and so on. At present, DME is usually made by the indirect method and technology development for the direct synthetic method is being implemented [Fujimoto 2004].

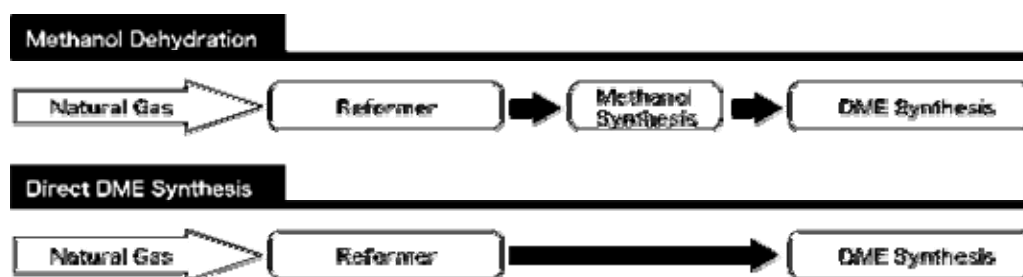


Figure 3.2 Schematic of DME production processes [Fujimoto 2004].

3.2.1 Methanol dehydration

DME for chemical use is currently produced by methanol dehydration process. The DME production by methanol dehydration is as follows Figure 3.3 [Fujimoto 2004].

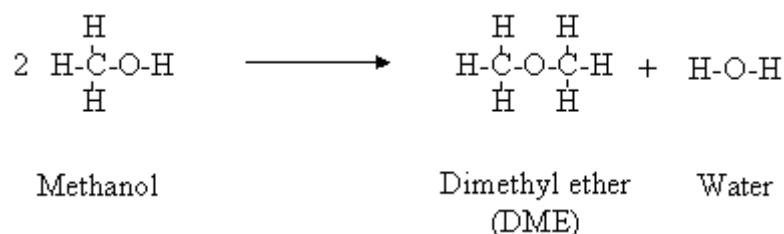


Figure 3.3 DME productions by methanol dehydration [Fujimoto 2004].

The gas phase exothermic reaction (heat of reaction= -22 kJ/mol) for the dehydration of methanol [Mii et al. 2005]. As shown in Figure 3.3, to produce 1 mol of DME, it is necessary for 1 mol of water to appear a by-product [Kim et al. 2006] Moreover, methanol can be reacted to produce other product as shown in Figure 3.4 [Techalertsuwan et al. 2005].

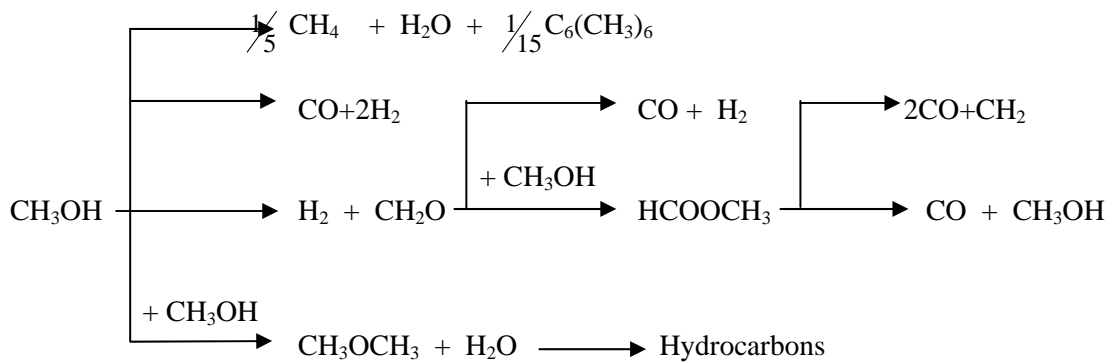


Figure 3.4 Other reaction from methanol [Techalertsuwan et al. 2005].

The reaction from methanol is as follows:

1. Decomposition of methanol to methane.
2. Decomposition of methanol to synthesis gas.
3. Dehydrogenation of methanol to formaldehyde and hydrogen. It also can be reacted with methanol to produce methylformate.
4. Dehydration of methanol to dimethyl ether and water. It also can be reacted to produce hydrocarbons.

The mechanism of dehydration of methanol to dimethyl ether over solid acid catalysts is shown in Figure 3.5 [Hattee 2003]. DME can be formed by protonation of hydroxyl group, coordination with Lewis site, cyclic transition state, and intermediate as methoxy species [Hattee 2003].

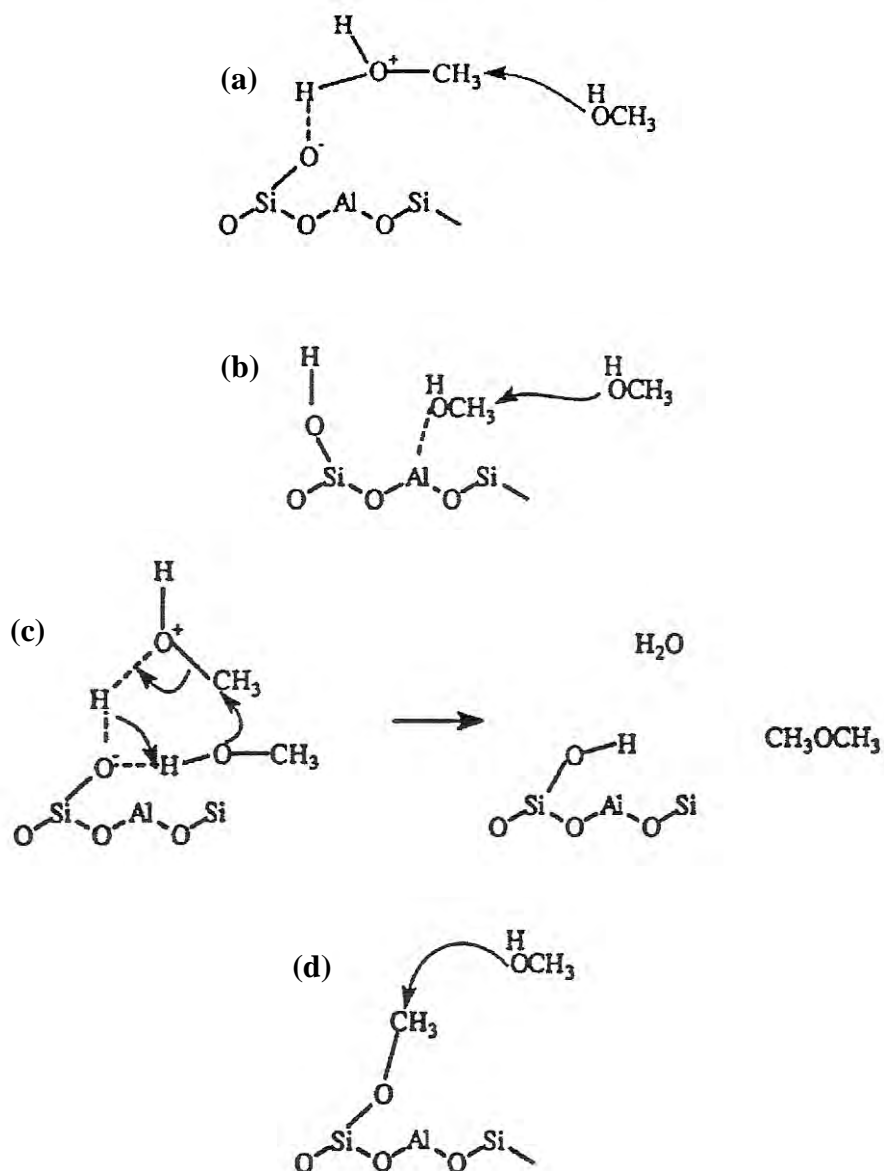


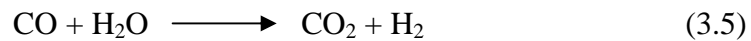
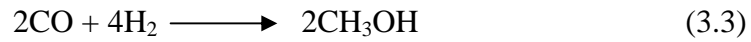
Figure 3.5 Mechanisms of Methanol dehydration to dimethyl ether over catalysts:

- (a) DME formation by protonation of hydroxyl group
- (b) DME formation by coordination with Lewis site
- (c) Cyclic transition state for DME formation
- (d) Methoxyl species as intermediate

[Hattee 2003].

3.2.2 Direct DME synthesis

The reaction formulas concerning DME synthesis are as follows [Ohno 2004 and Sudo 2002];



Reaction (3.1) synthesizes DME from synthesis gas (H_2 , CO) in three steps: methanol synthesis reaction (3.3), dehydration reaction (3.4), and shift reaction (3.5). When the shift reaction is slow, reactions (3.3) and (3.4) are combined into reaction (3.2). Overall, reaction is exothermic and the reaction heat at methanol synthesis step is dominant [Ohno 2004 and Sudo 2002].

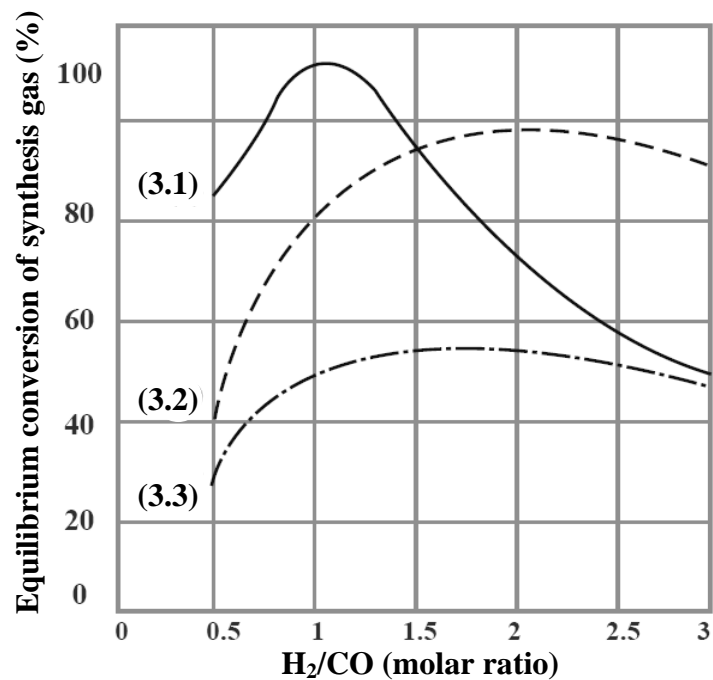


Figure 3.6 Equilibrium conversion of synthesis gas [Ohno 2004].

Figure 3.6 shows equilibrium conversion of synthesis gas (CO conversion plus H₂ conversion) for the two DME synthesis reactions, Formula (3.1) and Formula (3.2), and Formula (3.3) for the methanol synthesis reaction, as a function of hydrogen/carbon monoxide ratio (H₂/CO) of the synthesis gas. In each reaction, the equilibrium conversion has its maximum peak where the H₂/CO ratio correspond to the stoichiometric value, that is, with H₂/CO ratio of 1.0 for Formula (3.1) and 2.0 for both Formula (3.2) and (3.3). [Ohno 2004 and Sudo 2002].

When DME is synthesized by the reaction formula (3.1), it is possible to get H₂/CO=1 synthesis gas in an autothermal reformer with O₂ and by-product CO₂ from DME synthesis by the following reaction; [Ohno 2004 and Sudo 2002].



It is obvious that the reaction formula (3.1) is superior to the reaction formula (3.2) for equilibrium conversion of DME synthesis as well as for synthesis gas production. It depends on the catalyst characteristics which reaction, formula (3.1) or formula (3.2) is dominant. [Ohno 2004 and Sudo 2002].

3.3 The Aluminas

3.3.1 Properties of aluminas

Alumina which is Al₂O₃ in general form is a polymorphic material. Alumina can be easily synthesized small particles and obtained desirous surface area and pore distribution. Commercial alumina have surface area between 100-600 m²/g. High porosity solid cause high intra surface area, good metal dispersion and increasable effective of catalytic. There are many forms of alumina (α-, γ-, δ-, η-, κ-, χ-, θ-, ρ-, and ι- Al₂O₃) but the α- Al₂O₃ is the only stable form. The thermodynamically stable phase is alpha alumina (α- Al₂O₃, corundum) where all Al ions are equivalent in octahedral coordination in a hep oxide array. α- Al₂O₃ (corundum) powders are applied in catalysis as supports, for example, of silver catalysts for ethylene oxidation to ethylene oxide, just because they have low Lewis acidity, low catalytic activity, and

conversely, they are mechanically and thermally very strong. All other alumina polymorphs are metastable. [Evans 1993].

The other forms are frequently termed 'transition' aluminas. These transition aluminas are frequently termed 'activated' or 'active' aluminas. ρ - Al_2O_3 is amorphous but the other forms have reasonably well-defined X-ray diffraction patterns. The activated aluminas use as an adsorbent. Even though the surface of an activated alumina has a strong affinity for water, it makes very effective as a desiccant. Activated alumina can be used for removing water from a very wide range of compounds including acetylene, benzene, alkanes, alkenes and other hydrocarbons, air, ammonia, argon, chlorinated hydrocarbons, chlorine, natural gas and petroleum fuels, oxygen, sulfur dioxide and transformer oils [Evans 1993].

Activated alumina can dry a gas to a water content lower than that achievable with any other commercially available desiccant. In addition to water removal, activated alumina can be used selectively to adsorb certain other chemical species from gaseous or liquid streams. Polar molecules such as fluorides or chlorides are readily adsorbed and so activated alumina is used in petroleum refining to adsorb HCl from reformed hydrogen and organic fluorides from hydrocarbons produced by the HF-alkylation process [Evans 1993].

Activated aluminas find widespread application as both catalysts in their own right and as catalyst substrates. The more significant applications are summarized as the Claus catalyst for the removal of the hydrogen sulfide in natural gas processing, petroleum refining and coal treatment, as alcohol dehydration to give olefins or ethers, as hydrotreating to remove oxygen, sulfur, nitrogen and metal (V and Ni) impurities from petroleum feedstocks and to increase the H/C ratio, as reforming catalysts: Pt and Re catalysts on a γ - Al_2O_3 substrate are used to raise the octane-number of petrol, as automotive exhaust catalysts [Evans 1993].

Activated alumina has a surface with both Lewis and Bronsted acidic and basic sites. Acidity is derived from the Al^{3+} ions and H_2O molecules coordinated to

cationic sites, while basicity is due to basic hydroxide groups and O^{2-} anion vacancies [Evans 1993].

If alumina contact to humidity, surface are adsorped water molecules and when alumina were dried at 100 °C to 150 °C, water molecules are desorbed but remain hydroxyl group (-OH) cause acidity of alumina are weak Bronsted acid. (Figure 3.7) Calcination temperatures below 300 °C, the acid strength and concentration of alumina are low and at 500 °C reduce Bronsted acid sites. [Wittayakhun et al. 2004]

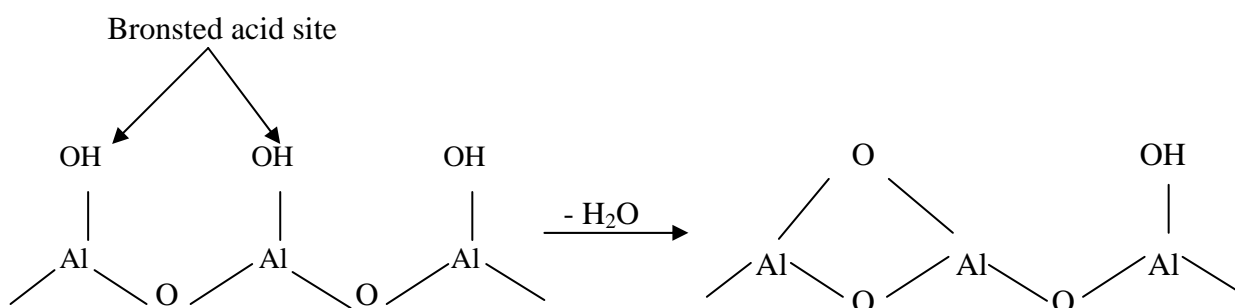


Figure 3.7 Desorption of water from alumina surface [Wittayakhun et al. 2004].

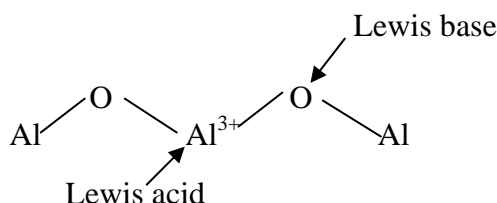


Figure 3.8 Lewis acid and Lewis basic sites on alumina [Wittayakhun et al. 2004].

As shown in Figure 3.8, further increasing temperatures above 600 °C, adjacent -OH combine and more emit H_2O and contribute to Al^{3+} are Lewis acid sites and O^{2-} are Lewis basic sites. Hardness of surface bring about no reaction between Lewis acid and Lewis base which both sites have high activity in various reaction such as Dehydration of alcohol and Isomerization of alkene. The decline in acidity for calcination temperatures above 800 °C can be attributed to the collapse in surface area as the alumina is converted to its alpha form [Wittayakhun et al. 2004].

3.3.1.1 Properties of γ - Al_2O_3 [Fierro et al.2006]

γ - Al_2O_3 which is the most used form of alumina in industry and any field of technologies is mostly obtained by decomposition of the boehmite oxyhydroxide γ - AlOOH (giving medium surface area lamellar powders, $\sim 100 \text{ m}^2/\text{g}$) or of a poorly crystallized hydrous oxyhydroxide called “pseudoboehmite” at 327 to 527 °C, giving high surface area materials ($\sim 500 \text{ m}^2/\text{g}$). However, the details of its structure are still matter of controversy. It has a cubic structure described by Lippens [Fierro et al. 2006] and de Boer [Fierro et al. 2006] to be a defective spinel, although it can be tetragonally distorted. Being the stoichiometry of the “normal” spinel MgAl_2O_4 (with Al ions virtually in octahedral coordination and Mg ions in tetrahedral coordination) the presence of all trivalent cations in γ - Al_2O_3 implies the presence of vacancies in usually occupied tetrahedral or octahedral coordination sites. Soled proposed that the cation charge can be balanced, more than by vacancies, by hydroxyl ions at the surface. In fact, γ - Al_2O_3 is always hydroxylated; dehydroxylation occurring only at a temperature where conversion to other alumina forms is obtained. XRD studies using the Rietveld method, performed by Zhou [Fierro et al. 2006] and Snyder [Fierro et al. 2006], suggested that Al^{3+} cations can be in positions different from those of spinels, that is, in trigonal coordination. The possibility of a structure of γ - Al_2O_3 , as “hydrogen-spinel” has been proposed based on IR spectroscopy. Calculations based on the composition HAl_5O_4 have been performed but found that this structure is very unstable. Sohlberg et al. [Fierro et al. 2006] arrived to a structure very similar to that proposed by Zhou [Fierro et al. 2006] and Snyder [Fierro et al. 2006], based on spinel but with occupation of extraspinel sites. On the contrary, Digne et al. [Fierro et al. 2006] and Krokidis et al. [Fierro et al. 2006] proposed a structure based on ccp oxide lattice but different from that of a spinel, with 25% of Al ions in tetrahedral interstice and no structural vacancies. According to these authors, this structure, although unstable with respect to corundum, is more stable than that of the spinel based structures. γ - Al_2O_3 is also active as an acidic catalyst. As for example it is very active in the dehydration of alcohols to olefins and to ether as well as both in double bond isomerization and in skeletal isomerization of olefins.

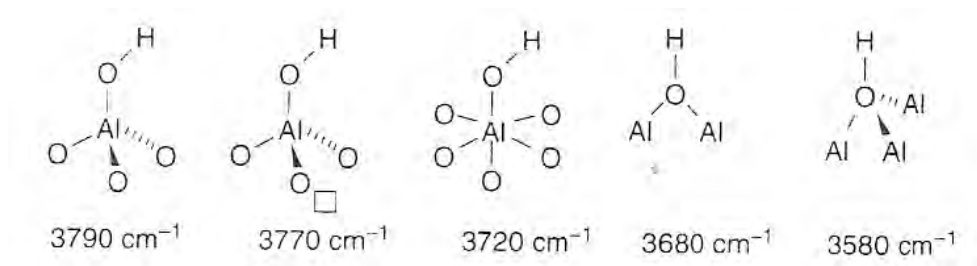


Figure 3.9 Assignment of the OH stretchings of transitional aluminas, following Busca et al., based on the comparison with the spectra of nondefective and partially defective spinel aluminates and ferrites. The square represents a vacancy in a normally occupied position of stoichiometric spinels [Fierro et al. 2006].

In Figure 3.9 the assignments of the five main νOH bands of the surface hydroxyl groups of transitional aluminas proposed by Busca et al. [Fierro et al. 2006]. The catalytic activity of transitional aluminas are undoubtedly mostly related to the Lewis acidity of a small number of low coordination surface aluminum ions, as well as to high ionicity of the surface Al-O bond. The alumina's Lewis sites have been well characterized by adsorption of probes such as pyridine, carbon monoxide, and several bases followed by IR, ammonia and amines followed by calorimetric, triphenylphosphine followed by ^{31}P NMR, to be the strongest among metal oxides, only weaker than those of Al halides. Volumetric, TPD and calorimetric experiment allowed also to determine the amount of such very strong Lewis sites present on transitional alumina surfaces, which however depend on the dehydroxylation degree (depending on the activation temperature) and the peculiar phase and preparation [Fierro et al. 2006].

3.3.2 Preparation of Al_2O_3 by solvothermal method

The synthesis method for producing Al_2O_3 has many methods, which are under intensive worldwide investigation for powder preparation.

Solvothermal method has been developed from hydrothermal method for synthesis of metal oxide and binary metal oxide, by using solvent as the reaction medium under pressure and at temperatures above its normal boiling point [Wiwattanapongpan 2004]. The advantages of the solvothermal method are given products with uniform morphology, well-controlled chemical composition, narrow particle size distribution, controlled crystal structures, and controlled grain sizes and morphologies can be controlled by process conditions such as solute concentration, reaction temperature, reaction time and the type of solvent [Pansanga et al. 2008]. The preparation method is described in the experimental section, Chapter IV.

CHAPTER IV

EXPERIMENTAL

This chapter consists of experimental systems and procedures used in this work which is divided into five parts. The chemicals and equipment for preparation and reaction are shown in section 4.1 and section 4.2, respectively and the preparation of Al_2O_3 catalysts are shown in section 4.3. Section 4.4 describes the details of catalyst characterization by various techniques such as X-ray diffraction (XRD), N_2 physisorption, Transmission Electron Microscopy (TEM), Ammonia temperature-programmed desorption (NH_3 -TPD), and Titration method involving ion exchange. The last part (section 4.5) describes the catalytic test in methanol dehydration to dimethyl ether (DME).

4.1 Materials and Chemicals

The commercial γ - Al_2O_3 catalyst is from JRC.

The details of chemicals for preparation of various phases Al_2O_3 catalysts and catalytic reaction are as follows:

1. Aluminum Isopropoxide: AIP, ($[(\text{CH}_3)_2\text{CHO}]_3\text{Al}$) from Aldrich
2. 1-Butanol, ($\text{C}_4\text{H}_9\text{OH}$) from Fluka
3. Toluene, ($\text{C}_6\text{H}_5\text{CH}_3$) from Fisher Scientific
4. Methanol, (CH_3OH) from Merck
5. Nitrogen, (N_2) from TIG
6. Helium, (He) from TIG

4.2 Equipment

4.2.1 The equipment for the synthesis of alumina by solvothermal method consisted of:

4.2.1.1 Autoclave reactor

- Made from stainless steel.
- Pressure gauge was connected.
- Relief valve used to prevent runaway reaction.
- Test tube was used to contain the reagent and solvent.

Autoclave reactor used for the experiment is shown in Figure 4.1.

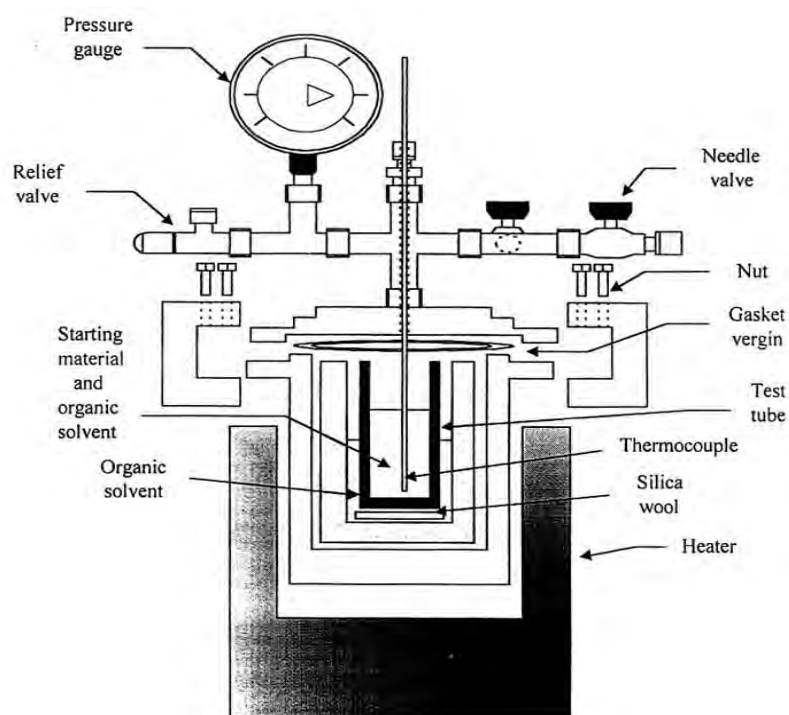


Figure 4.1 Autoclave reactor

Experiments

- Thermocouple is attached to the reagent in the autoclave.
- Amount of starting material = 15 g
- Amount of organic solvent in the test tube = 100 ml and amount of organic solvent in the gap between test tube and autoclave wall = 30 ml

4.2.1.2 Temperature program controller

A temperature program controller was connected to a thermocouple attached to the autoclave.

4.2.1.3 Electrical furnace (Heater)

Electrical furnace supplied the required heat to the autoclave for the reaction.

4.2.1.4 Gas controlling system

Nitrogen was set with a pressure regulator (0-150 bar) and needle valves were used to release gas from autoclave.

The diagram of the reaction equipment for the synthesis of catalyst is shown in Figure 4.2

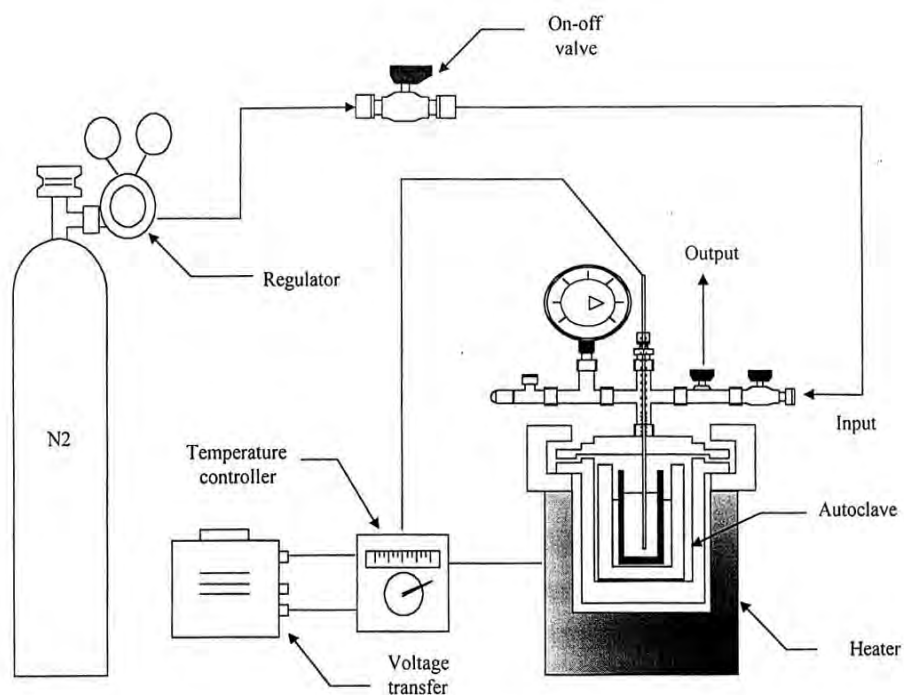


Figure 4.2 Diagram of the reaction equipment for the synthesis of catalyst.

4.2.2 The equipment for the synthesis of alumina by physical mixture method consisted of:

4.2.2.1 Magnetic stirrer and heater

The magnetic stirrer and heater (Figure 4.3) model RTC basis from IKA Labortechnik were used.

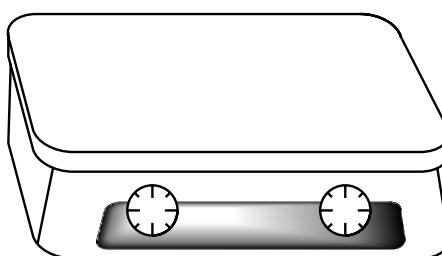


Figure 4.3 Magnetic stirrer and heater

4.2.2.2 Schlenk tube

Schlenk tube (Figure 4.4) was a tube with a ground glass joint and side arm, which was three-way glass valve. Sizes of Schlenk tubes which were 50, 100 and 200 mL were used to prepare catalyst

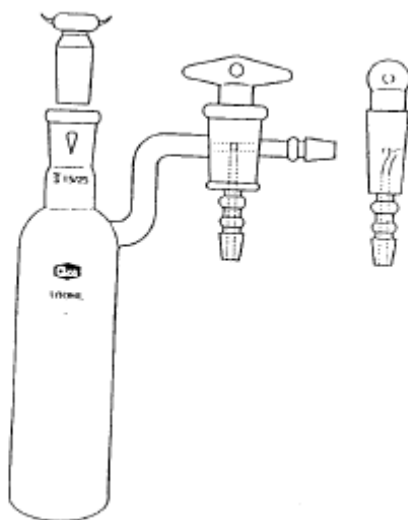


Figure 4.4 Schlenk tube

4.2.2.3 Vacuum pump

The vacuum pump model 195 from Labconco Corporation was used. A pressure of 10^{-1} to 10^{-3} mmHg was adequate for the vacuum supply to the vacuum line in the Schlenk line.

4.2.2.4 Schlenk line

Schlenk line (Figure 4.5) consists of vacuum and argon lines. The vacuum line was equipped with the solvent trap and vacuum pump, respectively. The argon line was connected with the trap and the mercury bubbler that was a manometer tube and contains enough mercury to provide a seal from the atmosphere when argon line was evacuated.

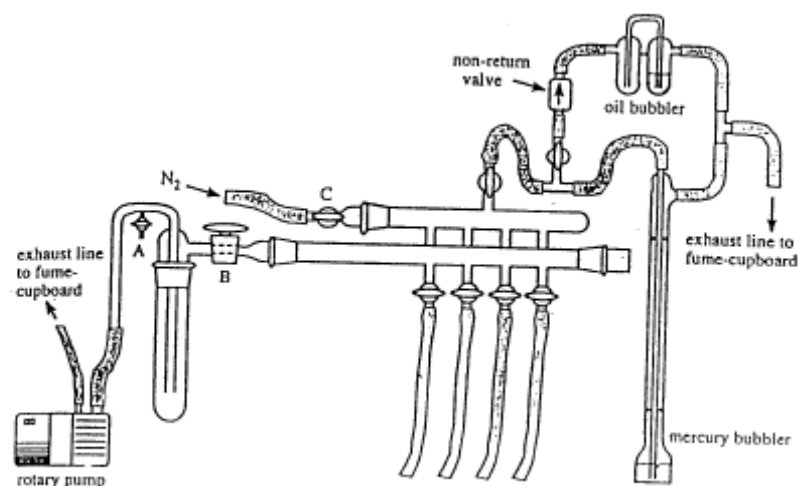


Figure 4.5 Schlenk line

4.2.3 The equipment for the reaction of alumina consisted of:

The flow diagram of the reaction that is methanol dehydration to dimethyl ether is shown in Figure 4.6

4.2.3.1 Saturator

Saturator was made from glass and set to bubble methanol and control pressure of methanol.

4.2.3.2 Reactor

Reactor tube was made from pyrex and had an inner diameter 6 mm and height 39.5 cm.

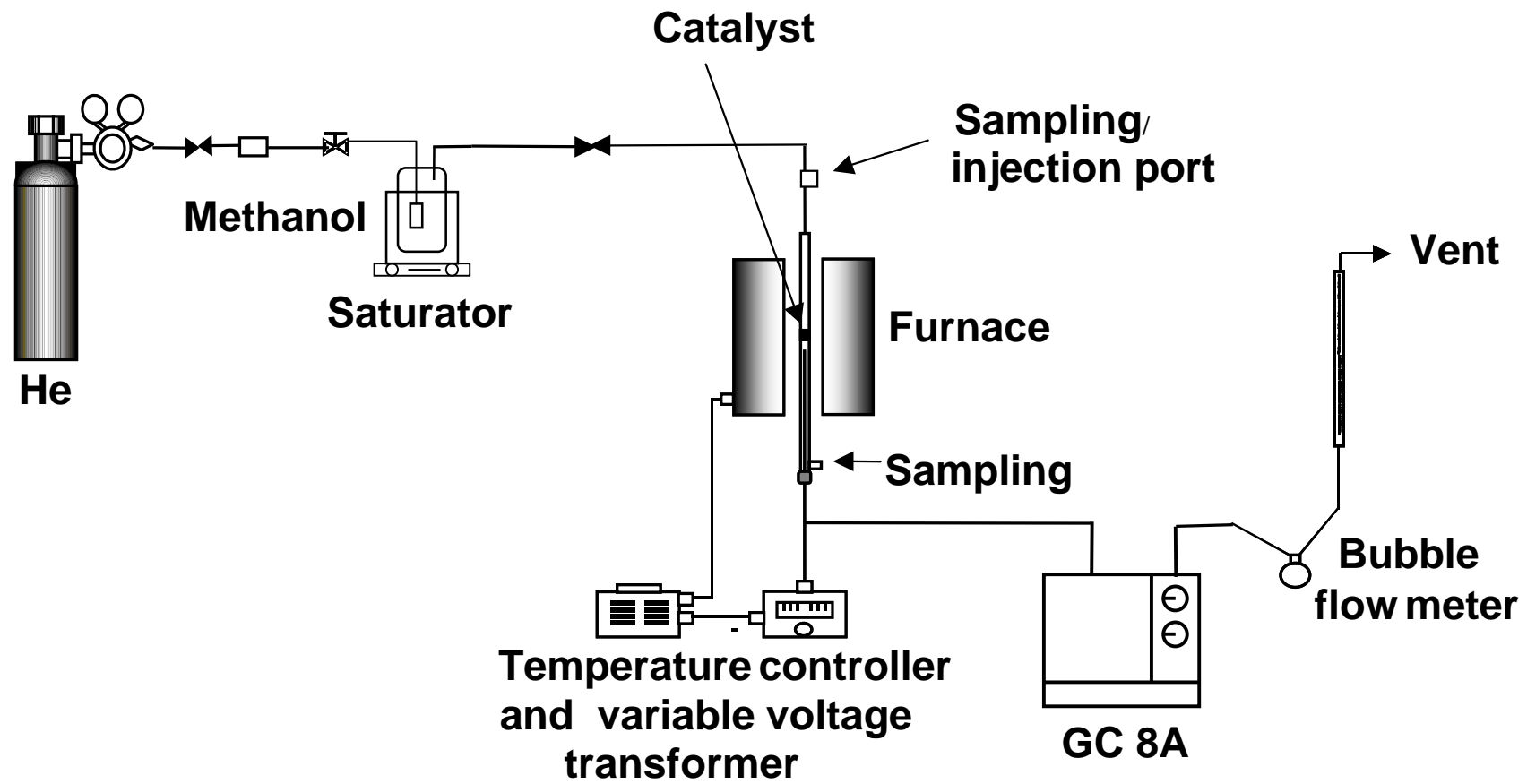


Figure 4.6 A schematic of methanol dehydration system

4.2.3.3 Heater and furnace

Heating cable was used to heat temperature of line preventing condensation of methanol. Variable voltage transformer was used to control the desired reactor temperature of furnace.

4.2.3.4 Temperature program controller

A temperature program controller was connected to a thermocouple attached to the reactor and variable voltage transformer and controlled the temperature.

4.2.3.5 Gas controlling system

Helium was set with a pressure regulator (0-150 bar) and regulator was used to release gas to line.

4.2.3.6 Gas chromatography

Gas chromatography (GC): Shimadzu model 8AIT was established for analyzing the reaction products with thermal conductivity detector (TCD). The TCD measures the conductivity of the analyte mixture which is a function of the concentration of the analyte in the gas. A carrier gas was Helium (He) and column was porapak Q (3 m×3 mmØ) for analyzing the concentration of methanol (CH₃OH), water (H₂O) and dimethyl ether (CH₃OCH₃).

Table 4.1 shows operating conditions of gas chromatograph for methanol dehydration to dimethyl ether.

Table 4.1 Operating conditions of gas chromatograph for methanol dehydration to dimethyl ether

Gas Chromatograph	SHIMADZU TCD GC 8AIT
Detector	TCD
Packed column	Porapak Q
Carrier gas	Ultra high purity He
Carrier gas flow rate (ml/min)	50
Injector temperature (°C)	110
Detector temperature (°C)	110
Initial column temperature (°C)	110
Initial holding time (min)	-
Programmed rate (°C/min)	-
Final column temperature (°C)	110
Final holding time (min)	-
Current (mA)	90
Analyzed gas	CH ₃ OH,H ₂ O,DME

4.3 Preparation of Al₂O₃ catalysts

4.3.1 Preparation of various phases Al₂O₃ catalysts by solvothermal method

15 g of aluminum isopropoxide was suspended in 100 ml of desired organic solvent in a test tube, the organic solvents using in this experiments were toluene, 1-butanol and the mix solvents between both solvents with desired composition, and then the test tube was placed in a 300 ml autoclave. An additional 30 ml of same solvent was placed in the gap between the autoclave wall and the test tube. The autoclave was completely purged with nitrogen, heated to a desired temperature at a rate of 2.5 °C min⁻¹ and kept at that temperature for 2 h. After the autoclave was cooled to room temperature, the resulting product was repeatedly washed with methanol by vigorous mixing and centrifuging and then dried in air. The as-synthesized powders were calcined in air at 600 °C for 6 h with a heating rate of 10 °C/min. The obtained catalysts comprised of χ/γ ratio 0/100, 10/90, 20/80, 50/50, 80/20, 90/10 and 100/0 derived from different amount of organic solvents as shown in Table 4.2.

4.3.2 Preparation of various phases Al₂O₃ catalysts by physical mixture method

Amount of γ -Al₂O₃ and χ - Al₂O₃ at desired χ/γ ratio were mixed in toluene in schlenk tube. The mixture was stirred and dried in vacuum with schlenk line at room temperature to obtain the catalyst. Example, preparation 10 g of 20/80 χ/γ ratio of Al₂O₃ catalyst, χ - Al₂O₃ 2 g and γ -Al₂O₃ 8 g were dissolved and well mixed in toluene then stirred and dried the solvent in vacuum to obtain the 20/80 χ/γ ratio of Al₂O₃ catalyst.

Table 4.2 χ/γ ratio in preparing catalysts of solvothermal method

χ/γ ratio	In test tube (ml)		In the gap between the autoclave wall and the test tube (ml)	
	Toluene	1-Butanol	Toluene	1-Butanol
0/100	0	100	0	30
10/90	10	90	3	27
20/80	20	80	6	24
50/50	50	50	15	15
80/20	80	20	24	6
90/10	90	10	27	3
100/0	100	0	30	0

4.4 Characterization of catalyst

The catalysts were characterized using a variety of techniques, which are briefly outlined below.

4.4.1 X-Ray Diffraction (XRD)

XRD was performed to determine the bulk phase of catalysts by SIEMENS D 5000 X-ray diffractometer connected with a computer with Diffract ZT version 3.3 program for fully control of the XRD analyzer using Cu K α radiation source with Ni filter in the 2θ range of 10-80 degrees resolution 0.04°. The crystallite size was estimated from line broadening using the Scherrer equation and α -Al₂O₃ was used as standard.

4.4.2 N₂ physisorption

BET surface area, pore volume and pore diameter were measured by N₂ adsorption–desorption isotherm at liquid nitrogen temperature (-196 °C) using a Micromeritics ASAP 2020. The surface area and pore distribution were calculated according to Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods, consecutively.

The reaction apparatus of BET surface area measurement consisted of two feed lines for helium and nitrogen. The flow rate of the gas was adjusted by means of fine-metering valve on the gas chromatograph. The sample cell made from pyrex glass. The mixture gases of helium and nitrogen flowed through the system at the nitrogen relative of 0.3. The catalyst sample (ca. 0.2 to 0.5 g) was placed in the sample cell, which was then heated up to 160 °C and held at this temperature for 2 h. After the catalyst sample was cooled down to room temperature, nitrogen uptakes were measure as follows.

Step (1) Adsorption step: The sample that set in the sample cell was dipped into liquid nitrogen. Nitrogen gas that flowed through the system was adsorbed on the surface of the sample until equilibrium was reached.

Step (2) Desorption step: The sample cell with nitrogen gas-adsorption catalyst sample dipped into the water at room temperature. The adsorbed nitrogen gas was desorbed from the surface of the sample. This step was completed when the indicator line was in the position of base line.

Step (3) Calibration step: 1 ml of nitrogen gas at atmospheric pressure was injected through the calibration port of the gas chromatograph and the area was measured. The area was the calibration peak.

4.4.3 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy (TEM) will be used to investigate morphology and crystallography of the catalyst particles. Model of TEM: JEOL JEM-2010 employs a LaB₆ electron gun operating in the voltage range of 80 to 200 kV, with an optimal point-to-point resolution of 0.23 nm. Facilities available on this instrument at National Metals and Materials Technology Center (MTEC) include a maximum specimen tilt of 30 degrees along both axes, single-tilt and double-tilt specimen holders, Oxford Instruments Link ISIS 300 X-ray microanalysis system, and Scanning Transmission Electron Microscopy (STEM) attachment.

4.4.4 Ammonia Temperature-Programmed Desorption (NH₃-TPD)

The acidity of the catalyst samples was determined by temperature-programmed desorption of ammonia using a Micromeritics Chemisorp 2750 with a computer. In an experiment, about 0.10 g of the catalyst sample was placed in a quartz tube and pretreated at 265 °C in a flow of helium. The sample was saturated with 15% NH₃/He. After saturation, the physisorbed ammonia was desorbed in a helium gas flow about 0.5 h. Then the sample was heated from 40 to 700 °C at a heating rate 10 °C /min. The amount of ammonia in effluent was measured via TCD signal as a function of temperature.

4.4.5 Titration method involving ion exchange

Titration method involving ion exchange will be used to determine the acidity of the catalyst samples. In an experiment, 0.2 g of catalyst was added to 10 mL of 3.42 M aqueous NaCl solution under stirring 30 h. After the ion exchange between the catalyst H⁺ ions and the Na⁺ ions in solution, the liquid was filtrated and titrated with 0.001 M aqueous NaOH solution. The end point (pH~7) of titration was determined using a pH meter and confirmed using pH paper.

4.5 Reaction study in dehydration of methanol

As shown in Figure 4.6, the diagram of methanol dehydration was used to investigate catalytic test. Catalytic experiments were performed at atmosphere pressure in fixed-bed reactor consisting of a Pyrex tube, a coaxially centered thermocouple with its tip located in the middle of the bed.

The dehydration of methanol over the catalyst samples was carried out in reactor with an inner diameter 6 mm. In an experiment, 0.2 g of each catalysts was loaded and the gas hourly space velocity (GHSV) was $5,300 \text{ h}^{-1}$. Methanol was bubbled by helium through a glass saturator maintained at $29 \text{ }^\circ\text{C}$ to keep a feed gas mixture consisting of 20% methanol balanced in helium. The partial pressure of methanol in the gas mixture was 169 mmHg. The calculation of the partial pressure of methanol was shown in Appendix A. The reactor was carried out in the temperature range: $100\text{-}300 \text{ }^\circ\text{C}$ under atmospheric pressure. The reaction products were analyzed on-line with a gas chromatograph with a TCD detector and a Porapak-Q column operating at 110°C [Ng 2002].

The product gas composition was analyzed on-line by a Shimadzu gas chromatograph (GC). The GC was equipped with a thermal conductivity detector (TCD). Helium was used as the carrier gas and separation of the constituents was achieved using molecular Porapak Q column. Porapak Q were used to analyze H_2O , CH_3OH and DME. The calibration curves for calculation of composition of reactant and products in methanol dehydration were shown in Appendix B.

CHAPTER V

RESULTS AND DISCUSSIONS

In preliminary experiments, the study was conducted so as to investigate the physical and chemical properties of commercial γ -Al₂O₃ and Al₂O₃ catalysts in various phases. These Al₂O₃ catalysts were synthesized by solvothermal technique, various χ/γ phase compositions are 0/100, 10/90, 20/80, 50/50, 80/20 90/10 and 100/0 as named C0G100, C10G90, C20G80, C50G0, C80G20, C90G10 and C100G0, respectively. The Al₂O₃ catalyst was synthesized by physical mixture method, χ/γ phase compositions is 20/80 as named PC20G80. The catalytic properties were evaluated using methanol dehydration to dimethyl ether. The results in this chapter are divided into three main parts. The first part describes the characteristics of commercial γ -Al₂O₃ and synthetic γ -Al₂O₃ catalysts (section 5.1). The catalytic properties and activities of commercial γ -Al₂O₃ and synthetic γ -Al₂O₃ catalysts (section 5.2). The second part describes the characteristics of Al₂O₃ catalysts consisting of various χ/γ phase compositions (section 5.3) and the catalytic properties and activities of Al₂O₃ catalysts for methanol dehydration to dimethyl ether (section 5.4). And, the last part describes the characteristics of the best Al₂O₃ catalyst of all various χ/γ phase Al₂O₃ catalysts in different synthetic method between solvothermal method and physical mixture (section 5.5) and the catalytic properties and activities of the best Al₂O₃ catalyst of all various χ/γ phase Al₂O₃ catalysts in different synthetic method between solvothermal method and physical mixture (section 5.6).

5.1 Characterization of commercial and synthetic γ -Al₂O₃ catalysts

5.1.1 X-ray diffraction (XRD)

Bulk crystal structure and chemical phase composition of a crystalline material can be detected by diffraction of an X-ray beam as a function of the angle of the incident beam. The measurements were carried out at the diffraction angles (2θ) between 10 and 80 degrees. Broadening of the diffraction peaks were used to estimate crystallite diameter from Scherrer Equation as shown in Appendix C.

Figure 5.1 shows the XRD patterns of commercial γ -Al₂O₃ and synthetic γ -Al₂O₃ catalysts. The XRD patterns both of commercial γ -Al₂O₃ and synthetic γ -Al₂O₃ were obvious at 32°, 37°, 39°, 45°, 61° and 66° as pure gamma phase [Meephoka et al. 2008]. Although the commercial γ -Al₂O₃ had a small peak at 27°, it was still shown γ -Al₂O₃ because each phase of transition alumina has a specific ratio of each peak. For commercial γ -Al₂O₃ and synthetic γ -Al₂O₃, the crystallite size were 4.2 nm and 4 nm, respectively as shown in Table 5.1 so the crystallite size of commercial γ -Al₂O₃ and synthetic γ -Al₂O₃ were about 4 nm.

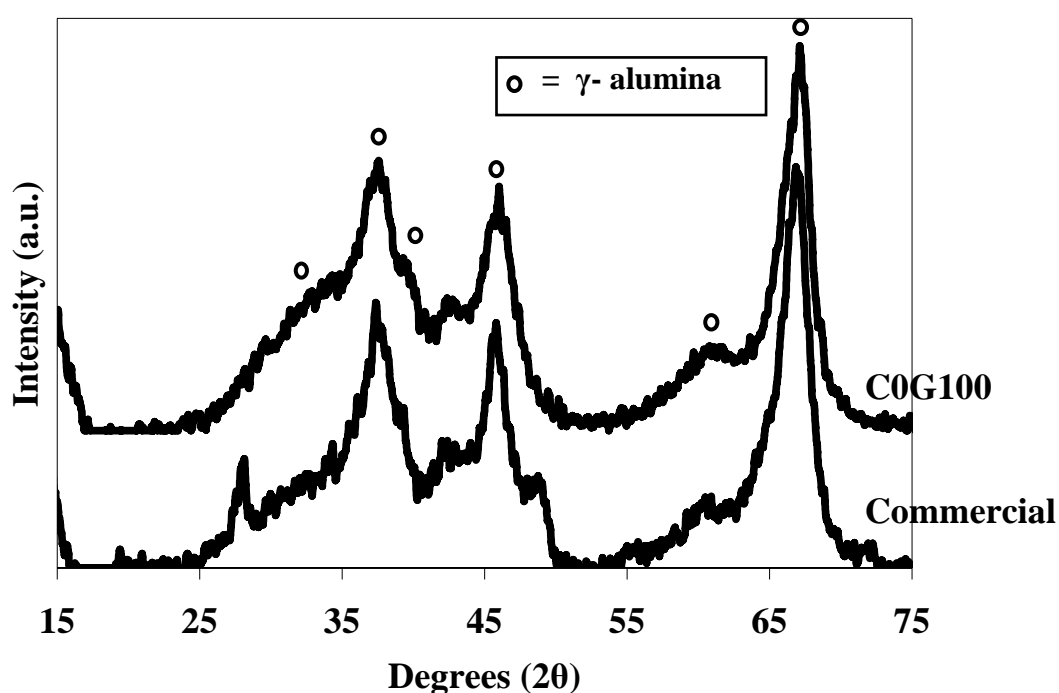


Figure 5.1 XRD patterns of commercial γ -Al₂O₃ and synthetic γ -Al₂O₃ catalysts.

Table 5.1 The crystallite size of commercial and synthetic γ -Al₂O₃ catalysts

Catalysts (γ -Al ₂ O ₃)	Crystallite size (nm)
Commercial	4.2
Synthetic (C0G100)	4.0

5.1.2 N₂ physisorption

Table 5.2 summarizes the physical properties of commercial γ -Al₂O₃ and the synthetic γ -Al₂O₃ catalysts. For commercial and synthetic γ -Al₂O₃, the BET surface areas decreased from 271 to 196 m²/g while the pore volume and the average pore diameter increased from 0.439 to 0.7778 cm³/g and 4.9 to 10.6 nm, respectively.

Table 5.2 Physical properties of commercial γ -Al₂O₃ and the synthetic γ -Al₂O₃ catalysts

Catalysts (γ -Al ₂ O ₃)	BET Surface Area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)
Commercial	271	0.439	4.9
Synthetic (COG100)	196	0.778	10.6

5.1.3 Transmission Electron Microscopy (TEM)

TEM images of commercial γ -Al₂O₃ and synthetic γ -Al₂O₃ catalysts are shown in Figure 5.2. For the commercial γ -Al₂O₃ and synthetic γ -Al₂O₃ catalysts, the wrinkled sheets morphology was observed. They were found to be similar to those obtained from the formation of γ -Al₂O₃ by decomposition of glycol or alkyl derivatives on boehmite [Pansanga et al. 2007].

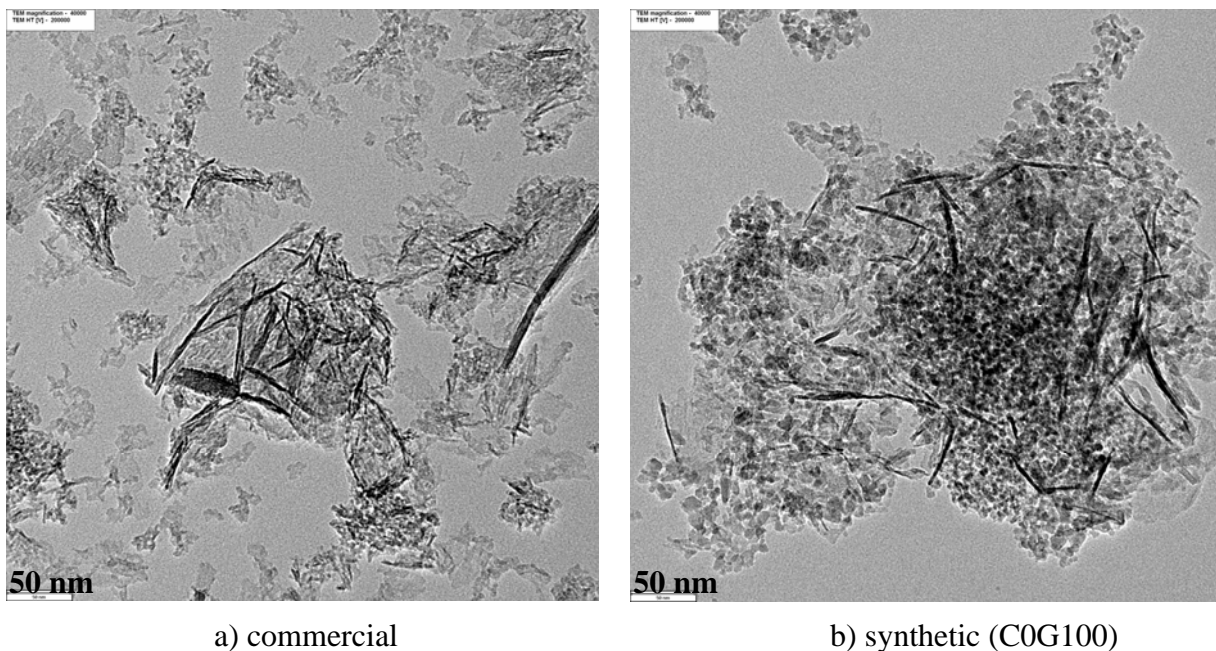


Figure 5.2 TEM images of γ -Al₂O₃ catalysts

5.1.4 Ammonia temperature-programmed desorption (NH₃-TPD)

Figure 5.3 shows the NH₃-TPD profiles of commercial γ -Al₂O₃ and the synthetic γ -Al₂O₃ catalysts. The profile for commercial γ -Al₂O₃, showed two broad peaks at the temperature ranged around 50 to 120°C and 180 to 380°C, respectively while the profiles for pure γ -alumina exhibited one sharp peak at the temperature ranged between 40 to 85°C. According to the literature [Corma et al. 1994], these peaks can be ascribed to the NH₃ desorbed from acid sites with low and medium to high strengths. From these results, it can be concluded that the synthetic γ -Al₂O₃ catalyst possesses weak surface acidic sites as compared to the commercial γ -Al₂O₃ catalyst which possesses weak and medium surface acidic sites.

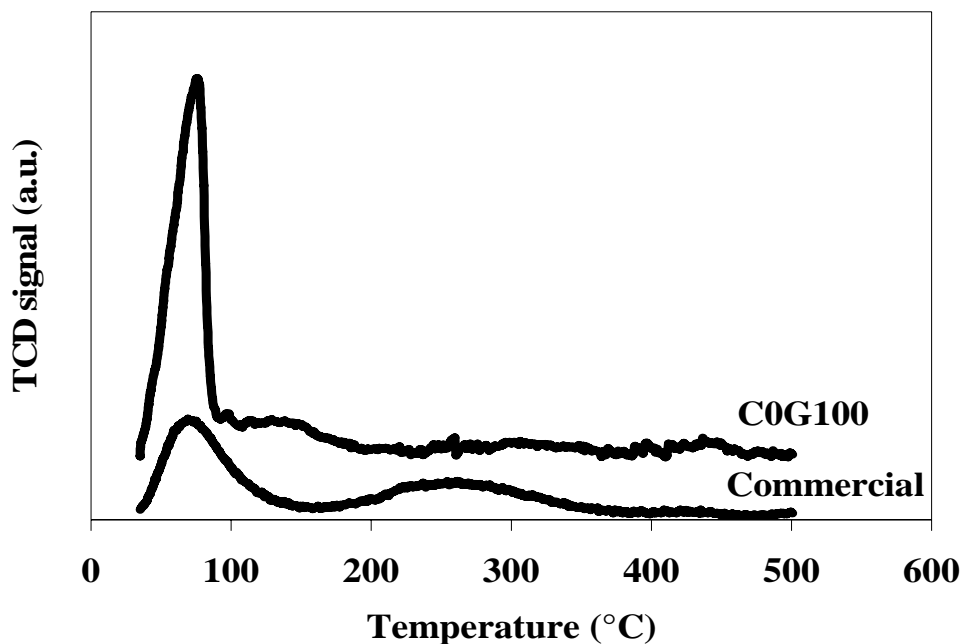


Figure 5.3 NH₃-TPD Profiles of commercial γ -Al₂O₃ and synthetic γ -Al₂O₃ catalysts.

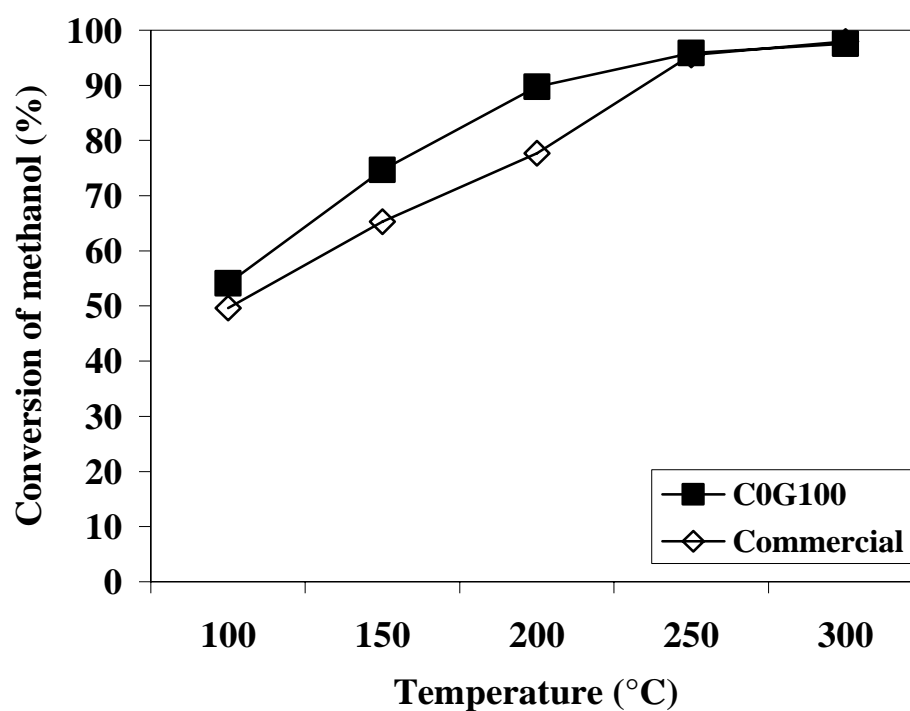
The acid properties of the alumina catalysts are also reported in Table 5.3. The calculation of the acidity is shown in Appendix D. The acidity of commercial γ -Al₂O₃ and the synthetic γ -Al₂O₃ was 0.370 and 0.490 $\mu\text{mol NH}_3/\text{g catalyst}$, respectively. Although the commercial γ -Al₂O₃ catalyst possesses weak and medium surface acidic sites, the acidity of the commercial γ -Al₂O₃ catalyst is lesser than the acidity of the synthetic γ -Al₂O₃. This result indicates that the synthetic γ -Al₂O₃ is appropriate synthesized method for improving the acidity of γ -Al₂O₃ catalysts.

Table 5.3 Acidity of commercial γ -Al₂O₃ and synthetic γ -Al₂O₃ catalysts.

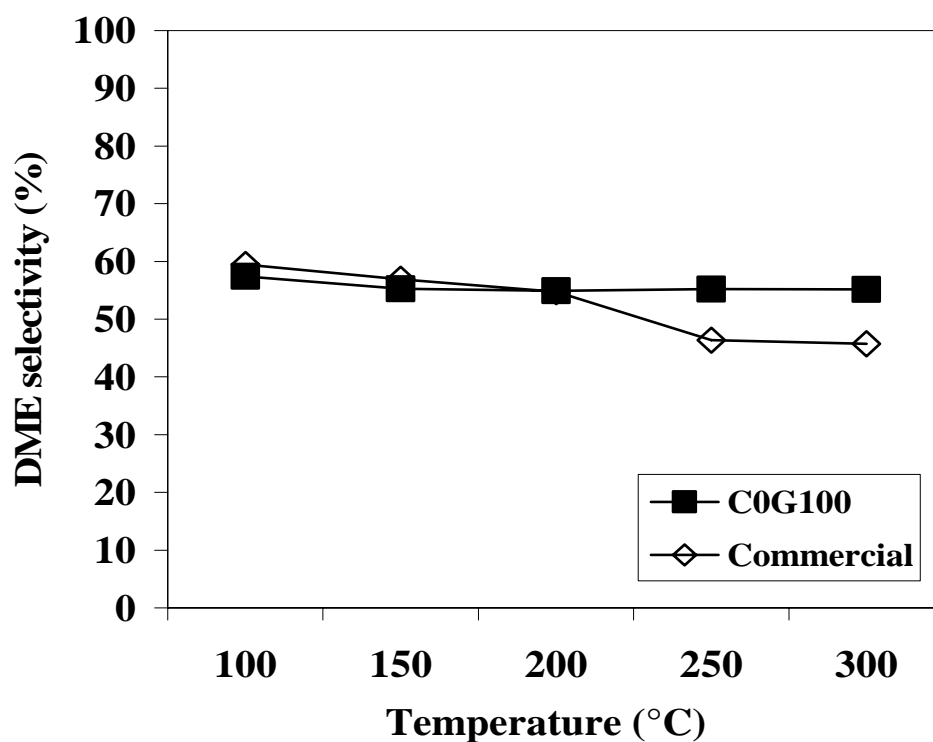
Catalysts (γ -Al ₂ O ₃)	Acidity ($\mu\text{mol NH}_3/\text{g catalyst}$)
Commercial	0.370
Synthetic (C0G100)	0.490

5.2 Reaction Study for commercial γ -Al₂O₃ and synthetic γ -Al₂O₃ catalysts

Figure 5.4 shows the results of methanol dehydration on alumina catalysts at the atmospheric pressure in the temperature range from 100 to 300°C. Methanol conversion over alumina catalyst increased with increasing reaction temperature as shown in Figure 5.4a, the conversion of commercial and synthetic γ -Al₂O₃ catalysts increased as the reaction temperature increased from 100 to 300°C. The activity of synthetic γ -Al₂O₃ was higher than commercial γ -Al₂O₃ catalyst. This result was in good agreement with the amount of acidity. This suggests that the acidity of Al₂O₃ catalyst play an important role on the catalytic activity for methanol dehydration reaction. The plot between DME selectivity and temperature of commercial and synthetic γ -Al₂O₃ catalysts are also shown in Figure 5.4b. The DME selectivity of commercial γ -Al₂O₃ catalysts decreased as the reaction temperature increased, while the selectivity of synthetic γ -Al₂O₃ catalysts remained constant at around 55%. The main by-product was CO obtained from CH₃OH decomposition reaction. Figure 5.4c shows the plot between DME yields and temperature of commercial and synthetic γ -Al₂O₃ catalysts. DME yields of commercial and synthetic γ -Al₂O₃ catalysts increased as the reaction temperature increased from 100 to 300°C. This result suggested that synthetic γ -Al₂O₃ catalysts exhibited the higher DME yield due to its high activity and DME selectivity.

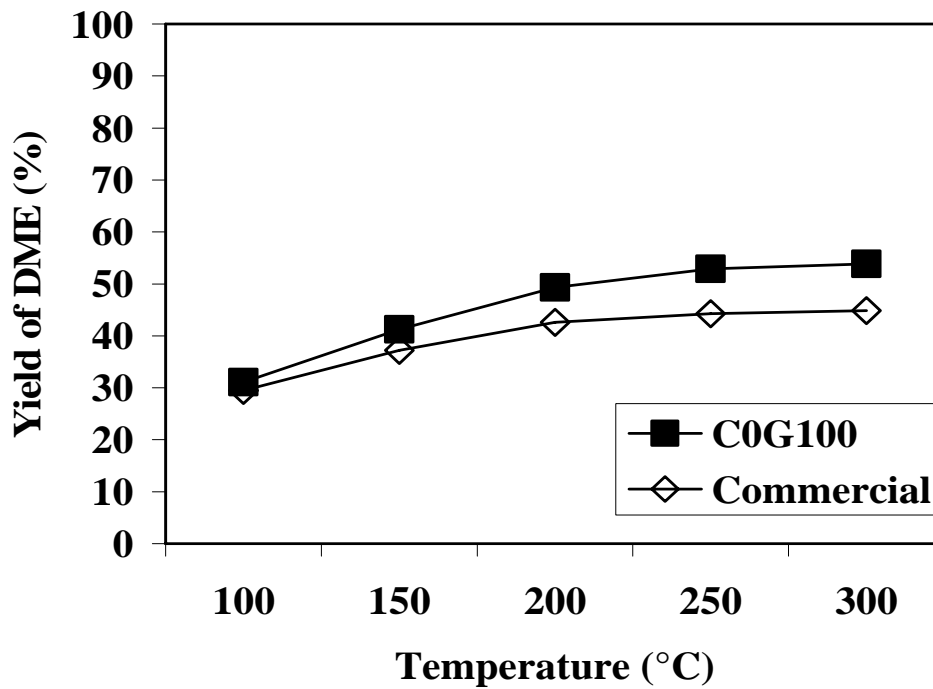


a) Methanol conversion profile



b) DME selectivity profile

Figure 5.4 Catalytic test of γ -Al₂O₃ catalysts (0.2 g of catalyst, GHSV=5,300 h⁻¹)



c) DME yield profile

Figure 5.4 (con.) Catalytic test of γ - Al_2O_3 catalysts

(0.2 g of catalyst, GHSV=5,300 h^{-1})

5.3 Characterization of synthetic Al_2O_3 catalysts with various χ/γ ratios

5.3.1 X-ray diffraction (XRD)

Figure 5.5 shows the XRD patterns of Al_2O_3 catalysts were synthesized by solvothermal technique with 0/100, 10/90, 20/80, 50/50, 80/20 90/10 and 100/0 χ/γ phase compositions. The XRD peaks of pure gamma phase (0/100) were obvious at 32° , 37° , 39° , 45° , 61° and 66° as same as Figure 5.1. When the ratio of toluene to 1-butanol increased, XRD peaks were apparent at 37° , 40° , 43° , 46° , 60° , and 67° and the higher ratio is, the more prominent peak at 43° is. From XRD pattern, the phase compositions of alumina samples were defined by the major peak (43°) of chi phase [Meephoka et al. 2008] of which the calibration curve was obtained by varying the ratio of pure gamma phase and pure chi phase of alumina in the physical mixtures.

Thus, %chi phase in samples was able to calculated and had error of the calculation method in a range of $\pm 10\%$ as shown in Appendix E.

Table 5.4 shows the crystallite size of Al_2O_3 catalysts with various χ/γ ratios. The crystallite size of Al_2O_3 increased from 4.0 to 8.7 nm as the χ -phase contents increased from 0 to 100 wt%. These results were in good agreement with the previously work reported by our group. [Meephoka et al. 2008]

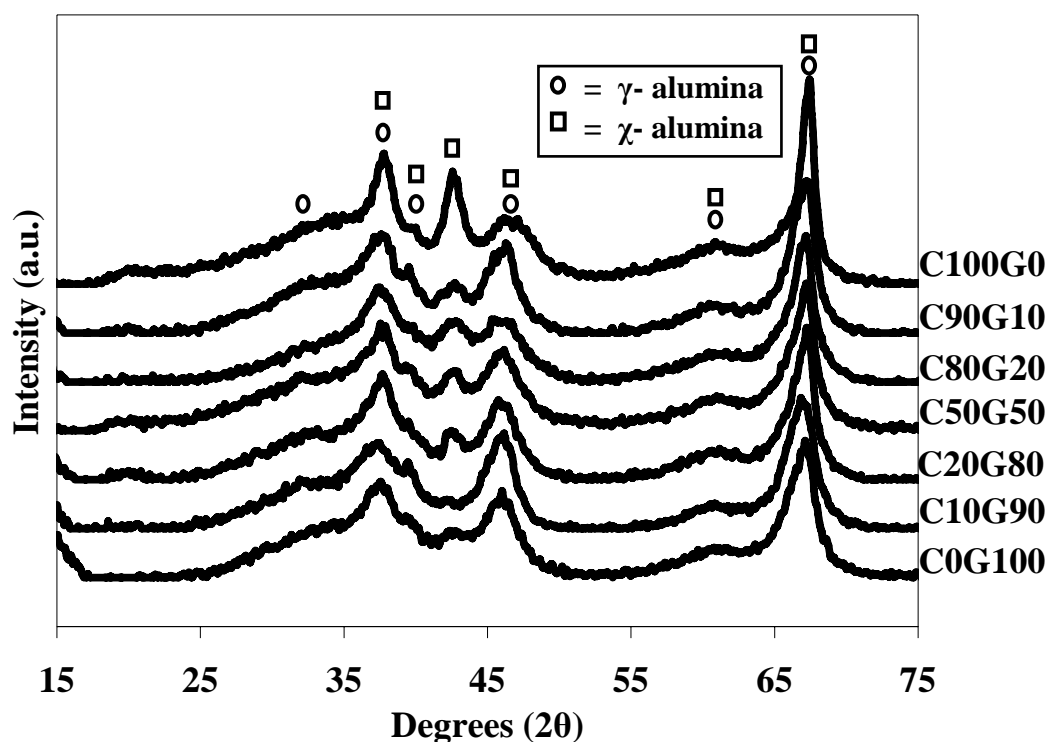


Figure 5.5 XRD patterns of synthetic Al_2O_3 catalysts with various χ/γ ratios

Table 5.4 The crystallite size of synthetic Al₂O₃ catalysts with various χ/γ ratios

Catalysts (χ/γ ratios)	Crystallite size (nm)
C0G100 (0/100)	4.0
C10G90 (10/90)	4.2
C20G80 (20/80)	5.5
C50G50 (50/50)	4.8
C80G20 (80/20)	5.1
C90G10 (90/10)	4.7
C100G0 (100/0)	8.7

5.3.2 N₂ physisorption

Table 5.5 summarized the physical properties of the Al₂O₃ catalysts. The BET surface areas and pore volume of Al₂O₃ decreased from 196 to 125 m²/g and 0.78 to 0.52 cm³/g, respectively as the χ -phase contents increased from 0 to 100 wt%. While the average pore diameter remained constant at around 10 nm. These results were in good agreement with the previously work reported by our group [Meephoka et al. 2008].

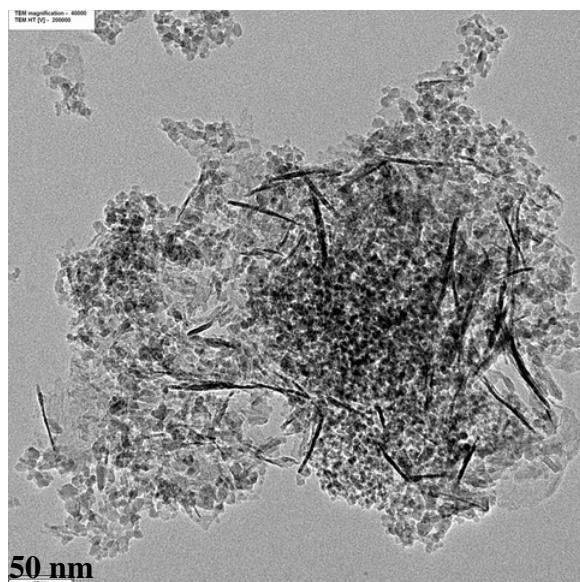
Table 5.5 Physical properties of synthetic Al₂O₃ catalysts with various χ/γ ratios

Catalysts (χ/γ ratios)	BET Surface Area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)
C0G100 (0/100)	196	0.778	10.6
C10G90 (10/90)	185	0.496	8.3
C20G80 (20/80)	187	0.768	12.1
C50G50 (50/50)	180	0.617	12.1
C80G20 (80/20)	173	0.565	8.2
C90G10 (90/10)	168	0.636	10.6
C100G0 (100/0)	125	0.515	11.1

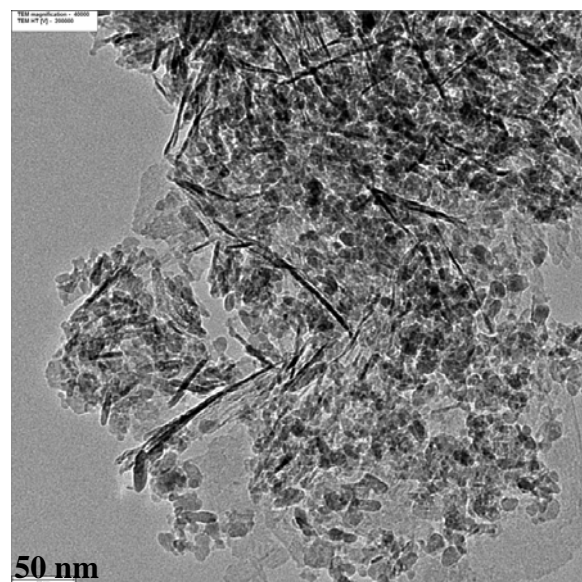
5.3.3 Transmission Electron Microscopy (TEM)

TEM images of alumina powders prepared with different amounts of mixed solvent between 1-butanol and toluene are shown in Figure 5.6. For the ones prepared with 1-butanol, the wrinkled sheets morphology was observed. They were found to be similar to those obtained from the formation of γ -alumina by decomposition of glycol or alkyl derivatives on boehmite [Pansanga et al. 2007]. As the amounts of toluene increased, the wrinkled sheets morphology became less apparent and spherical particles were observed [Pansanga et al. 2007]. The presence of spherical particles was probably due to the formation of χ -alumina, which was normally formed by thermal decomposition reaction of AIP in inert organic solvents at 300 °C. For the

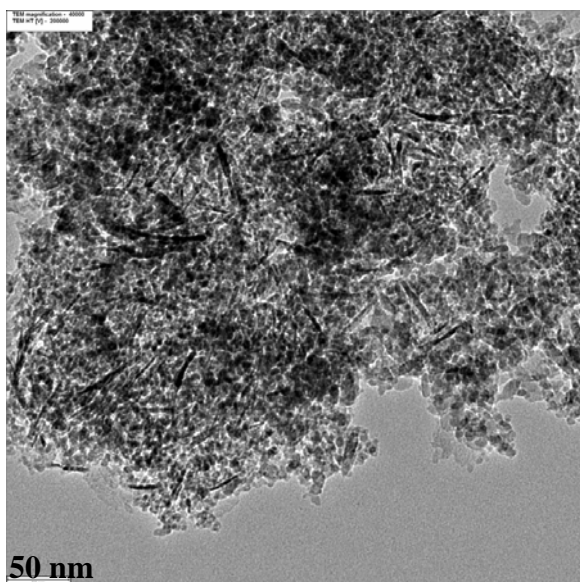
ones prepared with toluene, the spherical particles morphology was observed. TEM results were in a good agreement with the XRD patterns that the mixture of γ -alumina and χ -alumina was observed when volume of toluene increased. These results were in good agreement with the previously work reported by our group [Pansanga et al. 2007].



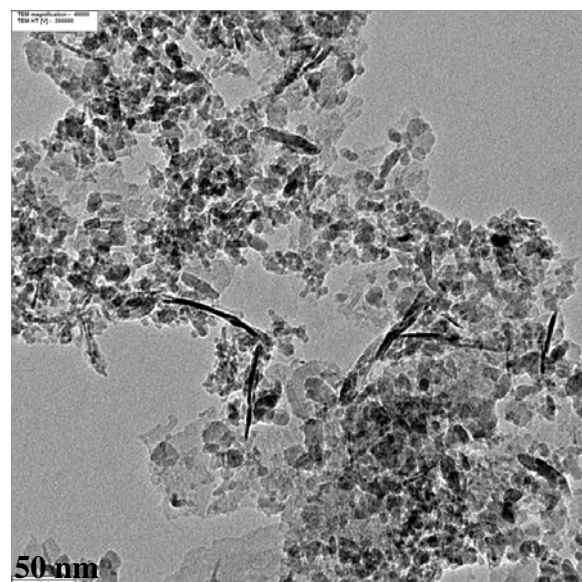
a) C0G100



b) C10G90

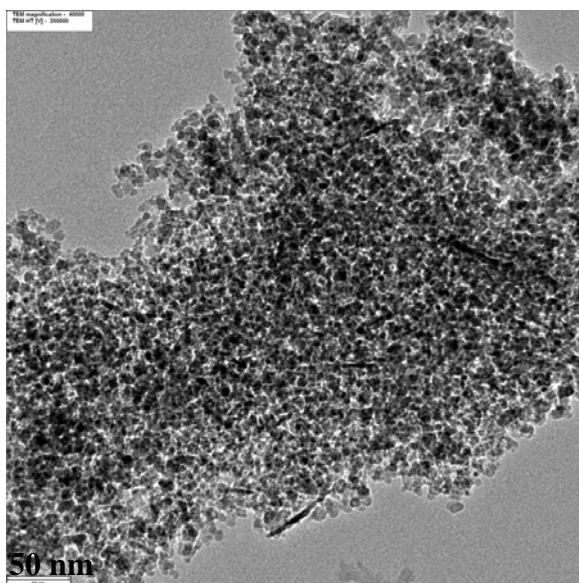


c) C20G80

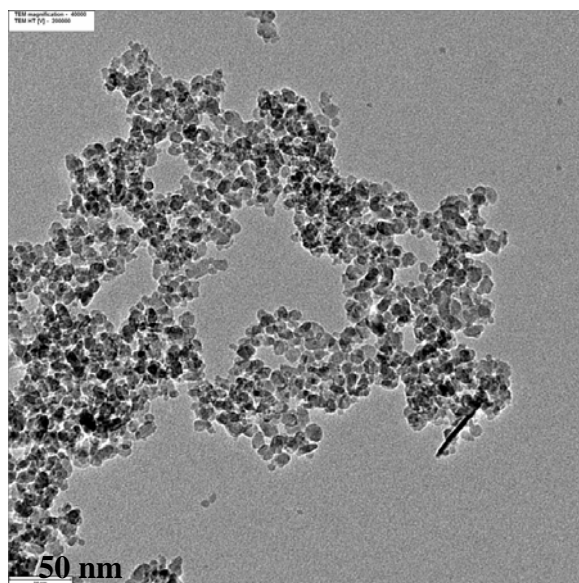


d) C50G50

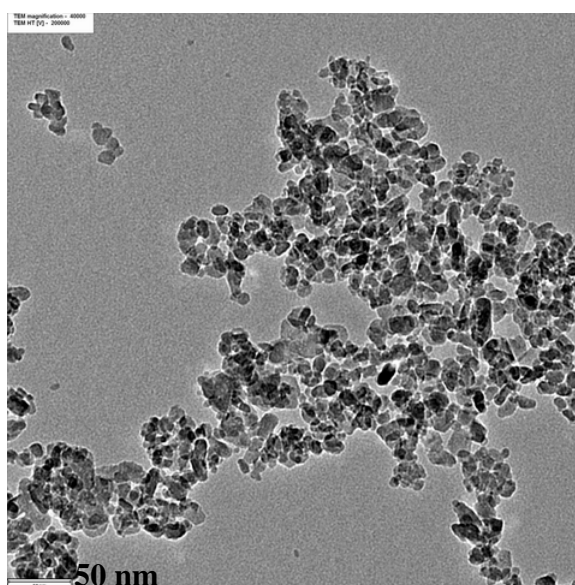
Figure 5.6 TEM Images of synthetic Al_2O_3 catalysts with various χ/γ ratios



e) C80G20



f) C90G10



g) C100G0

Figure 5.6 (con.) TEM Images of synthetic Al_2O_3 catalysts with various χ/γ ratios

5.3.4 Ammonia temperature-programmed desorption (NH₃-TPD)

Figure 5.7 shows the NH₃-TPD profiles of all Al₂O₃ catalysts with different wt% of χ -phase contents. The profiles for pure γ -alumina exhibited one sharp peak at the temperature ranged between 40 to 85°C, while the profiles for pure χ -alumina showed two broad peaks at the temperature ranged around 50 to 180°C and 200 to 400°C, respectively. According to the literature [Corma et al. 1994], these peaks can be ascribed to the NH₃ desorbed from acid sites with low and medium to high strengths. From these results, it can be concluded that the solvothermal-made χ -alumina powder possesses strong surface acidic sites as compared to the γ -alumina powder. When the wt% of χ -phase content increased, the first NH₃-TPD peak of γ -alumina became broader and slightly shifted to the higher temperature. Moreover the second peak was also observed. Such result suggests that the presence of χ -phase in Al₂O₃ catalyst significantly enhanced the surface acidity of the γ -alumina.

The acid properties of the alumina catalysts are also reported in Table 5.6. The calculation of the acidity was shown in Appendix D. The acidity of pure gamma and pure chi alumina is 0.490 and 1.684 $\mu\text{mol NH}_3/\text{g catalyst}$, respectively. The acidity increased from 0.49 to 4 $\mu\text{mol NH}_3/\text{g catalyst}$ as the χ phase contents increased from 0 to 20 wt% and then decreased to 1.684 as the χ phase contents increased further to 100 wt%. This result indicates that there are appropriate amount of χ phase content for improving the acidity of γ -Al₂O₃ catalysts. The total acidity concentration ($\mu\text{mol NH}_3/\text{g catalyst}$) improved as following order: C20G80 > C50G50 > C100G0 > C90G10 > C10G90 > C80G20 > C0G100.

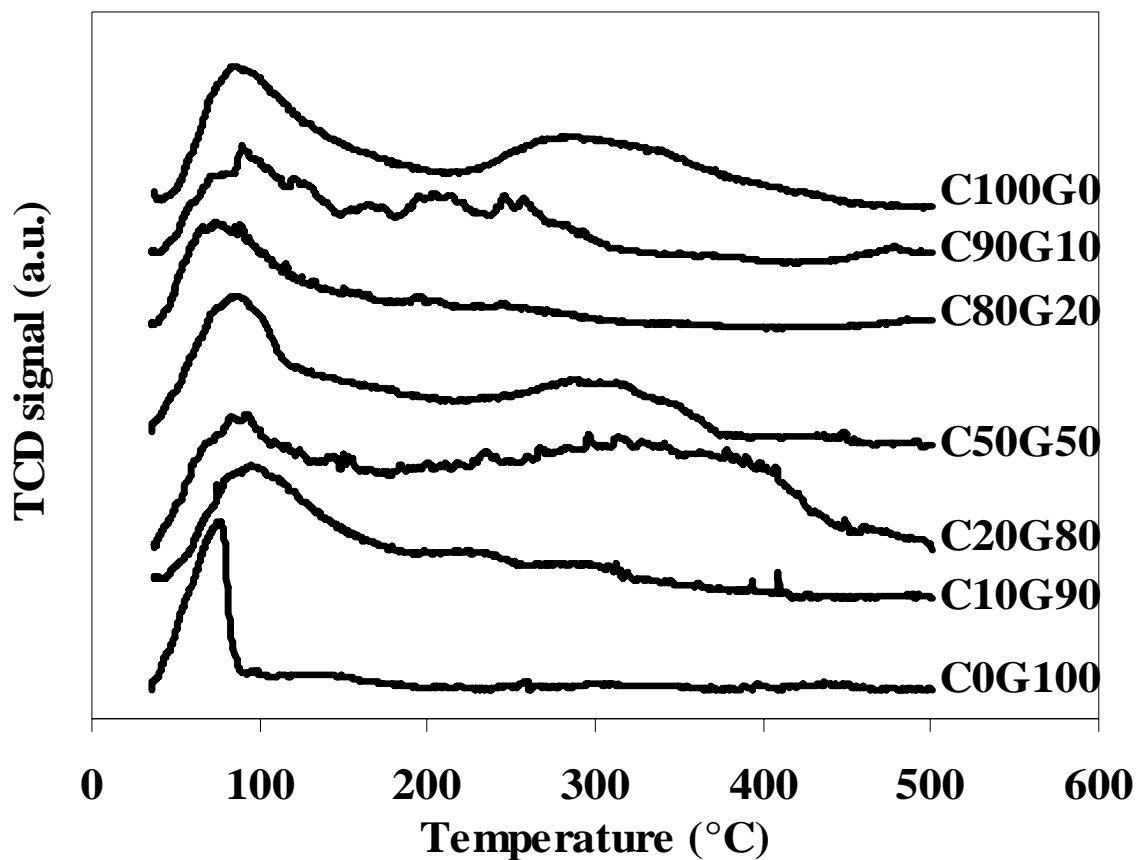


Figure 5.7 NH₃-TPD Profiles of synthetic Al₂O₃ catalysts with various χ/γ ratios

Table 5.6 Acidity of synthetic Al₂O₃ catalysts with various χ/γ ratios

Catalysts (χ/γ ratios)	Acidity ($\mu\text{mol NH}_3/\text{g catalyst}$)
C0G100 (0/100)	0.490
C10G90 (10/90)	1.188
C20G80 (20/80)	4.004
C50G50 (50/50)	2.053
C80G20 (80/20)	0.988
C90G10 (90/10)	1.347
C100G0 (100/0)	1.684

5.3.5 Titration method involving ion exchange

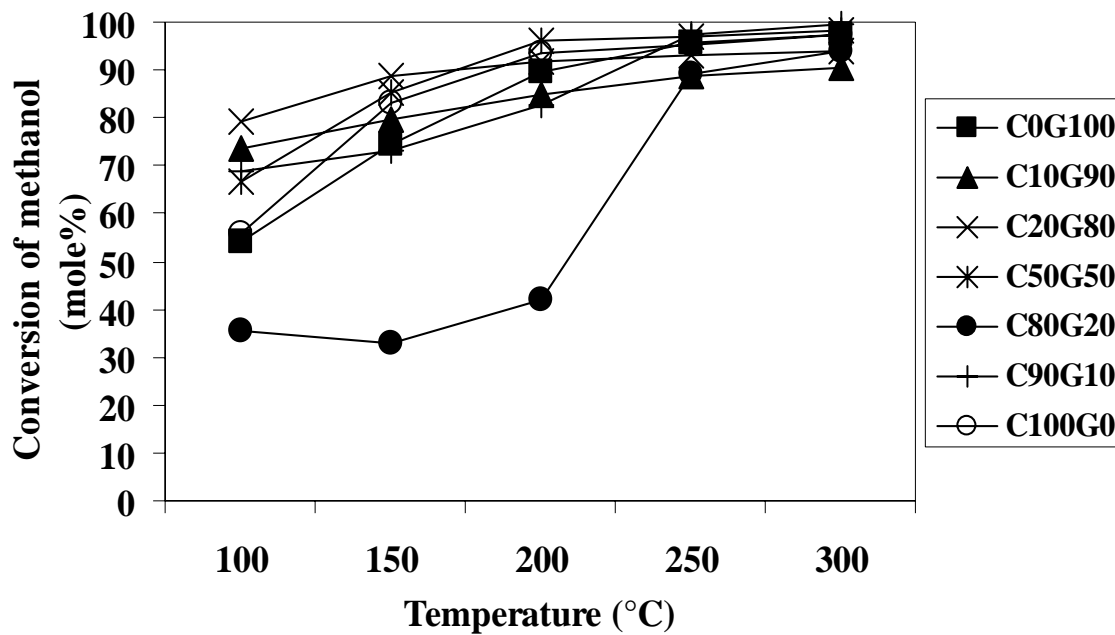
The acid properties of the alumina catalysts from Titration method involving ion exchange are also studied and reported in Table 5.7. The calculation of the acidity was shown in Appendix D. The acidity of pure gamma and pure chi alumina is 5 and 10 $\mu\text{mol/g}$ catalyst, respectively. The acidity increased from 5 to 25 $\mu\text{mol/g}$ catalyst as the χ phase contents increased from 0 to 20 wt% and then decreased to 10 $\mu\text{mol/g}$ catalyst as the χ phase contents increased further to 100 wt%. This result indicates that there are appropriate amount of χ phase content for improving the acidity of $\gamma\text{-Al}_2\text{O}_3$ catalysts. In compare to $\text{NH}_3\text{-TPD}$ estimation, the number of acid sites ($\mu\text{mol/g}$ catalyst) determined by the ion-exchange/titration method exhibited nearly same order as: C20G80 > C50G50 > C100G0 > C10G90 > C0G100 > C90G10 > C80G20 except for the last four orders. The different between those values had been reported by López et al. [López et al. 2007]

Table 5.7 Acidity of synthetic Al_2O_3 catalysts with various χ/γ ratios

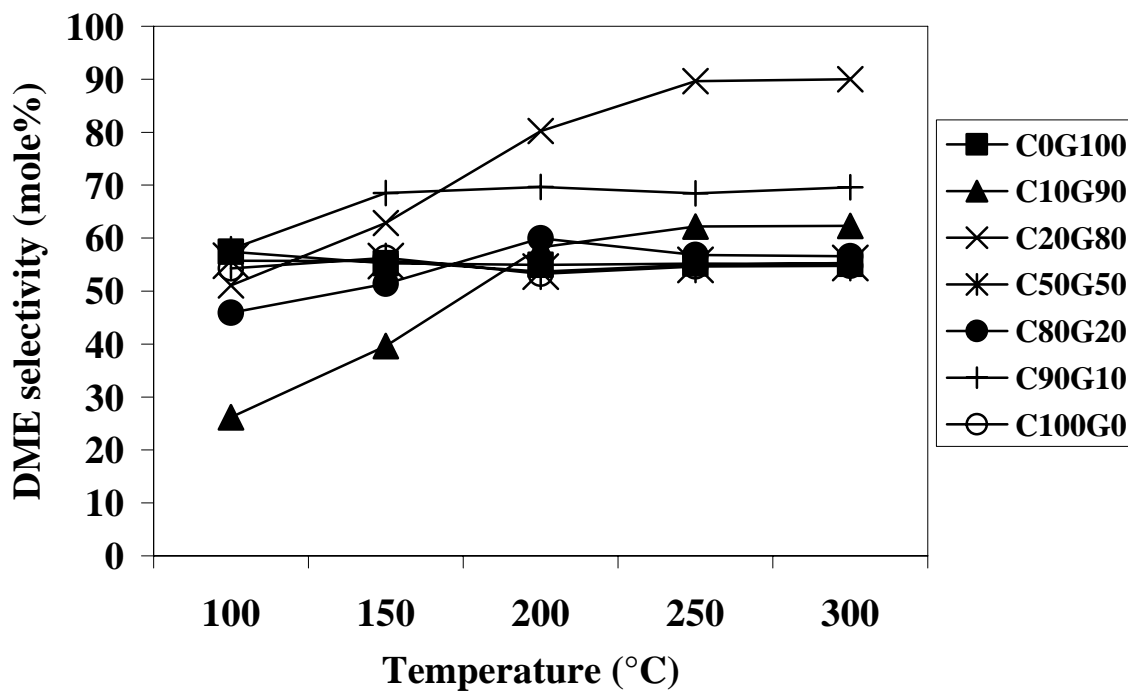
Catalysts (χ/γ ratios)	Acidity ($\mu\text{mol/g}$ catalyst)
C0G100 (0/100)	5
C10G90 (10/90)	7.5
C20G80 (20/80)	25
C50G50 (50/50)	15
C80G20 (80/20)	0.5
C90G10 (90/10)	2.5
C100G0 (100/0)	10

5.4 Reaction Study for synthetic Al₂O₃ catalysts with various χ/γ ratios

Figure 5.8 shows the results of methanol dehydration on alumina catalysts at the atmospheric pressure in the temperature range from 100 to 300°C. According to literatures [Fu et al. 2005, Jiang et al. 2004, Jun et al. 2002, Kim et al. 2006, Vishwanathan et al. 2004, and Xu et al. 1997], the effect of temperature on the catalytic activity of γ -Al₂O₃ has been examined. Methanol conversion over alumina catalyst increased with increasing reaction temperature. The results are in agreement with our result as shown in Figure 5.8a, the conversion over all Al₂O₃ catalysts increased as the reaction temperature increased from 100 to 300°C. At 150°C, activity of Al₂O₃ catalysts was improved in order of C20G80 > C50G50 > C100G0 > C10G90 > C0G100 > C90G10 > C80G20. This result is in good agreement with the increasing order of acidity concentration determined by the ion-exchange/titration method. This suggests that the acidity of Al₂O₃ catalyst play an important role on the catalytic activity for methanol dehydration reaction. Since methanol dehydration reaction is an acid-catalyzed reaction, the methanol conversion is mainly related to the acidity with weak and medium. [Xia et al. 2006, Yaripour et al.2005] The plot between DME selectivity and temperature of all Al₂O₃ catalysts is also shown in Figure 5.8b. The DME selectivity of C0G100, C10G90 and C20G80 increased as the reaction temperature increased, while the selectivity of other catalysts remained constant at around 55%. The main by-product was CO obtained from CH₃OH decomposition reaction. Figure 5.8c shows the plot between DME yields and temperature of all Al₂O₃ catalysts. DME yields of all Al₂O₃ catalysts increased as the reaction temperature increased from 100 to 300°C. Among the Al₂O₃ catalysts, C20G80 exhibited the highest DME yield for 86% at 300°C, which due to its high activity and DME selectivity. A review for previous studies of DME synthesis from methanol dehydration over various catalyst systems has been summarized in Table 5.8. Compared to many studies reported earlier [Fu et al. 2005, Jiang et al. 2004, Kim et al. 2006, Vishwanathan et al. 2004, Xu et al. 1997, and Yaripour et al. 2005], C20G80 Al₂O₃ catalyst showed higher yield for DME under similar reaction conditions. Figure 5.9 shows the stability of C20G80 catalyst in methanol dehydration at 300°C. The methanol conversion of C20G80 was stable at around 93% over 24 h time-on-stream.



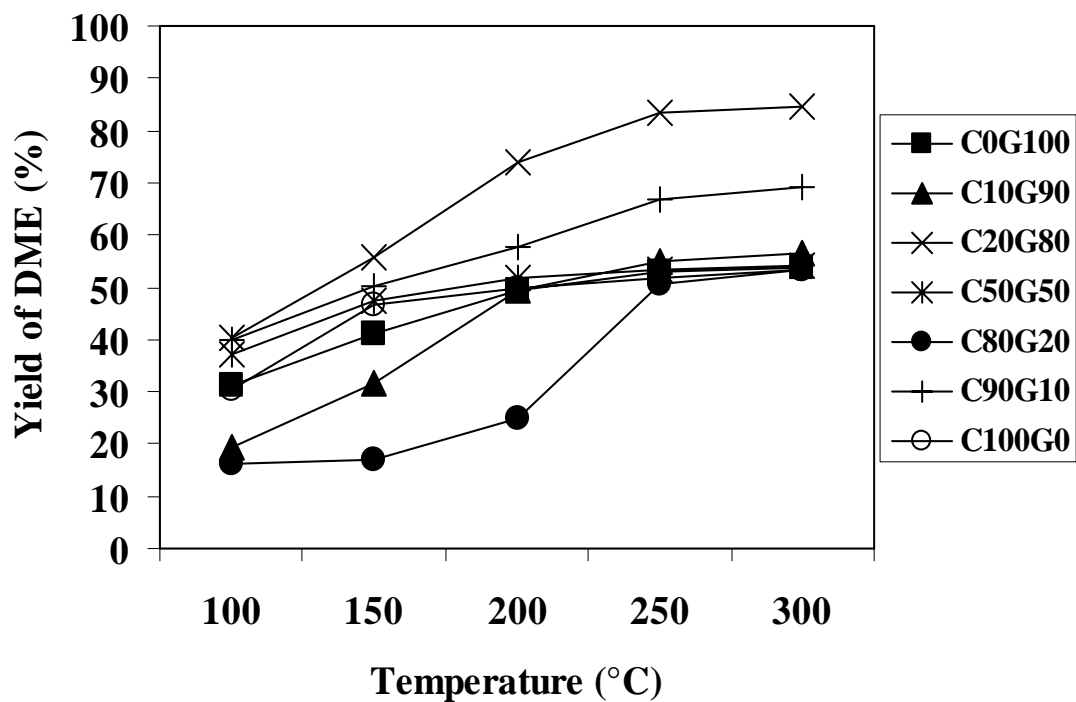
a) Methanol conversion profile



b) DME selectivity profile

Figure 5.8 Catalytic test of synthetic Al_2O_3 catalysts with various χ/γ ratios.

(0.2 g of catalyst, $\text{GHSV}=5,300 \text{ h}^{-1}$)



c) DME yield profile

Figure 5.8 (con.) Catalytic test of synthetic Al_2O_3 catalysts with various χ/γ ratios.

(0.2 g of catalyst, $\text{GHSV}=5,300 \text{ h}^{-1}$)

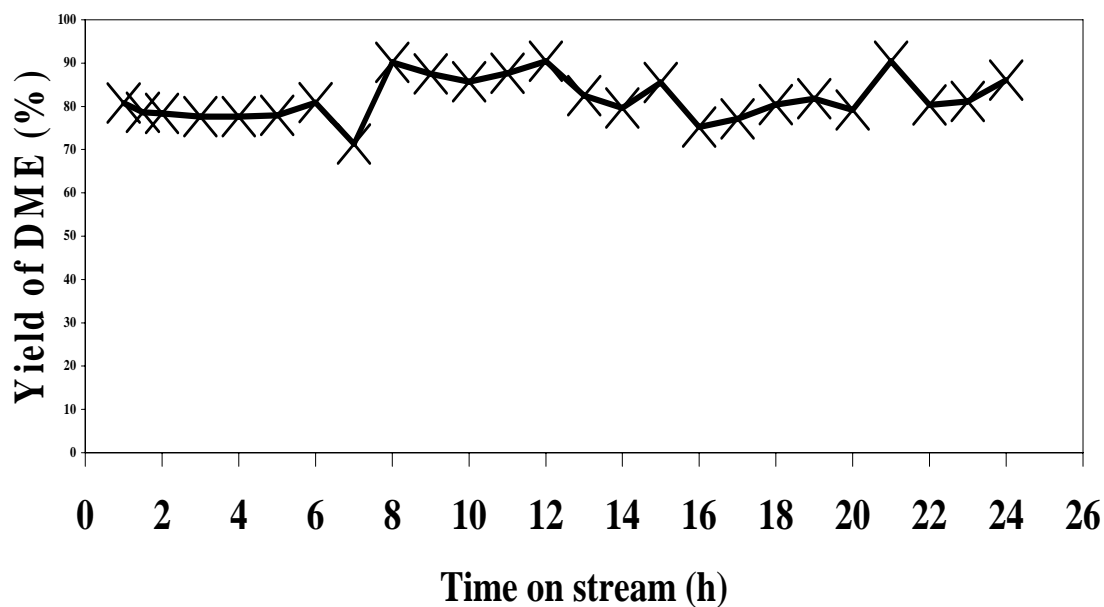


Figure 5.9 Long term study of C20G80 catalyst.

(0.2 g of catalyst, $\text{GHSV}=5,300 \text{ h}^{-1}$, $300 \text{ }^\circ\text{C}$)

Table 5.8 Summary of DME synthesis from methanol dehydration reaction.

Source	Catalyst	BET surface area (m ² /g)	Amount of Catalyst (g)	Space velocity (h ⁻¹)	Reaction Temperature (°C)	DME yields (%)
Fu et al. 2005	Ti(SO ₄) ₂ / γ-Al ₂ O ₃	291	0.2	GHSV 3,400	240	85
Jiang et al. 2004	NaH-ZSM-5 (Si/Al = 30)	-	0.2	WHSV 4	250	62
Kim et al. 2006	γ-Al ₂ O ₃ / NaZSM-5 (Si/Al=40)	240-439	1.8 ml	LHSV 10	210-380	15-85
Vishwanathan et al. 2004	NaH-ZSM-5 (Si/Al = 20)	-	1.5 ml	LHSV 10	270-340	73-84
Vishwanathan et al. 2004	TiO ₂ /SiO ₂	73-206	1.5	WHSV 0.316	340	53-83
Xu et al. 1997	amorphous SiO ₂ /Al ₂ O ₃	-	0.51	-	140-190	4-43
Yaripour et al. 2005.	Aluminium phosphate	156-385	0.5	GHSV 15,600	300	64-75
Yaripour et al. 2005	Alumino Silicate	252-383	0.5	GHSV 15,600	300	73-86
Yaripour et al. 2005	SiO ₂ -TiO ₂	46-60	0.5	GHSV 15,600	300	0.2-25

5.5 Characterization of Al₂O₃ (χ/γ ratios: 20/80) synthesized by solvothermal and physical mixture method

5.5.1 X-ray diffraction (XRD)

Figure 5.10 shows the XRD patterns of 20 wt% χ -Al₂O₃ synthesized by solvothermal and physical mixture. The XRD peaks of 20 wt% χ -Al₂O₃ synthesized by solvothermal and physical mixture were obvious at 32°, 37°, 39°, 43°, 45°, 61° and 66° as the same. Table 5.9 shows the crystallite size of 20 wt% χ -Al₂O₃ synthesized by solvothermal and physical mixture. The crystallite size of 20 wt% χ -Al₂O₃ synthesized by solvothermal and physical mixture was about 5 nm.

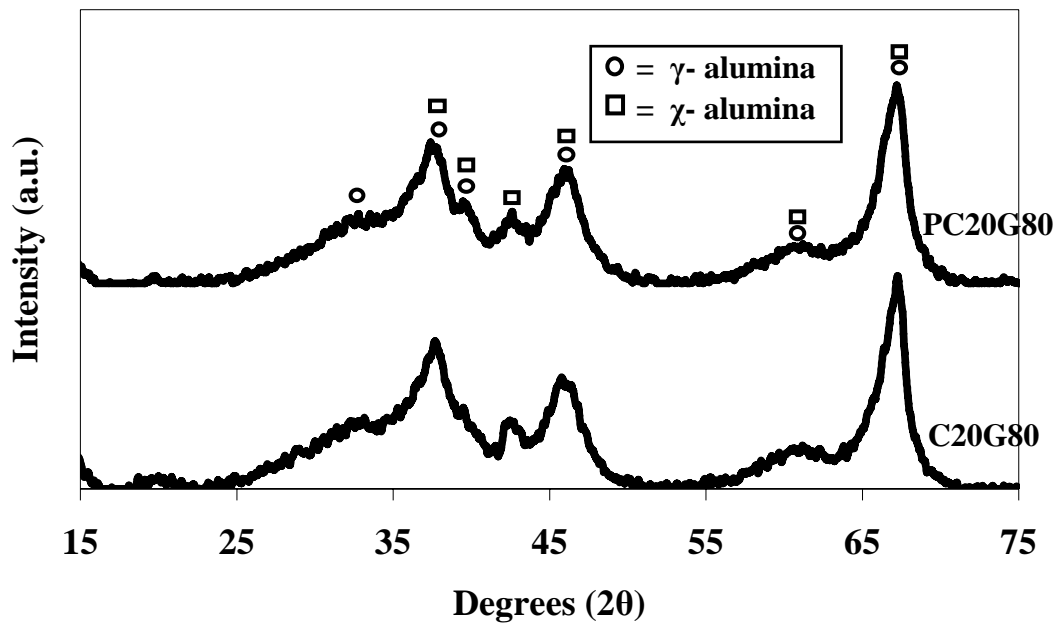


Figure 5.10 XRD patterns of 20 wt% χ -Al₂O₃ synthesized by solvothermal and physical mixture.

Table 5.9 The crystallite size of 20 wt% χ -Al₂O₃ synthesized by solvothermal and physical mixture.

Catalysts (χ/γ ratios)	Crystallite size (nm)
C20G80 (20/80)	5.5
PC100G0 (20/80)	5.1

5.5.2 N₂ physisorption

Table 5.10 summarized the physical properties of 20 wt% χ -Al₂O₃ synthesized by solvothermal and physical mixture. The BET surface areas were not significant difference; 187 and 183 m²/g for 20 wt% χ -Al₂O₃ synthesized by solvothermal and physical mixture, respectively. The pore volume was slightly difference; 0.768 to 0.714 cm³/g for 20 wt% χ -Al₂O₃ synthesized by solvothermal and physical mixture, respectively. The average pore diameter of 20 wt% χ -Al₂O₃ synthesized by solvothermal (12.1 nm) was slightly larger than 20 wt% χ -Al₂O₃ synthesized by physical mixture (10.7 nm).

Table 5.10 Physical properties of 20 wt% χ -Al₂O₃ synthesized by solvothermal and physical mixture.

Catalysts (χ/γ ratios)	BET Surface Area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)
C20G80 (20/80)	187	0.768	12.1
PC100G0 (20/80)	183	0.714	10.7

5.5.3 Transmission Electron Microscopy (TEM)

TEM images of 20 wt% χ -Al₂O₃ synthesized by solvothermal and physical mixture are shown in Figure 5.11. For the 20 wt% χ -Al₂O₃ synthesized by solvothermal and physical mixture, the wrinkled sheets morphology was observed however the amount of the wrinkled sheets morphology of 20 wt% χ -Al₂O₃ is less than the amount of the wrinkled sheets morphology of γ -Al₂O₃.

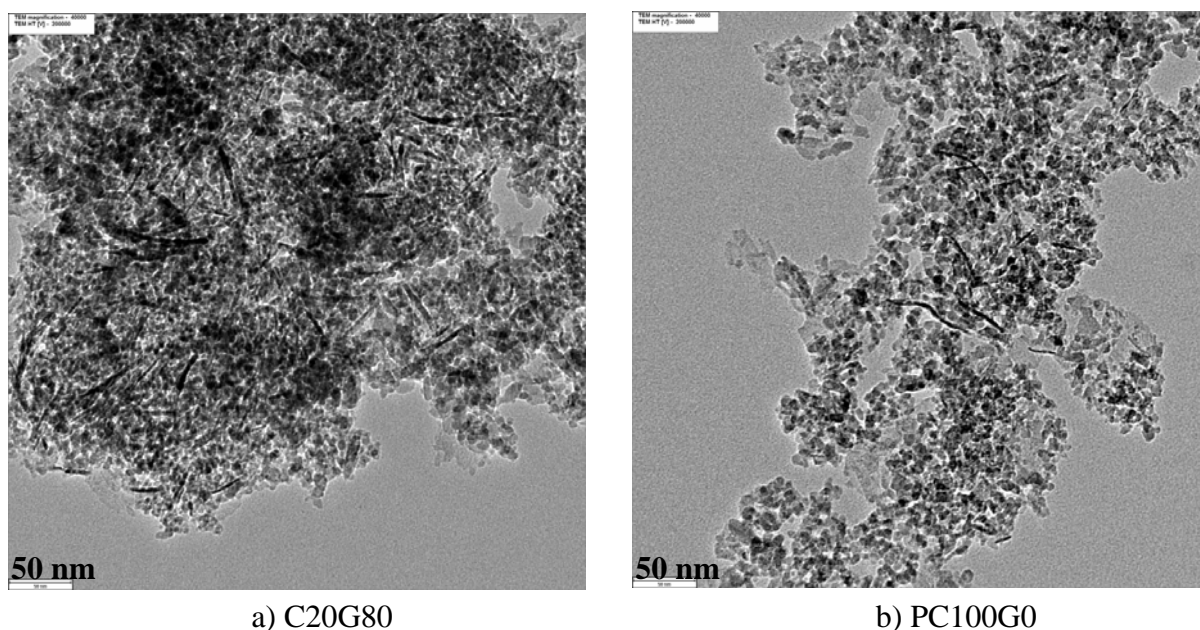


Figure 5.11 TEM Images of 20 wt% χ -Al₂O₃ synthesized by solvothermal and physical mixture.

5.5.4 Ammonia temperature-programmed desorption (NH₃-TPD)

Figure 5.12 shows the NH₃-TPD profiles of 20 wt% χ -Al₂O₃ catalysts synthesized by solvothermal and physical mixture. The profile for 20 wt% χ -Al₂O₃ catalysts synthesized by physical mixture, showed one sharp peak at the temperature ranged between 40 to 300°C while the profiles for 20 wt% χ -Al₂O₃ catalysts synthesized by solvothermal exhibited two broad peaks at the temperature ranged around 50 to 120°C and 180 to 380°C. According to described above, it can be concluded that the 20 wt% χ -Al₂O₃ catalysts synthesized by physical mixture possesses weak surface acidic sites as compared to the 20 wt% χ -Al₂O₃ catalysts synthesized by solvothermal which possesses weak and medium surface acidic sites.

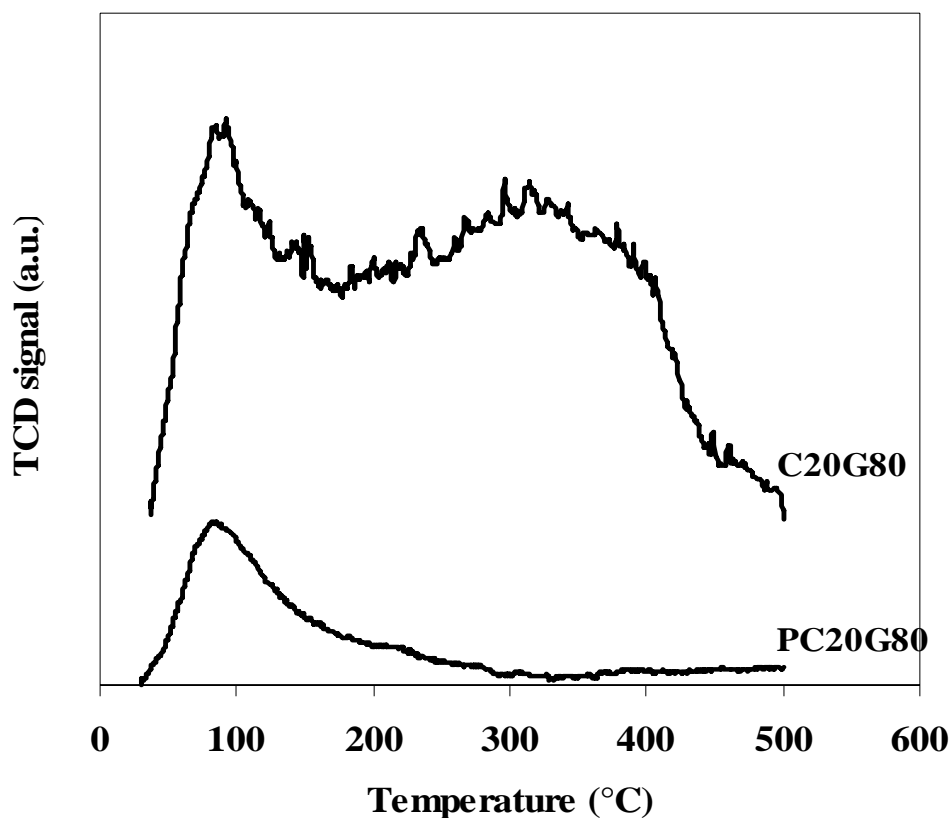


Figure 5.12 NH₃-TPD Profiles of 20 wt% γ -Al₂O₃ synthesized by solvothermal and physical mixture

The acid properties of the alumina catalysts are also reported in Table 5.11. The acidity of 20 wt% γ -Al₂O₃ synthesized by solvothermal and physical mixture is 4.004 and 0.999 $\mu\text{mol NH}_3/\text{g catalyst}$, respectively. The acidity of 20 wt% γ -Al₂O₃ catalyst synthesized by solvothermal is higher than the acidity of 20 wt% γ -Al₂O₃ synthesized by physical mixture. This result indicates that the 20 wt% γ -Al₂O₃ synthesized by solvothermal is appropriate synthesized method for improving the acidity of γ -Al₂O₃ catalysts.

Table 5.11 Acidity of 20 wt% χ -Al₂O₃ synthesized by solvothermal and physical mixture

Catalysts (χ/γ ratios)	Acidity ($\mu\text{mol NH}_3/\text{g catalyst}$)
C20G80 (20/80)	4.004
PC100G0 (20/80)	0.999

5.5.5 Titration method involving ion exchange

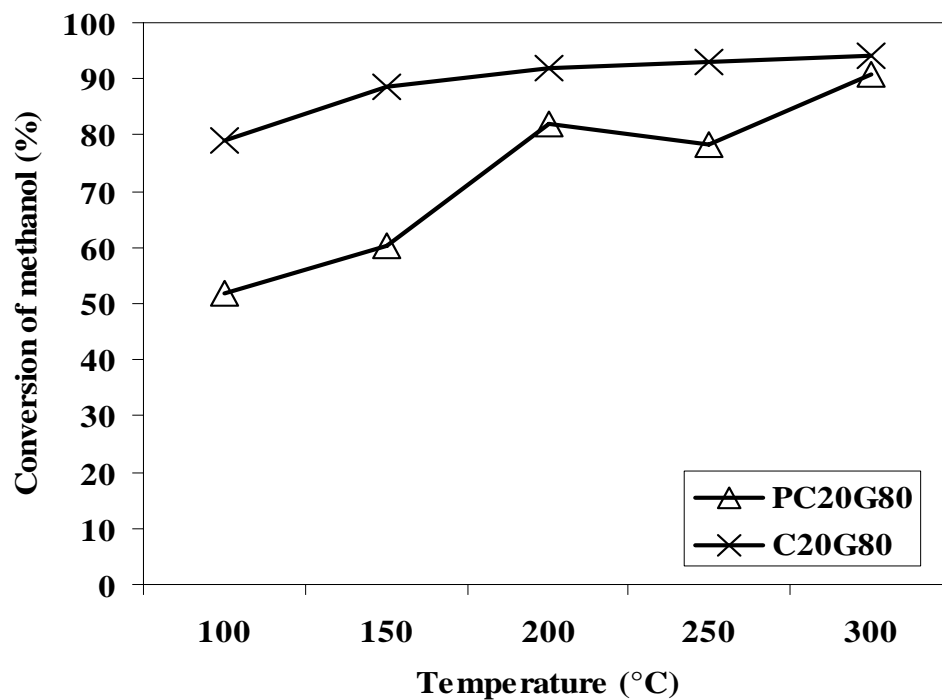
The acid properties of the alumina catalysts from titration method involving ion exchange are also studied and reported in Table 5.12. The acidity of 20 wt% χ -Al₂O₃ synthesized by solvothermal and physical mixture is 25 and 1 $\mu\text{mol/g}$ catalyst, respectively. The acidity of 20 wt% χ -Al₂O₃ catalyst synthesized by solvothermal is higher than the acidity of 20 wt% χ -Al₂O₃ synthesized by physical mixture. This result support the result from NH₃-TPD and indicate that solvothermal is appropriate synthesized method for improving the acidity of γ -Al₂O₃ catalysts.

Table 5.12 Acidity of 20 wt% χ -Al₂O₃ synthesized by solvothermal and physical mixture

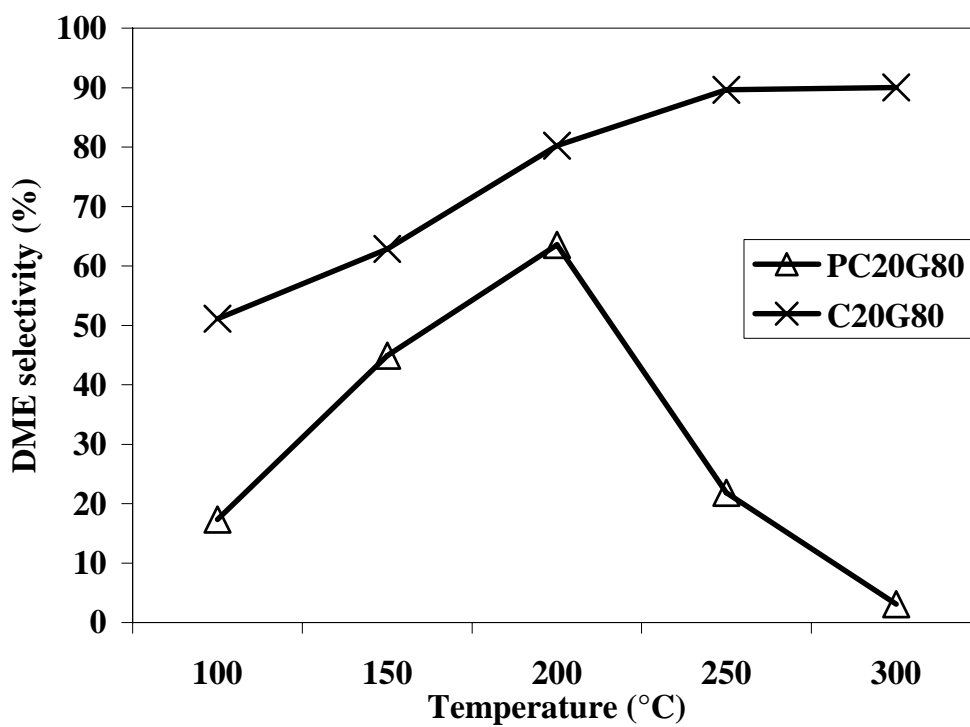
Catalysts (χ/γ ratios)	Acidity ($\mu\text{mol/g catalyst}$)
C20G80 (20/80)	25
PC100G0 (20/80)	1

5.6 Reaction Study for Al₂O₃ (χ/γ ratios: 20/80) synthesized by solvothermal and physical mixture method

Figure 5.13 shows the results of methanol dehydration on alumina catalysts at the atmospheric pressure in the temperature range from 100 to 300°C. Methanol conversion over alumina catalyst increased with increasing reaction temperature as shown in Figure 5.13a. The conversion of 20 wt% χ -Al₂O₃ synthesized by solvothermal and physical mixture increased as the reaction temperature increased from 100 to 300°C. The activity of 20 wt% χ -Al₂O₃ synthesized by solvothermal is higher than 20 wt% χ -Al₂O₃ synthesized by physical mixture. This result is in good agreement with the amount of acidity. This suggests that the acidity of Al₂O₃ catalyst play an important role on the catalytic activity for methanol dehydration reaction as the same result of described above. The plot between DME selectivity and temperature of 20 wt% χ -Al₂O₃ synthesized by solvothermal and physical mixture is also shown in Figure 5.13b. The DME selectivity of 20 wt% χ -Al₂O₃ synthesized by solvothermal increased as the reaction temperature increased, while the selectivity of 20 wt% χ -Al₂O₃ synthesized by physical mixture increased the highest selectivity at 200°C then decreased after that temperature and hydrocarbons were occurred. Figure 5.13c shows the plot between DME yields and temperature of 20 wt% χ -Al₂O₃ synthesized by solvothermal and physical mixture. DME yields of 20 wt% χ -Al₂O₃ synthesized by solvothermal and physical mixture showed the same trend of DME selectivity. This result suggested that 20 wt% χ -Al₂O₃ catalyst synthesized by solvothermal exhibited the higher DME yield than 20 wt% χ -Al₂O₃ catalyst synthesized by physical mixture because of its high activity and DME selectivity.

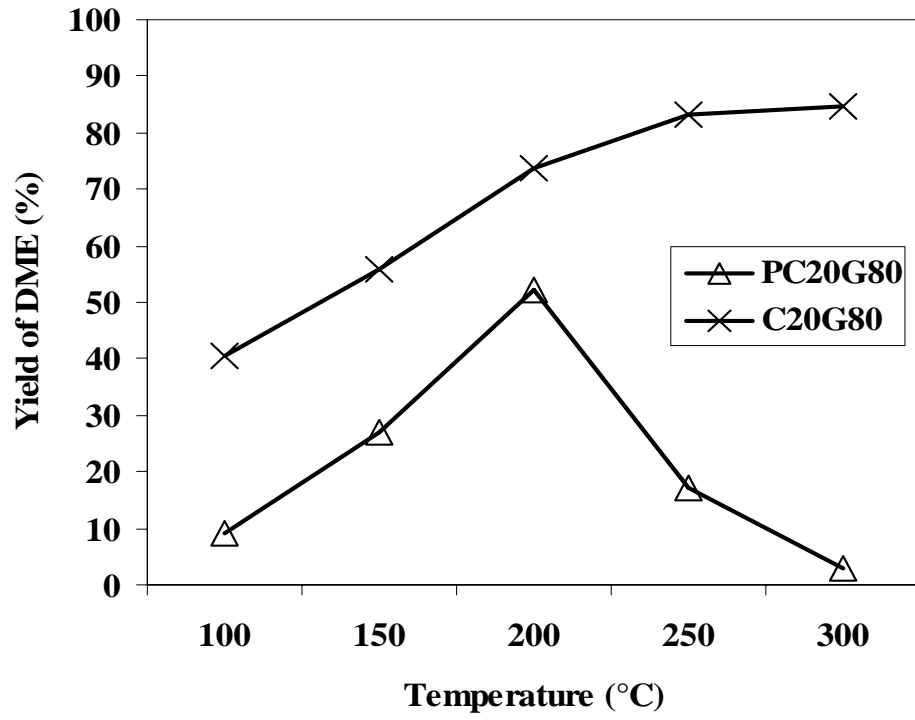


a) Methanol conversion profile



b) DME selectivity profile

Figure 5.13 Catalytic test of 20 wt% χ -Al₂O₃ synthesized by solvothermal and physical mixture (0.2 g of catalyst, GHSV=5,300 h⁻¹)



c) DME yield profile

Figure 5.13 (con.) Catalytic test of 20 wt% χ -Al₂O₃ synthesized by solvothermal and physical mixture.

(0.2 g of catalyst, GHSV=5,300 h⁻¹)

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

The conclusions of the present research are the following:

1. Commercial and synthetic γ -Al₂O₃ are compared.
 - Both of them exhibited the wrinkled sheets morphology.
 - The synthetic γ -Al₂O₃ via solvothermal method showed much higher acidity as revealed by NH₃ temperature programmed desorption and exhibited the higher yield.
- 2 Pure γ -Al₂O₃, pure χ -Al₂O₃ and the mixed χ/γ phase Al₂O₃ catalyst are compared.
 - As the formation of χ -alumina increased, the wrinkled sheets morphology became less apparent and spherical particles were observed.
 - Mixed χ/γ phase Al₂O₃ catalyst with 20 wt% χ -phase showed much higher density and strength of surface acidity as revealed by NH₃ temperature programmed desorption and ion-exchanged/titration method.
 - The 20 wt% χ -Al₂O₃ catalyst exhibited the highest yield for synthesis of dimethyl ether (86%) by dehydration of methanol reaction with high stability.
3. The synthesis method of 20 wt% χ -Al₂O₃ is compared between solvothermal method and physical mixture method.
 - Both of them exhibited the wrinkled sheets morphology.
 - 20 wt% χ -Al₂O₃ synthesized by solvothermal method showed much higher density and strength of surface acidity and exhibited the higher yield.

6.2 Recommendations

From this experiment, we have expected to improve acidity of catalyst for dimethyl ether (DME) production. Recommendations for the future work are the following.

1. To determine type of acidity (Bronsted and Lewis) with Fourier Transform Infrared Spectrophotometer (FTIR) and/or solid state Nuclear Magnetic Resonance (NMR).
2. To study effect of physical mixture synthesis method to characteristic catalyst and find reaction products distribution.
3. To study interaction of 20 wt% χ -Al₂O₃ to give higher acidity than γ -Al₂O₃.

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APPENDICES

APPENDIX A

CALCULATION OF VAPOR PRESSURE

Antione equation :

$$\ln P = A - \frac{B}{(T + C)} \quad (1)$$

Define: P = vapor pressure

A, B, C = constant value

T = temperature, (K)

Constant value of methanol for calculation vapor pressure

A = 7.89750

B = 1474.08

C = 229.13

For methanol, substitute in Antione equation

$$\begin{aligned} \ln P &= 7.8975 - \frac{1474.08}{((273.15 + 29) + 229.13)} \\ &= 5.1286 \end{aligned}$$

$$P = 168.7807 \text{ mmHg}$$

Pressure from tank = 16.25 psig

$$= 840.136 \text{ mmHg}$$

Volume of methanol = $\frac{168.7807}{840.136}$

$$= 20.09 \%$$

APPENDIX B

CALIBRATION CURVES

This appendix showed the calibration curves for calculation of composition of reactant and products in methanol dehydration. The reactant is methanol. The products are water and dimethyl ether.

The thermal conductivity detector (TCD), gas chromatography Shimadzu model 8AIT was used for analyzing the concentration of methanol, water and dimethyl ether by using Parapak Q column.

Mole of reagent in y-axis and area in x-axis, which was reported by gas chromatography, is exhibited in the curves. The calibration curves of methanol, water, and dimethyl ether.

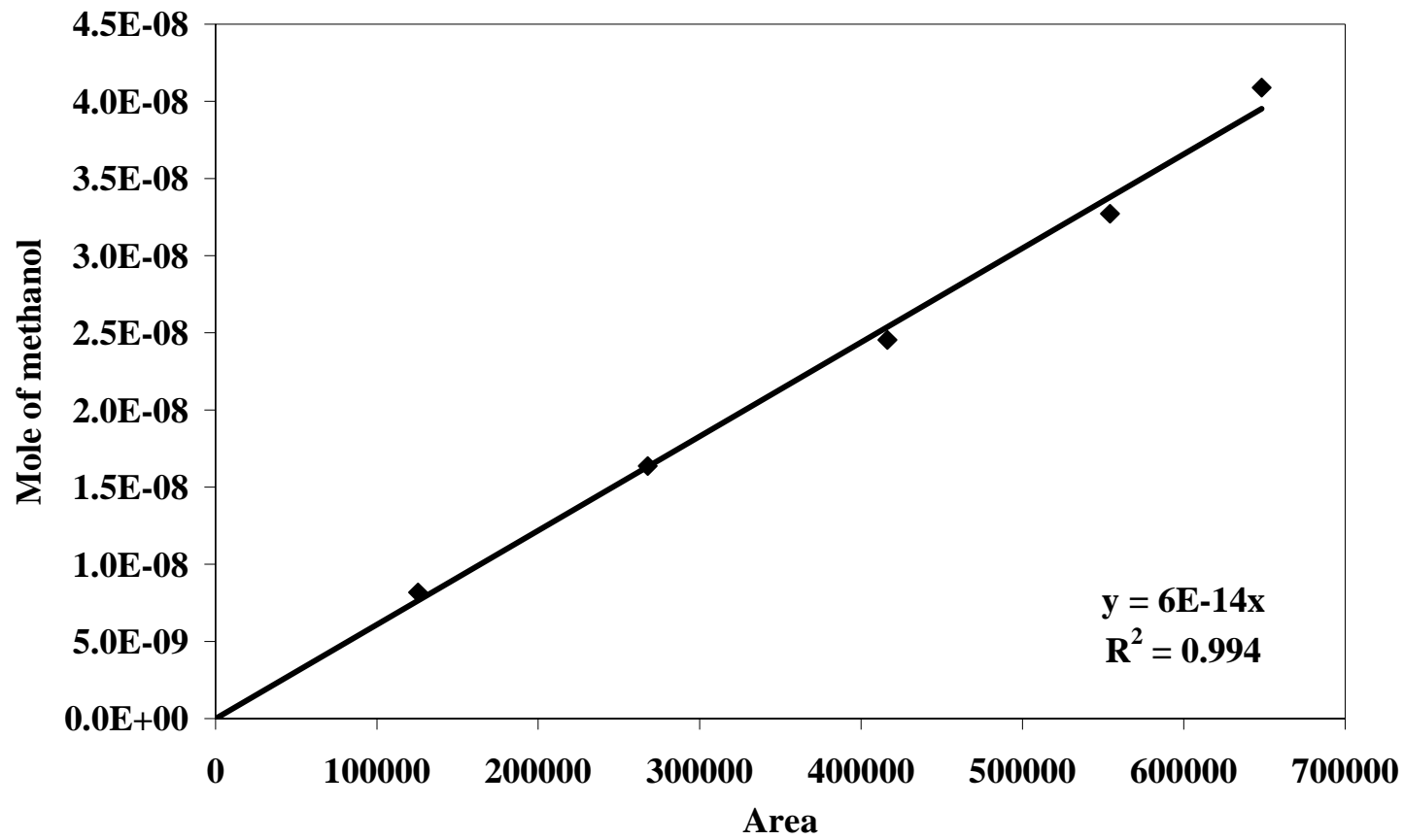


Figure B.1 The calibration curve of methanol.

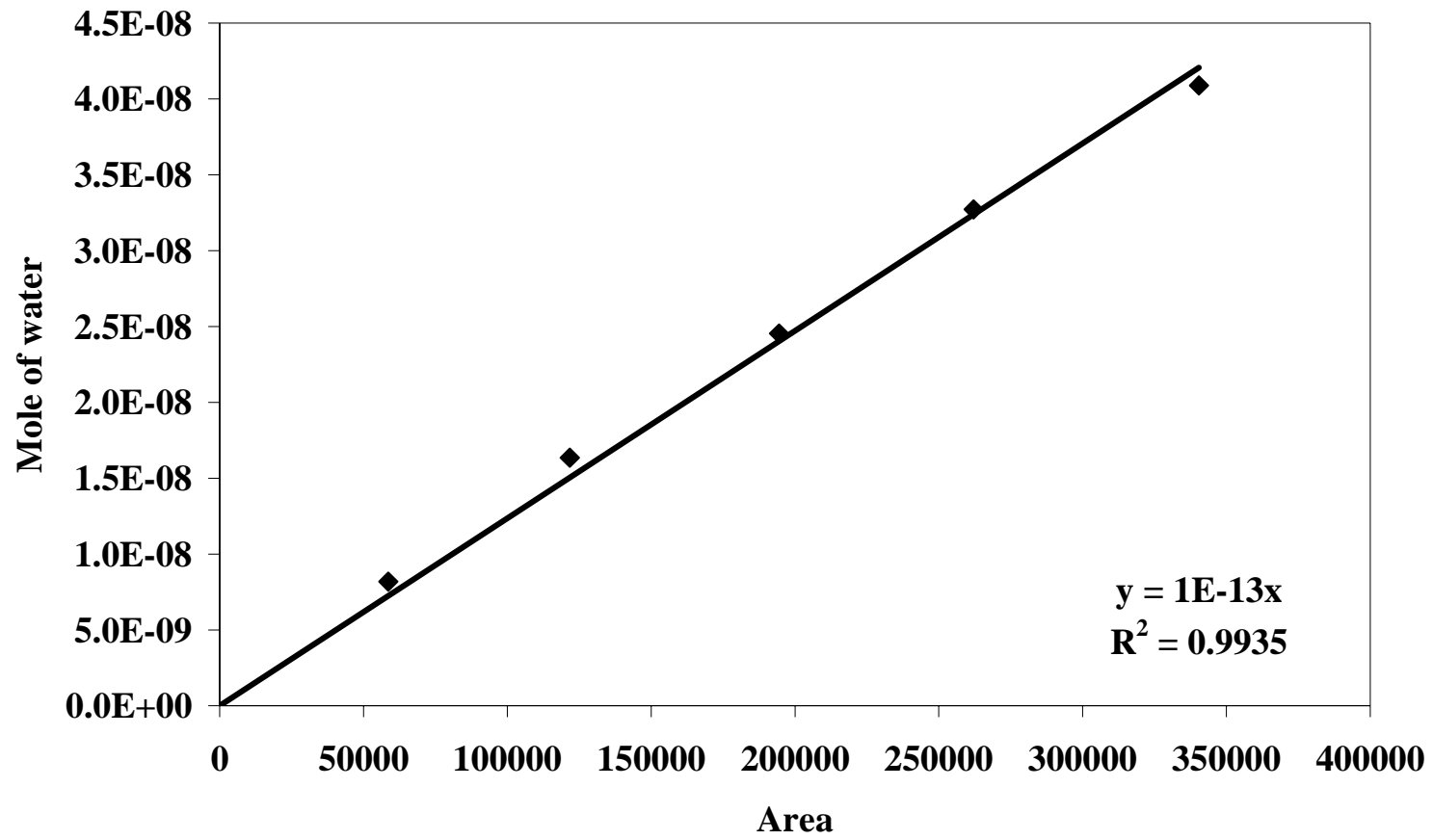


Figure B.2 The calibration curve of water.

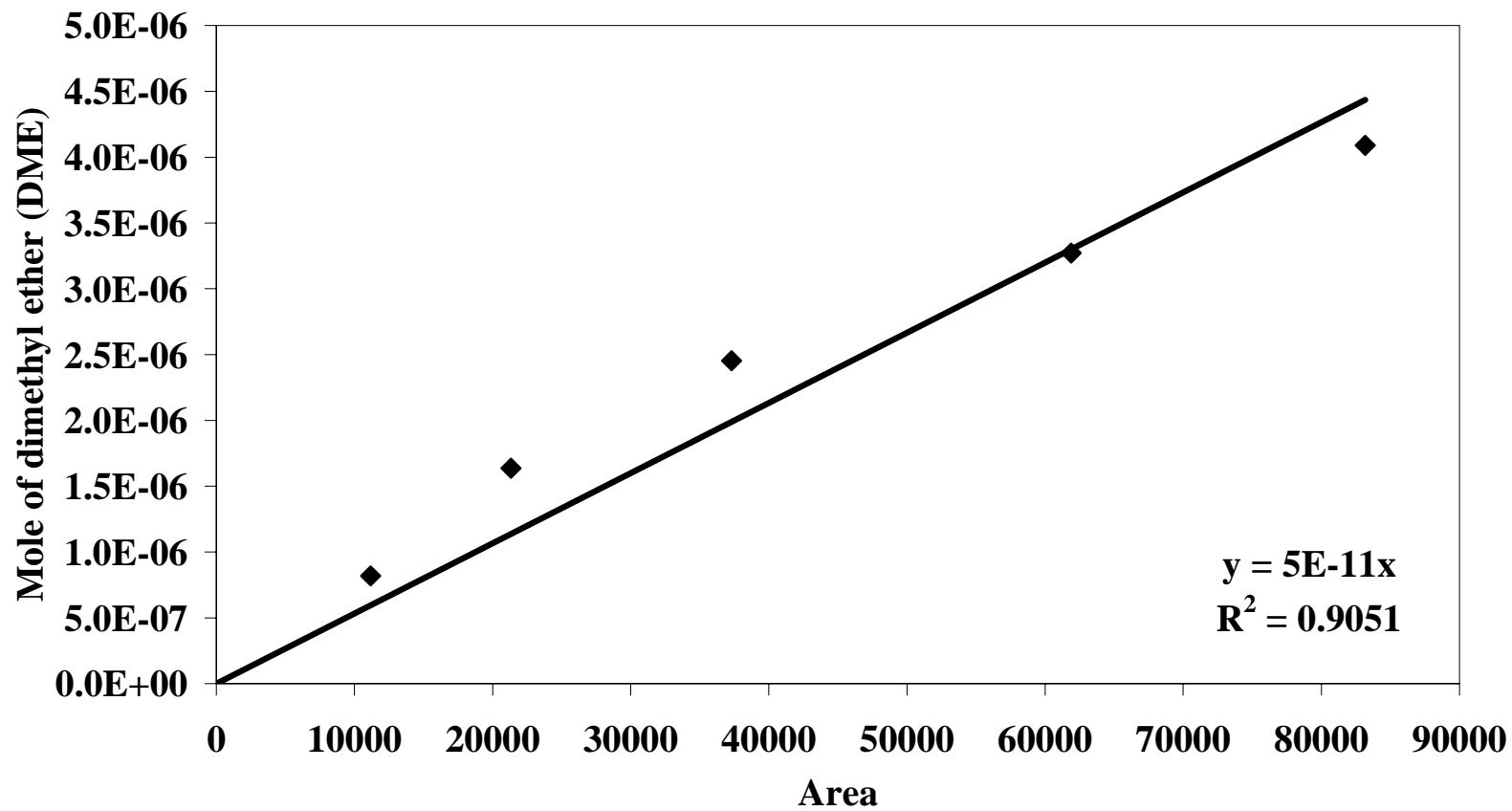


Figure B.3 The calibration curve of dimethyl ether.

APPENDIX C

CALCULATION OF THE CRYSTALLITE SIZE

Calculation of the crystallite size by Debye-Scherrer equation

The crystallite size was calculated from the half-height width of the highest intensity diffraction peak of XRD patterns of transition alumina.

From Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (\text{C.1})$$

where D = Crystallite size, Å

K = Crystallite-shape factor = 0.9

λ = X-ray wavelength, 1.5418 Å for CuK α

θ = Observed peak angle, degree

β = X-ray diffraction broadening, radian

The X-ray diffraction broadening (β) is the pure width of a powder diffraction free from all broadening due to the experimental equipment. α -Alumina is used as a standard sample to observe the instrumental broadening since its crystallite size is larger than 2000 Å. The X-ray diffraction broadening (β) can be obtained by using Warren's formula.

From Warren's formula:

$$\beta = \sqrt{B_M^2 - B_S^2} \quad (\text{C.2})$$

where B_M = The measured peak width in radians at half peak height.

B_S = The corresponding width of the standard material.

Example: Calculation of the crystallite size of χ -Al₂O₃

$$\begin{aligned}
 \text{The half-height width of peak} &= 1.153^\circ \text{ (from the figure C.1)} \\
 &= (1.153 \times \pi) / 180 \\
 &= 0.0201 \text{ radian}
 \end{aligned}$$

The corresponding half-height width of peak of α -alumina (from the B_s value at the 2θ of 67.44° in figure C.2) = 0.0057 radian

$$\begin{aligned}
 \text{The pure width, } \beta &= \sqrt{B_M^2 - B_S^2} \\
 &= \sqrt{0.0201^2 - 0.0057^2} \\
 &= 0.01927 \text{ radian}
 \end{aligned}$$

Scherrer equation:

$$B = 0.01927 \text{ radian}$$

$$2\theta = 67.44^\circ$$

$$\theta = 33.72^\circ$$

$$\lambda = 1.5418 \text{ \AA}$$

$$\begin{aligned}
 \text{The crystallite size} &= \frac{0.9 \times 1.5418}{0.01927 \cos 33.72} \\
 &= 86.6 \text{ \AA} \\
 &= 8.7 \text{ nm}
 \end{aligned}$$

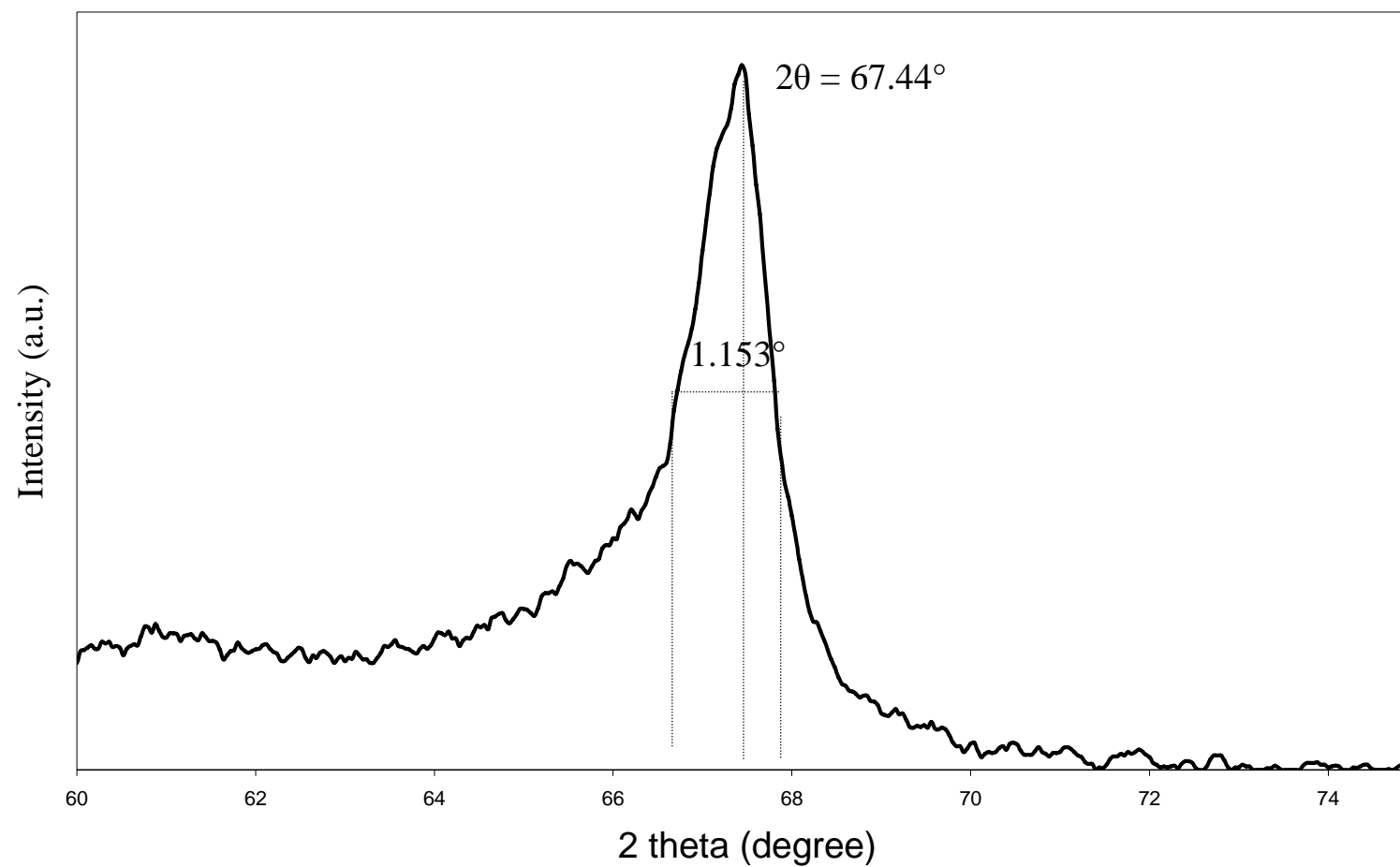


Figure C.1 The diffraction peak of pure chi alumina for calculation of the crystallite size.

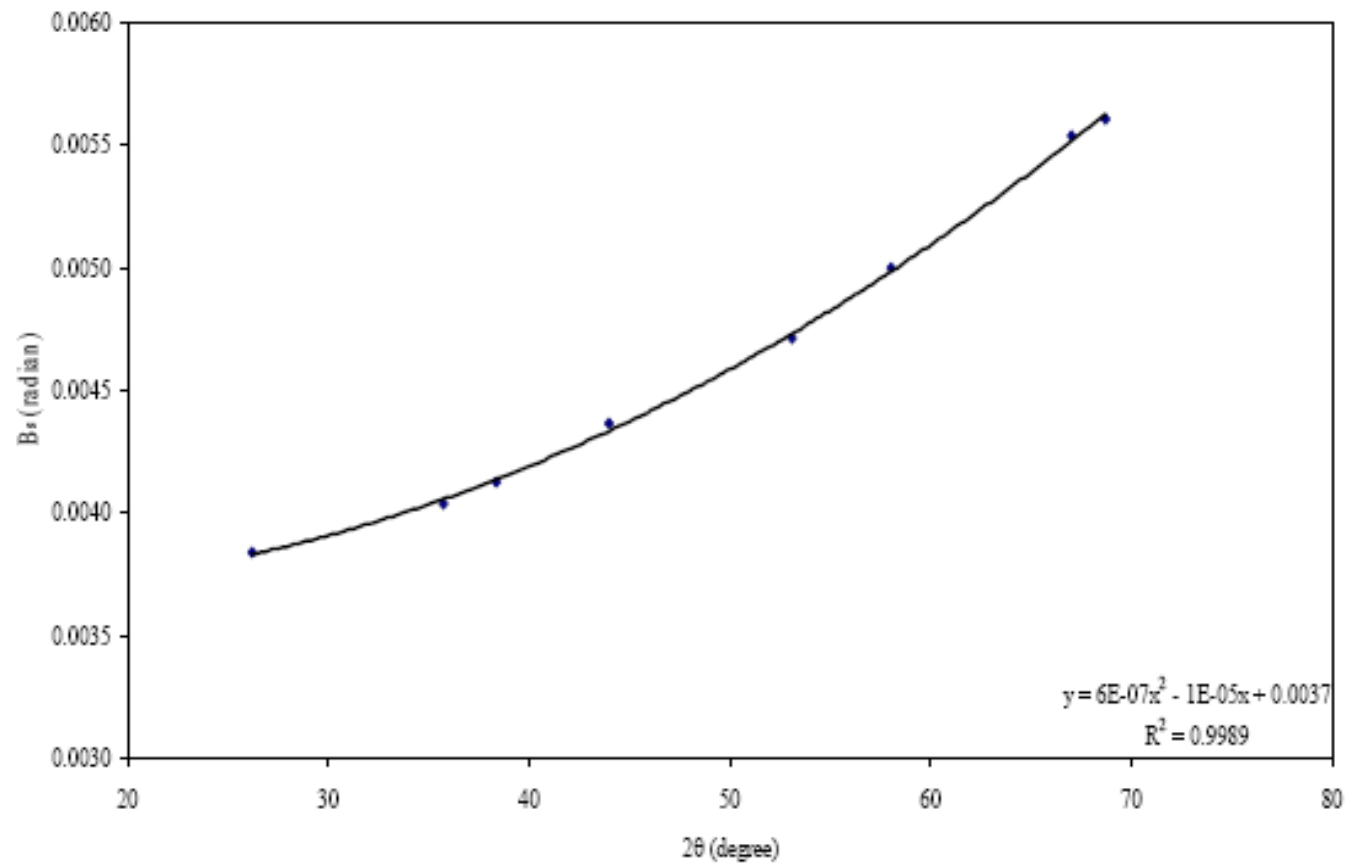


Figure C.2 The plot indicating the value of line broadening due to the equipment. The data were obtained by using α -alumina as a standard.

APPENDIX D

CALCULATION OF THE ACIDITY

This appendix showed the calculation of the acidity of alumina catalysts from the NH₃-TPD Profiles and Titration involving ion exchange of alumina catalysts.

$$\text{The acidity} = \frac{\text{mole}}{\text{amount of dry catalyst}}$$

Example: Calculation of the acidity of χ -Al₂O₃

The NH₃-TPD Profiles:

Under area of the NH₃-TPD Profiles of χ -Al₂O₃ = 0.000572 (from Figure D.1)

The mole of NH₃ was calculated from the calibration curves of NH₃ in Figure D.2.

$$\begin{aligned} \text{The mole of NH}_3 \text{ of } \chi\text{-Al}_2\text{O}_3 &= 0.000572 \times 0.0003 \\ &= 1.717 \times 10^{-7} \text{ mole} \end{aligned}$$

$$\text{Amount of } \chi\text{-Al}_2\text{O}_3 = 0.102 \text{ g}$$

$$\begin{aligned} \text{The acidity of } \chi\text{-Al}_2\text{O}_3 &= \frac{1.717 \times 10^{-7}}{0.102} \text{ mol NH}_3 / \text{g catalyst} \\ &= 1.684 \times 10^{-6} \text{ mol NH}_3 / \text{g catalyst} \\ &= 1.684 \text{ } \mu\text{mol NH}_3 / \text{g catalyst} \end{aligned}$$

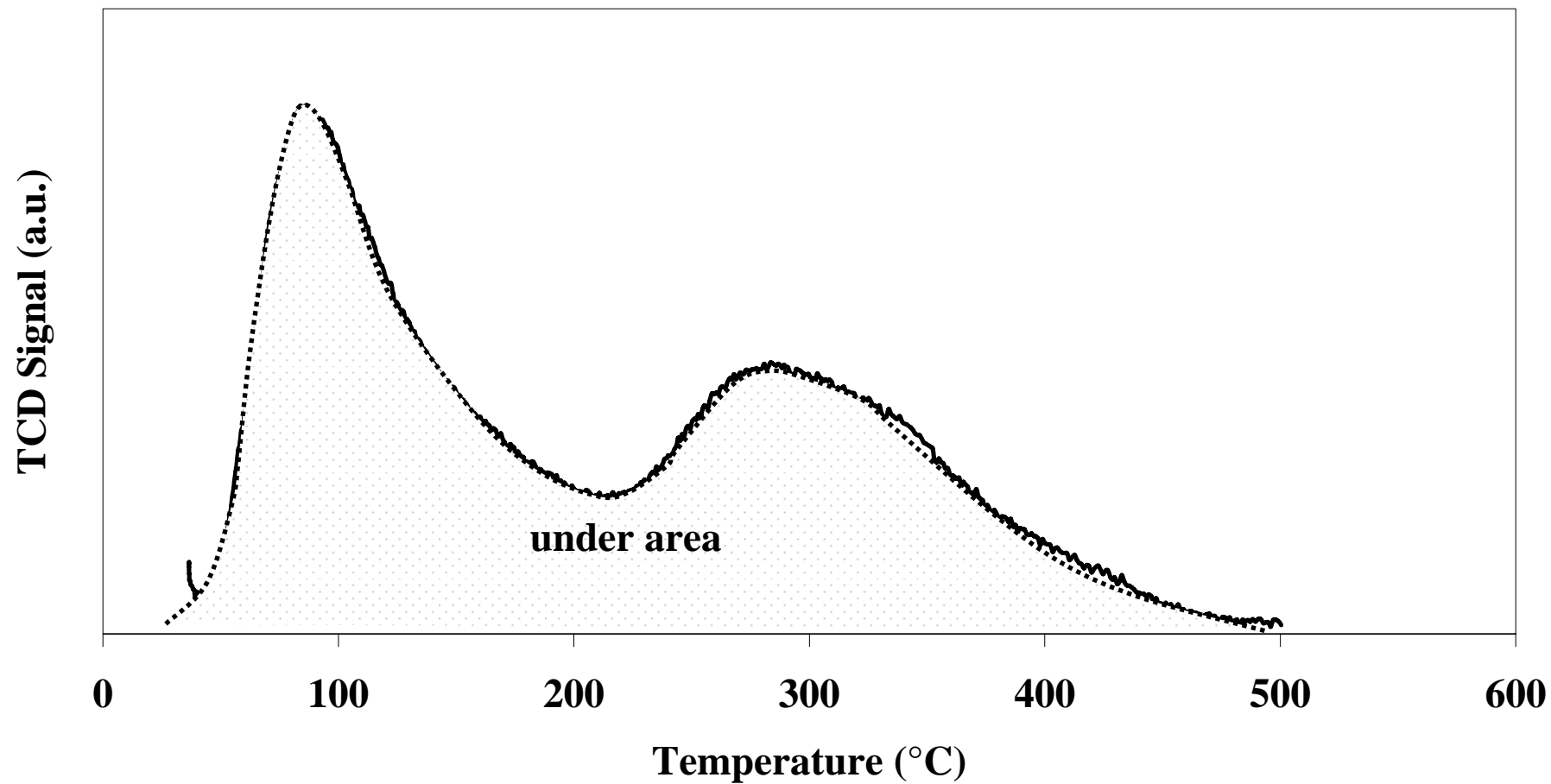


Figure D.1 The NH₃-TPD Profiles of pure chi alumina for calculation of the acidity.

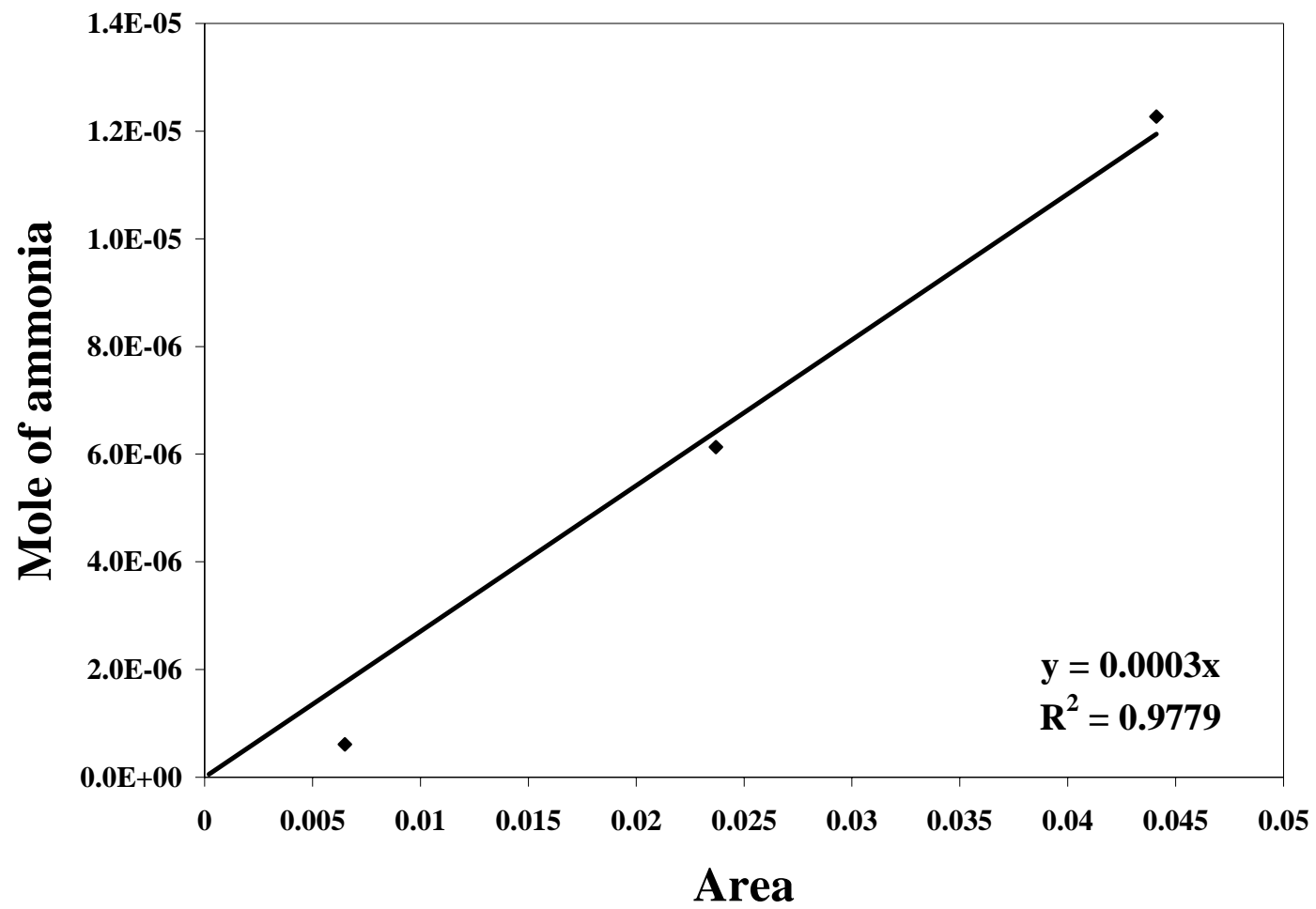


Figure D.2 The Calibration curve of ammonia.

Titration involving ion exchange:

From the experiment of γ -Al₂O₃:

The amount of catalyst = 0.200 g

The concentration of aqueous NaOH solution = 0.001 M

The amount of aqueous NaOH solution for titration to endpoint = 2 ml

$$\begin{aligned}\text{Mole of Na}^+ \text{ ions} &= \frac{0.001 \times 2}{1000} \text{ mole} \\ &= 2 \times 10^{-6} \text{ mole} \\ &= \text{Mole of H}^+ \text{ ions}\end{aligned}$$

$$\begin{aligned}\text{The acidity} &= \frac{2 \times 10^{-6}}{0.2} \text{ mol/g catalyst} \\ &= 10 \mu\text{mol /g catalyst}\end{aligned}$$

APPENDIX E

CALIBRATION CURVE OF CHI PHASE PERCENT

This appendix showed the calibration curves for calculation of chi phase percent in alumina catalysts which derived from the XRD pattern of physical mixtures between pure γ - and χ - alumina with various contents.

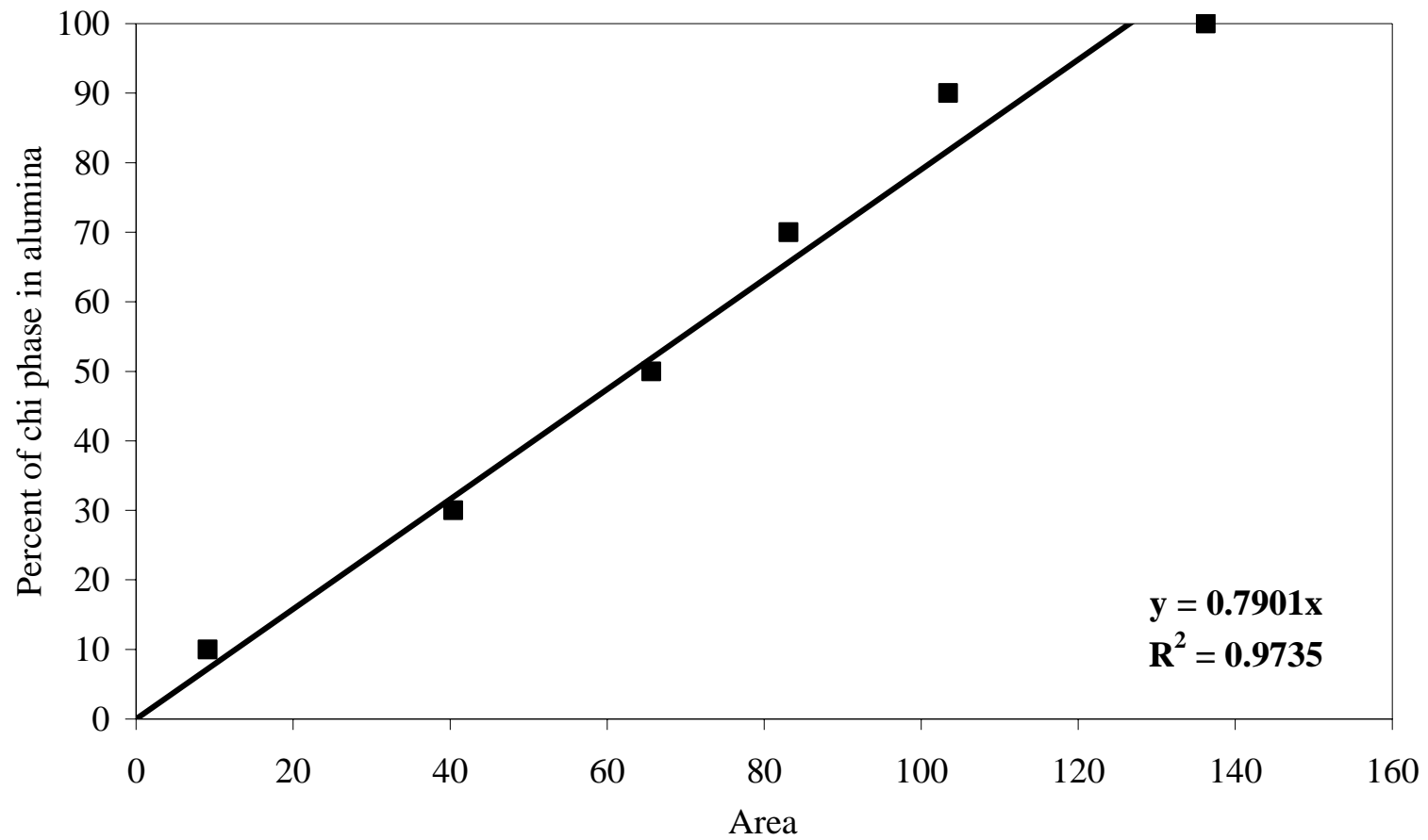


Figure E.1 The calibration curve of chi phase percent in alumina.

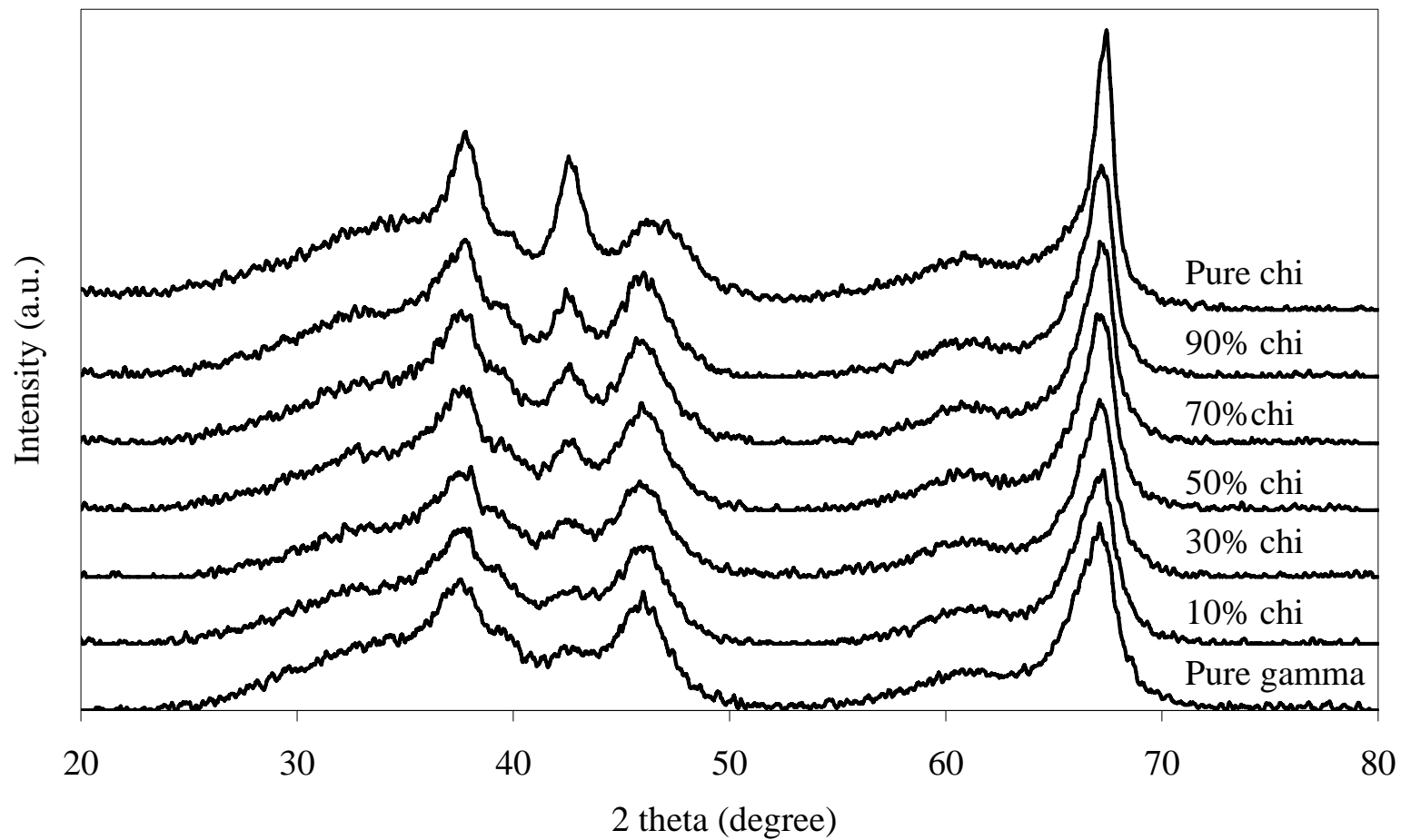


Figure E.2 The XRD pattern of physical mixtures between pure γ - and χ - alumina with various contents

APPENDIX F

LIST OF PUBLICATIONS

1. Jutharat Khom-in, Piyasan Praserthdam, Joongjai Panpranot and Okorn Mekasuwandumrong, "Synthesis of dimethyl ether (DME) from methanol dehydration using γ -Al₂O₃ and χ -Al₂O₃", Pure and Applied Chemistry International Conference, Bangkok, Thailand, January 30-February 1, 2008

2. Jutharat Khom-in, Piyasan Praserthdam, Joongjai Panpranot and Okorn Mekasuwandumrong, "Dehydration of Methanol to Dimethyl Ether over Nanocrystalline Al₂O₃ with Mixed γ - and χ -Crystalline Phases", Catalysis Communications, 2008, Accepted Manuscript

**Synthesis of dimethyl ether (DME) from
methanol dehydration using γ -Al₂O₃ and χ -Al₂O₃**

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ABSTRACT

Dehydration of methanol to dimethyl ether (DME) was investigated over nanocrystalline Al₂O₃ with γ - and χ -crystalline phases. The catalysts were characterized by X-ray diffraction (XRD), N₂ physisorption, and NH₃-temperature programmed desorption (NH₃-TPD). The catalytic test was studied in fixed-bed reactor at a range of temperatures: 100-300 °C under atmospheric pressure and a GHSV of 5,300 h⁻¹. It was found that the BET specific surface areas and pore volume of γ - Al₂O₃ and χ - Al₂O₃ catalysts were 196 m²/g, 0.778 cm³/g and 125 m²/g, 0.515 cm³/g, respectively. While the acidity of γ - Al₂O₃ and χ - Al₂O₃ catalysts increased from 0.490 to 1.684 mmol NH₃/g dry sample. The conversion over of γ - Al₂O₃ and χ - Al₂O₃ catalysts increased as the reaction temperature increased from 100 to 300°C however χ -Al₂O₃ catalyst exhibited higher conversion than γ -Al₂O₃. Because methanol dehydration reaction is an acid-catalyzed reaction, the methanol conversion is mainly related to the acidity.

Keywords

χ - Al₂O₃, γ - Al₂O₃, Dimethyl ether (DME), Methanol dehydration

1. INTRODUCTION

Dimethyl ether (DME) is a potential alternative fuel for future diesel engine operation because of its lower NO_x emission, near-zero smoke amounts, and lesser engine noise than conventional diesel oil [1-3]. It can also be used to replace chlorofluorocarbons (CFCs) which destroy ozone layer of the atmosphere and used as an aerosol propellant, due to its liquefaction property, such as hair spray and shaving cream [3-8].

Dimethyl ether can be produced by methanol dehydration over a solid acid catalyst or direct synthesis from syngas over a bifunctional catalyst [1, 3, 9]. Methanol dehydration to dimethyl ether is a potential process and more favorable in views of thermodynamics and economy [2, 5]. Such reaction occurs in different path-ways on different type of solid-acid catalysts such as γ -Al₂O₃, HZSM-5, HY zeolite, silica-alumina, phosphorus-alumina, fluorinated alumina, etc. [1-12]. Al₂O₃ is used as a common catalyst because of its fine particle size, high surface area, surface catalytic activity, excellent thermal stability, and wide range of chemical, physical, and catalytic properties and Al₂O₃ has received much intensive study both for academic and commercial purposes [13-15]. Among the various crystalline phases of Al₂O₃, γ -Al₂O₃ has received much attention due to its high selectivity [3, 7]. In order improve the acidity of γ -Al₂O₃, addition of some dopants such as borate, silica, phosphorous, and fluorine has been studied [2-3, 8-9, 11-12].

χ -Al₂O₃ is one of the metastable polymorphs of transition alumina [13] with relatively high acidity compared to γ -Al₂O₃. It can be prepared directly by solvothermal method using appropriate solvent. The advantages of the solvothermal method are given products with uniform morphology, well-controlled chemical composition, narrow particle size distribution, controlled crystal structures, and controlled grain sizes. Moreover, the morphologies of products can be controlled by process conditions such as solute concentration, reaction temperature, reaction time and the type of solvent.[16-26]

PUBLICATION 1

This research studied dehydration of methanol to dimethyl ether over γ - Al_2O_3 and χ - Al_2O_3 catalysts which were prepared by solvothermal method.[16-22] Effect of characteristic catalysts by XRD, N_2 -adsorption, and NH_3 -TPD techniques to DME productivity in methanol dehydration were examined and discussed.

2. EXPERIMENTAL

2.1 Catalysts preparation

Nanocrystalline transition Al_2O_3 catalysts were prepared by using solvothermal method according to the procedure described in Meephoka et.al. [15]. 15 g of aluminum isopropoxide (AIP) was suspended in 100 ml of desired organic solvent in a test tube, and then the test tube was placed in a 300 ml autoclave. An additional 30 ml of same solvent was placed in the gap between the autoclave wall and the test tube. The autoclave was completely purged with nitrogen, heated to a desired temperature 300 °C at a rate of 2.5°C/ min and kept at that temperature for 2 h. After the autoclave was cooled to room temperature, the resulting product was repeatedly washed with methanol by vigorous mixing and centrifuging and then dried in air. The as-synthesized powders were calcined in air at 600°C for 6 h with a heating rate of 10°C/min. The organic solvents used in this study were 1-butanol and toluene. The obtained catalysts comprised of 100% gamma phase and 100% chi phase, respectively.

2.2 Characterization

XRD was performed to determine the bulk phase of catalysts by SIEMENS D 5000 X-ray diffractometer connected with a computer with Diffract ZT version 3.3 program for fully control of the XRD analyzer using Cu $K\alpha$ radiation source with Ni filter in the 2θ range of 10-80 degrees. The crystallite size was estimated from line broadening according to the Scherrer equation.

Specific surface area, pore volume and pore diameter were measured by N_2 adsorption-desorption isotherm at liquid nitrogen temperature (-196 °C) using a Micromeritics ASAP 2020. The specific surface area and pore distribution were calculated according to Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods, consecutively.

The acidity of the catalyst samples was determined by temperature-programmed desorption of ammonia using a Micromeritics Chemisorp 2750 with a computer. In an experiment, about 0.10 g of the catalyst sample was placed in a quartz tube and pretreated at 265 °C in a flow of helium.

The sample was saturated with 15% NH_3/He . After saturation, the physisorbed ammonia was desorped in a helium gas flow about 0.5 h. Then the sample was heated from 40 to 700 °C at a heating rate 10 °C /min. The amount of ammonia in effluent was measured via TCD signal as a function of temperature.

2.3 Catalytic test

The dehydration of methanol over the catalyst samples was carried out in a fixed-bed reactor with an inner diameter 6 mm. In an experiment, 0.2 g of each catalyst was loaded and the gas hourly space velocity (GHSV) was 5,300 h^{-1} . Methanol was bubbled by helium through a glass saturator maintained at 29 °C. The reactor was carried out in the temperature range: 100-300 °C under atmospheric pressure. The reaction products were analyzed by an on-line gas chromatograph with a Porapak-Q column operating at 110°C and a TCD detector.

3. RESULTS AND DISCUSSION

3.1 Catalyst characterization

Figure 1 shows XRD pattern of the alumina catalysts produced gamma and chi. Each phase of transition alumina has a specific ratio of each peak. The XRD peaks of pure gamma phase are obvious at 32° , 37° , 39° , 45° , 61° and 66° . γ -alumina was formed as seen by the XRD characteristic peaks at $2\theta = 32^\circ$ [14]. For pure chi phase, XRD peaks are apparent at 37° , 40° , 43° , 46° , 60° , and 67° . The XRD characteristic peaks of χ -alumina was observed at $2\theta = 43^\circ$ [14,15].

In Table 1, some physical properties of the alumina catalysts are listed. According to previously work of our group [15], the BET specific surface area decreased slightly and the average pore diameter was rather similar. The results are in agreement with the reported; showed 196 and 125 m^2/g for pure gamma and pure chi phases and the pore diameter is about 11 nm. The pore volume of pure gamma and pure chi phases is 0.778 and 0.515 cm^3/g , respectively but the crystallite size of pure gamma and pure chi phases is 4 nm and 8.7 nm, respectively.

The result of the acid properties of the alumina catalysts are summarized in Table 1. The acidity of pure gamma and pure chi phases is 0.490 and 1.684 $\text{mmol NH}_3/\text{g}$ dry sample, respectively. Also, NH_3 -TPD profiles are depicted in Figure 2. The profiles for pure γ -alumina exhibited one sharp peak at the temperature ranged between 40 to 85°C , while the profiles for pure χ -alumina showed two broad peaks at the temperature ranged around 50 to 180°C and 200 to 400°C , respectively. According to Corma et. al.[27], these peaks can be ascribed to the NH_3 desorbed from acid sites with low and medium to high strengths. From these results, it can be concluded that the solvothermal-made χ -alumina powder possesses strong surface acidic sites as compared to the γ -alumina powder.

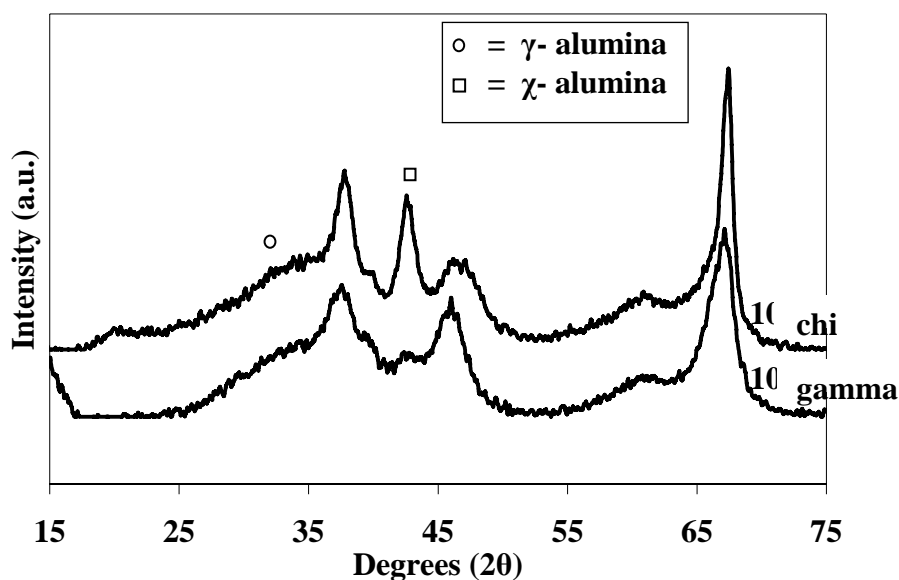


Figure 1. XRD patterns of alumina samples

PUBLICATION 1

Table 1. Acidity contents and some properties of the alumina catalysts

Samples	BET Specific surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	Crystallite size (nm)	Acidity (mmol NH ₃ /g dry sample)
gamma	196	0.778	10.6	4	0.490
chi	125	0.515	11.1	8.7	1.684

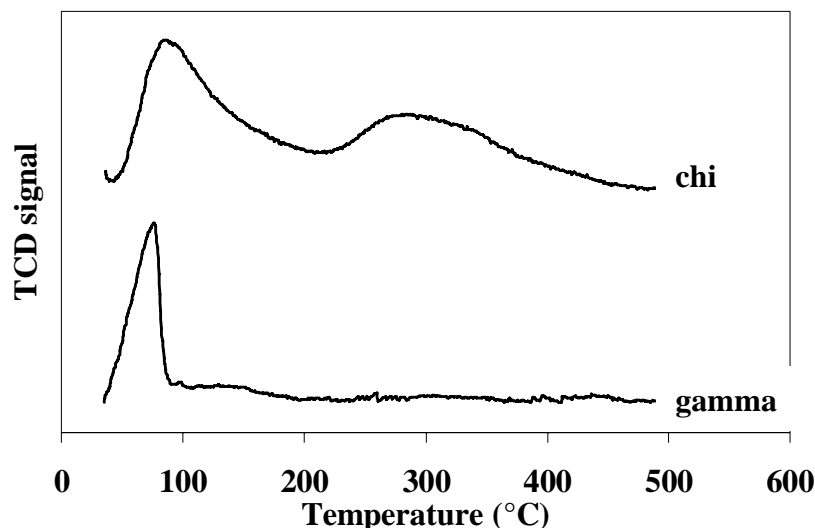


Figure 2. Temperature program desorption profiles of catalyst samples.

3.2 Catalytic reaction

Figure 3 shows the results of methanol dehydration on alumina catalysts at the atmospheric pressure in the temperature range from 100 to 300 °C. According to Jun et.al. [4], Jiang et.al. [5], Kim et.al. [7], Xu et.al. [8], Fu et.al. [9], and Vishwanathan et.al. [10], the effect of temperature on the catalytic activity of γ -Al₂O₃ was examined. The methanol conversion over alumina catalyst increased with an increasing on the reaction temperature. The results are in agreement with our result as shown in Figure 3a, the conversion over all Al₂O₃ catalysts increase as the reaction temperature increase from 100 to 300 °C. At high temperature the conversion is close to 100%, it is difficult to define the effect of temperature so the purpose aims at low temperature. The activity of Al₂O₃ catalysts was improved in order of pure chi phase > pure gamma phase. Our result is in good agreement with the increasing order of acidity. This suggests that the acidity of Al₂O₃ catalyst play an important role on the catalytic activity for methanol dehydration reaction. According to the literatures Xia et.al. [3], Jun et.al. [4], and Jiang et.al. [5], the methanol dehydration reaction is an acid-catalyzed reaction, hence the methanol conversion is mainly related to the acidity with weak and medium. The plot between DME selectivity and temperature of all Al₂O₃ catalysts is also shown in Figure 3b. The DME selectivity of pure gamma and pure chi phase remained constant at around 55%. Figure 3c shows the plot between DME yields and temperature of Al₂O₃ catalysts. DME yields of Al₂O₃ catalysts increased as the reaction temperature increased from 100 to 300°C. At 150°C, pure chi phase exhibited the higher DME yield due to its high activity. This is shown that pure chi phase is better than pure gamma phase at 150°C.

PUBLICATION 1

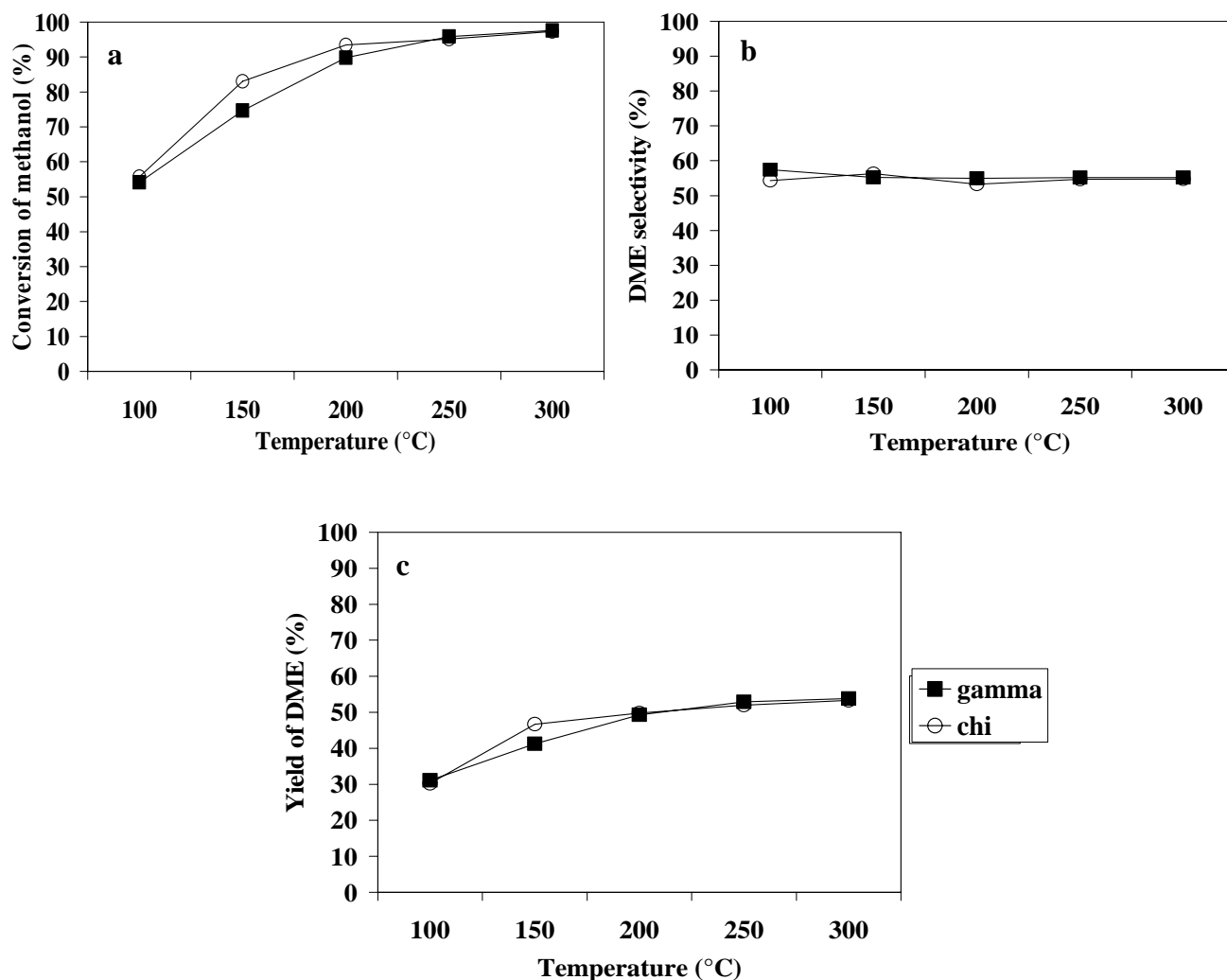


Figure 3. Catalytic test of catalyst samples: a) conversion of methanol, b) DME selectivity, and c) yield of DME.

4. CONCLUSIONS

Nanocrystalline Al_2O_3 catalysts with γ and χ phases have been successfully prepared by solvothermal method which is one-step synthesis and simple method. BET specific surface area of γ and χ phases alumina decreased from 196 to 125 m^2/g , respectively and pore volume of γ and χ phases alumina decreased from 0.78 to 0.52 cm^3/g , respectively. While the average pore diameter was still constant at around 11 nm. The NH_3 -TPD results revealed that χ - Al_2O_3 catalyst increased the densities and strength of surface acidity, which improve the catalytic activity for methanol dehydration to DME.

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“REVISED”

Dehydration of Methanol to Dimethyl Ether over Nanocrystalline Al₂O₃ with
Mixed γ - and χ -Crystalline Phases

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Abstract

Dehydration of methanol to dimethyl ether (DME) was investigated over a wide range of nanocrystalline Al_2O_3 with mixed γ - and χ -crystalline phases. The catalysts were characterized by X-ray diffraction (XRD), N_2 physisorption, ion-exchange titration, and NH_3 -temperature programmed desorption (NH_3 -TPD). It was found that γ - Al_2O_3 catalyst containing 20 wt% of χ -phase exhibited the highest yield (86%) with good stability for DME synthesis. The NH_3 -TPD and ion-exchange titration results revealed 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.

KEYWORDS: methanol dehydration; dimethyl ether (DME); γ - Al_2O_3 ; χ - Al_2O_3 ; mixed phases

1. Introduction

Dimethyl ether (DME) is a potential alternative fuel for future diesel engine operation because of its lower NO_x emission, near-zero smoke amounts, and lesser engine noise compared to conventional diesel oil [1-3]. It can also be used to replace chlorofluorocarbons (CFCs) which destroy ozone layer of the atmosphere and used as an aerosol propellant, aided by its liquefaction property, such as hair spray and shaving cream [3-8].

Dimethyl ether can be produced by methanol dehydration over a solid acid catalyst or direct synthesis from syngas over a bifunctional catalyst [1, 3, 9]. Methanol dehydration to dimethyl ether is a potential process and more favorable in views of thermodynamics and economy [2, 5]. Such reaction occurs in different pathways on different type of solid-acid catalysts such as γ -Al₂O₃, HZSM-5, HY zeolite, silica-alumina, phosphorus-alumina, fluorinated alumina, etc. [1-12]. Al₂O₃ is used as a common catalyst because of its fine particle size, high surface area, surface catalytic activity, excellent thermal stability, high mechanical resistance, and wide range of chemical, physical, and catalytic properties [13-15]. Among the various crystalline phases of Al₂O₃, γ -Al₂O₃ has received much attention due to less generation of by product [3, 7]. In order improve the acidity of γ -Al₂O₃, addition of some dopants such as borate, silica, phosphorous, and fluorine has been studied [2-3, 8-9, 11-12].

χ -Al₂O₃ is one of the metastable polymorphs of transition alumina [13] with relatively high acidity compared to γ -Al₂O₃. It can be prepared directly by solvothermal method using appropriate solvent. In this study, nanocrystalline γ -Al₂O₃, χ -Al₂O₃, and mixed γ - and χ - crystalline phase Al₂O₃ with various χ/γ ratios were prepared by the solvothermal method and evaluated in methanol dehydration reaction to dimethyl ether. The catalysts were also characterized by X-ray diffraction

(XRD), N₂ physisorption, ion-exchange titration, and NH₃-temperature programmed desorption (NH₃-TPD).

2. Experimental

2.1 Catalyst Preparation

Nanocrystalline transition Al₂O₃ catalysts with various χ/γ phase compositions were prepared by using solvothermal method according to the procedure described in Meephoka et al. [15]. Approximately 15 g of aluminum isopropoxide (AIP) was suspended in 100 ml of desired organic solvent in a test tube, and then the test tube was placed in a 300-ml autoclave. An additional 30 ml of same solvent was placed in the gap between the autoclave wall and the test tube. The autoclave was completely purged with nitrogen, then heated to 300°C at a rate of 2.5°C min⁻¹ and kept at that temperature for 2 h. After the autoclave was cooled to room temperature, the resulting product was repeatedly washed with methanol by vigorous mixing and centrifuging and then dried in air. The organic solvents used in this study were toluene, 1-butanol, and the mixed solvents between toluene and 1-butanol with various compositions. The as-synthesized powders were calcined in air at 600°C for 6 h with a heating rate of 10°C/min. The obtained catalysts comprised of 0, 10, 20, 50, 80, 90 and 100% χ -phase and are referred herein as 0C, 10C, 20C, 50C, 80C, 90C and 100C, respectively.

2.2 Catalyst Characterization

XRD was performed to determine the bulk phase of catalysts using a SIEMENS D5000 X-ray diffractometer connected with a computer with Diffract ZT

version 3.3 program for fully control of the XRD analyzer using Cu K_{α} radiation source with Ni filter in the 2θ range of 10-80 degrees. The average crystallite size was estimated from line broadening using the Scherrer equation. Surface area, pore volume and pore diameter were measured by N_2 adsorption–desorption isotherm at liquid nitrogen temperature (-196°C) using a Micromeritics ASAP 2020. The surface area and pore distribution were calculated according to Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods, consecutively. Acidity of the catalyst samples was determined by temperature-programmed desorption of ammonia using a Micromeritics Chemisorp 2750 system and ion-exchange/titration method. For the ion-exchange/titration method, similar procedure as that described in Ref.[17] was used. Approximately 0.2 g of catalyst was added to 10 ml of 3.42 M aqueous NaCl solution under stirring 30 h. After the ion exchange between the catalyst H^+ ions and the Na^+ ions in solution, the liquid was filtrated and titrated with 0.001 M aqueous NaOH solution. The endpoint (pH~7) of titration was determined using a pH meter and confirmed using pH paper.

2.3 Reaction Study

Dehydration of methanol was carried out in a fixed-bed reactor with an inner diameter 6 mm. In an experiment, approximately 0.2 g of catalyst was loaded and the gas hourly space velocity (GHSV) was $5,300\text{ h}^{-1}$. Methanol was bubbled by helium through a glass saturator maintained at 29°C . The partial pressure of methanol in the gas mixture was 169 mmHg. The reaction was carried out in the temperature range $100\text{-}300^{\circ}\text{C}$ under atmospheric pressure. The products were analyzed on-line using a gas chromatograph with a TCD detector and a Porapak-Q column operating at 110°C .

196 to 125 m²/g and 0.78 to 0.52 cm³/g, respectively as the χ -phase content increased from 0 to 100 wt% while the average pore diameter remained constant at around 10 nm. The results were in good agreement with the previous work reported by our group for the mixed γ - and χ -phase alumina [15]. The acid properties of the alumina catalysts are also reported in **Table 1**. The total acidity concentration determined by NH₃ temperature program desorption experiments in $\mu\text{mol NH}_3/\text{g cat.}$ was found to be in the order: 20C > 50C > 100C > 90C > 10C > 80C > 0C. In addition, acidity of the Al₂O₃ catalysts was also measured by the ion-exchange/titration method. The acidity determined by such technique was in the order: 20C > 50C > 100C > 10C > 0C > 90C > 80C. There was a slight difference from those determined by NH₃-TPD for last four orders. Discrepancy of the number of acid sites determined by these two techniques has also been reported by other researchers [17]. However, it is clearly shown that acidity of γ -Al₂O₃ catalyst was improved when it contained an appropriate amount of χ -phase Al₂O₃.

Figure 3 shows the results of methanol dehydration on alumina catalysts at the atmospheric pressure in the temperature range from 100 to 300°C. According to literatures, the effect of temperature on the catalytic activity of γ -Al₂O₃ has been examined [4-5, 7-10]. Typically, methanol conversion increased with increasing reaction temperature. Similar trend was observed for all the Al₂O₃ catalysts in this study under the reaction conditions used (**Figure 3a**). At 150°C, the activity of Al₂O₃ catalysts was improved in order of 20C > 50C > 100C > 10C > 0C > 90C > 80C which is in good agreement with the increasing order of acidity concentration determined by the ion-exchange/titration method. It is known that acidity of Al₂O₃ catalyst plays an important role on the catalytic activity for methanol dehydration reaction. Since methanol dehydration reaction is an acid-catalyzed reaction, the

methanol conversion is mainly related to acidity with weak and medium strong [3-5]. The plot between DME selectivity and temperature of all Al_2O_3 catalysts is also shown in Figure 3b. The DME selectivity of 0C, 10C and 20C increased as the reaction temperature increased, while the selectivity of other catalysts remained constant at around 55 mole%. The main by-products were CO and H_2 obtained from CH_3OH decomposition reaction. Figure 3c shows the plot between DME yields and temperature of all Al_2O_3 catalysts. DME yields of all the Al_2O_3 catalysts increased as the reaction temperature increased from 100 to 300°C with the 20C catalyst exhibited the highest DME yield of 86% at 300°C. A review for previous studies of DME synthesis from methanol dehydration over various catalyst systems has been summarized in Table 2. Compared to many studies reported earlier [2, 5-11], our 20C Al_2O_3 catalyst showed higher yield for DME under similar reaction conditions. Figure 4 shows the stability of the 20C catalyst for methanol dehydration at 300°C. The methanol yield of 20C was stable at around 83% over 24 h time-on-stream. A good stability of our 20C catalyst sample was probably due to high stability of the alumina supports. Phase transformation or changes in the physical properties of alumina did not occur under the reaction conditions used.

4. Conclusions

Compared to pure χ - Al_2O_3 and γ - Al_2O_3 , the mixed χ/γ phase Al_2O_3 catalyst with 20 wt% χ -phase showed much higher density and strength of surface acidity as revealed by NH_3 temperature programmed desorption and ion-exchanged/titration method. As a consequence, the 20 wt% χ - Al_2O_3 catalyst exhibited the highest yield for synthesis of dimethyl ether (86%) by dehydration of methanol reaction with high stability.

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FIGURE CAPTIONS

- Figure 1 Powder X-ray diffraction patterns of alumina catalysts with various phase composition
- Figure 2 NH_3 -temperature programmed desorption (NH_3 -TPD) profiles of alumina catalysts with various phase composition.
- Figure 3 Catalytic test of catalyst samples (reaction conditions were 0.2 g of catalyst and GHSV = 5,300 h^{-1})
- a) Methanol conversion profiles
 - b) DME selectivity profiles
 - c) DME Yield profiles
- Figure 4 Long-term test of catalyst samples (reaction conditions were 300°C, 0.2 g of catalyst, and GHSV = 5,300 h^{-1}).

TABLES

Table 1 Acidity contents and some properties of the alumina catalysts

Samples	BET Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	Crystallite size (nm)	Acidity	
					NH ₃ -TPD (μ mol NH ₃ / g catalyst)	Exchange/titra tion (μ mol/g catalyst)
0C	196	0.778	10.6	4	0.490	5
10C	185	0.496	8.3	4.2	1.188	7.5
20C	187	0.768	12.1	5.5	4.004	25
50C	180	0.617	12.1	4.8	2.053	15
80C	173	0.565	8.2	5.1	0.988	0.5
90C	168	0.636	10.6	4.7	1.347	2.5
100C	125	0.515	11.1	8.7	1.684	10

Table 2 Summary of DME synthesis from methanol dehydration reaction

Catalyst	BET surface area (m ² /g)	Amount of Catalyst (g)	Space velocity (h ⁻¹)	Reaction Temperature (°C)	DME yields (%)	Source
Aluminosilicate	252-383	0.5	GHSV 15,600	300	73-86	[2]
NaH-ZSM-5 (Si/Al = 30)	-	0.2	WHSV 4	250	62	[5]
TiO ₂ /SiO ₂	73-206	1.5	WHSV 0.316	340	53-83	[6]
γ-Al ₂ O ₃ /NaZSM-5 (Si/Al=40)	240-439	1.8 ml	LHSV 10	210-380	15-85	[7]
amorphous SiO ₂ /Al ₂ O ₃	-	0.51	-	140-190	4-43	[8]
Ti(SO ₄) ₂ /γ-Al ₂ O ₃	291	0.2	GHSV 3,400	240	85	[9]
NaH-ZSM-5 (Si/Al = 20)	-	1.5 ml	LHSV 10	270-340	73-84	[10]
Aluminium phosphate	156-385	0.5	GHSV 15,600	300	64-75	[11]
SiO ₂ -TiO ₂	46-60	0.5	GHSV 15,600	300	0.2-25	[11]

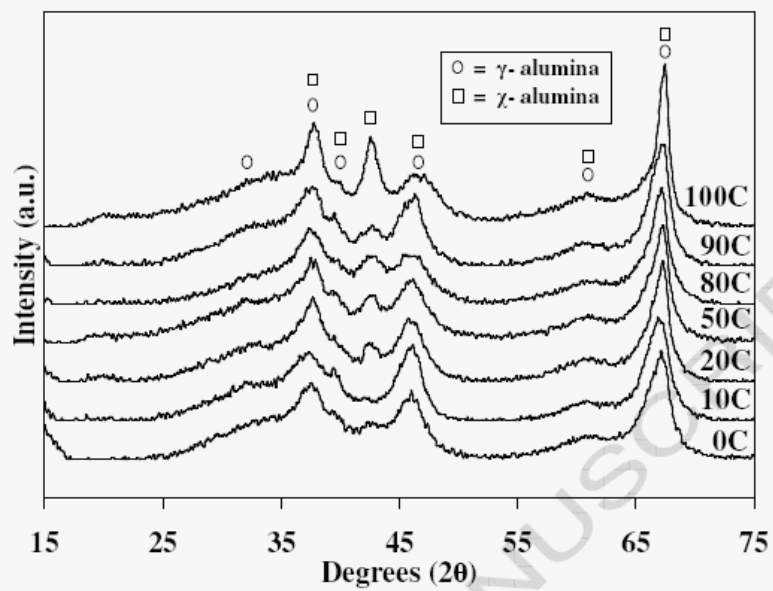


Figure 1

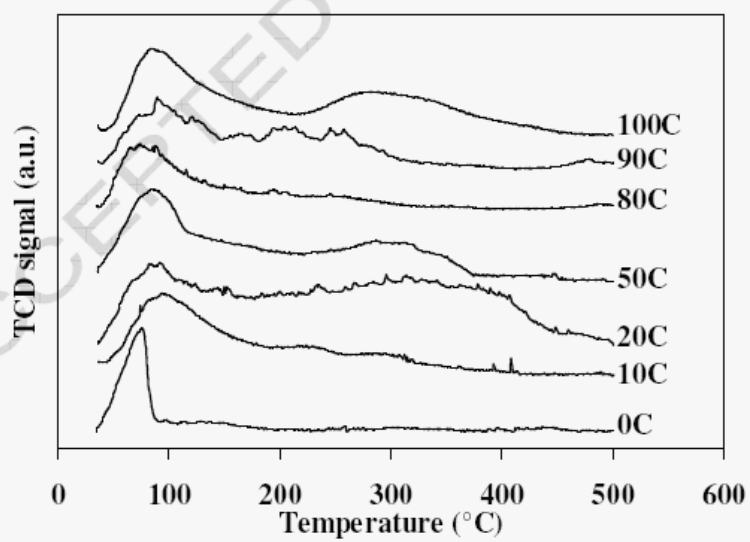


Figure 2

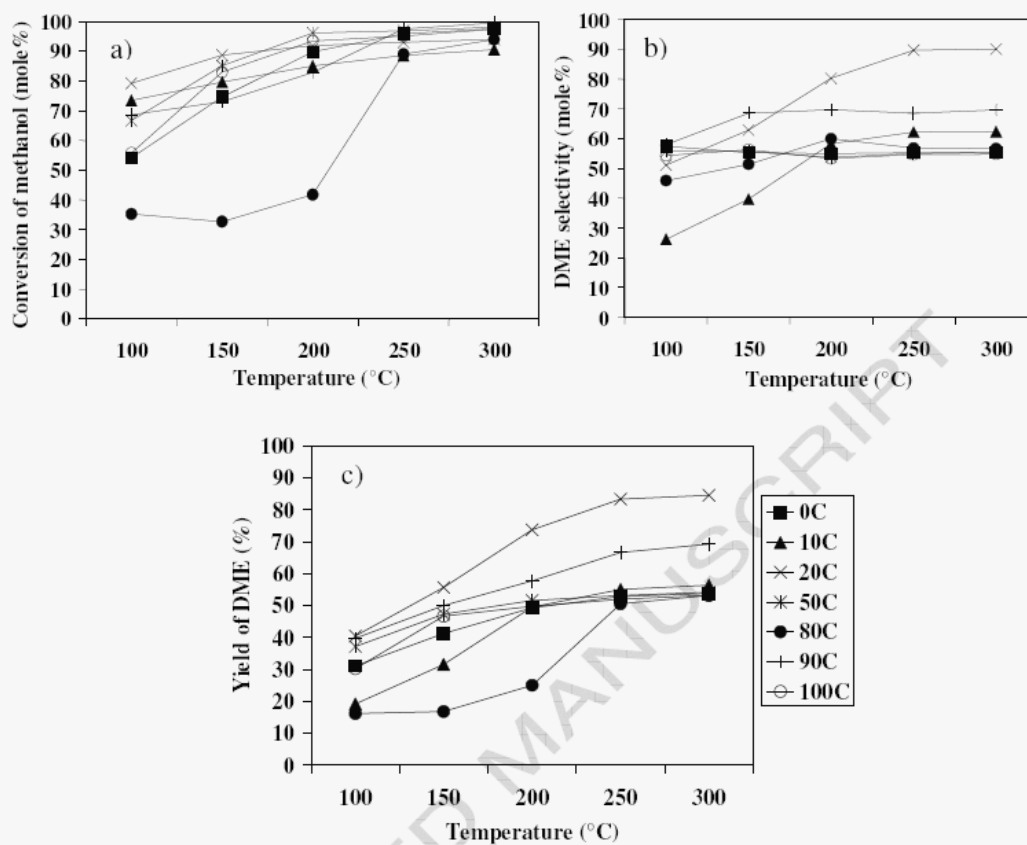


Figure 3

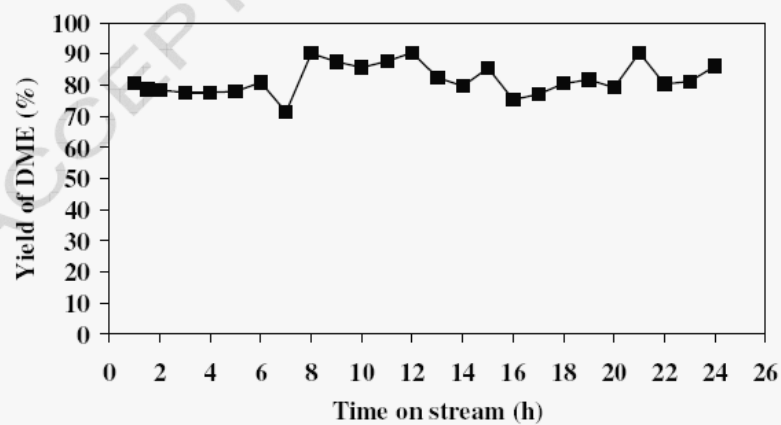


Figure 4

VITA

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