จุฬาลงกรณ์มหาวิทยาลัย
ทุนวิจัย
กองทุนรัชดาภิเษกสมโภช

รายงานวิจัย

การผลิตไดเมทิลอีเทอร์จากเมทานอลเพื่อเป็นพลังงานทางเลือก

โดย

จูงใจ ปั้นประณต

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กิตติกรรมประกาศ

งานวิจัยนี้ได้รับทุนสนับสนุนจากทุนวิจัยกองทุนรัชดาภิเษกสมโภช จุฬาลงกรณ์มหาวิทยาลัย

โครงการวิจัยงบประมาณแผ่นดิน ประจำปีงบประมาณ 2553 ที่ได้รับการอนุมัติด้วย

งบประมาณกระตุ้นเศรษฐกิจ (บัญชีเงินกู้)

ชื่อโครงการวิจัย การผลิตไดเมทิลอีเทอร์จากเมทานอลเพื่อเป็นพลังงานทางเลือก

ชื่อผู้วิจัย ผศ.ดร.จูงใจ ปั้นประณต

เดือนและปีที่ทำวิจัยเสร็จ กันยายน พ.ศ.2554

บทคัดย่อ

งานวิจัยนี้ศึกษาการผลิตไดเมทิลอีเทอร์จากปฏิกิริยาการคายน้ำของเมทานอลโดยใช้ตัวเร่งปฏิกิริยาประเภทอะลูมินาที่สังเคราะห์ขึ้นสองชนิดคือแกมมาอะลูมินาที่สังเคราะห์โดยวิธีโซลโวเทอร์มอลและอะลูมิเนียมฟอสเฟตที่สังเคราะห์โดยวิธีการตกตะกอน โดยเปรียบกับตัวเร่งปฏิกิริยาแกมมาอะลูมินาเชิงพาณิชย์ อุณหภูมิที่ทำปฏิกิริยาคือ 150 ถึง 300 องศาเซลเซียส ความดันบรรยากาศ และความเร็วเชิงสเปซของแก๊ส 5,300 ต่อชั่วโมง พบว่าความว่องไวของตัวเร่งปฏิกิริยาเรียงลำดับได้ดังนี้ อะลูมิเนียมฟอสเฟตที่สังเคราะห์โดยวิธีการตกตะกอน > แกมมาอะลูมินาที่สังเคราะห์โดยวิธีโซลโวเทอร์มอล > แกมมาอะลูมินาเชิงพาณิชย์ โดยได้ค่าผลได้ของไดเมทิลอีเทอร์เท่ากับ 85% โดยน้ำหนัก เมื่อใช้ตัวเร่งปฏิกิริยาอะลูมิเนียมฟอสเฟตที่อุณหภูมิ 250 องศาเซลเซียส ความว่องไวของตัวเร่งปฏิกิริยาขึ้นกับปริมาณของตำแหน่งที่มีความเป็นกรดและพื้นที่ผิวเป็นหลัก เนื่องจากอะลูมิเนียมฟอสเฟตให้ความว่องไวสูงที่อุณหภูมิในการทำปฏิกิริยาต่ำกว่าจึงเป็นตัวเร่งปฏิกิริยาที่มีความเหมาะสมในการนำไปใช้ในระดับอุตสาหกรรม ตัวเร่งปฏิกิริยาที่ผ่านการใช้งานแล้วสามารถนำกลับมาใช้ได้ใหม่โดยไม่พบการเสื่อมสภาพของตัวเร่งปฏิกิริยา การวิเคราะห์ด้วยเทคนิคฟูริเยร์ทรานสฟอร์มอินฟาเรดสเปกโตรสโกปี รามานสเปกโตรสโกปี และการไทเทรตด้วยเอมมีน แสดงหมู่ P-OH ที่เพิ่มขึ้นหลังการใช้งานในปฏิกิริยาการคายน้ำของเมทานอล

Project: Synthesis of dimethyl ether from methanol for use as alternative fuels
Name of the Investigators: Asst. Prof. Joongjai Panpranot
Year: 2011

Abstract

Dimethyl ether (DME) was synthesized from the dehydration of methanol using three types of alumina-based catalysts (γ-Al_2O_3 prepared by solvothermal method, commercial γ-Al_2O_3, and amorphous $AlPO_4$ prepared by precipitation method) at 150-300°C, atmospheric pressure, and gas hourly space velocity (GHSV) 5300 h^{-1}. The catalyst activity was in the order: amorphous $AlPO_4$ > solvothermal γ-Al_2O_3 > commercial γ-Al_2O_3. The total yield of DME was 85% over $AlPO_4$ at 250°C. Because relatively high activity can obtained at much lower reaction temperature than γ-Al_2O_3, amorphous $AlPO_4$ appeared to be more suitable for industrial application. The catalysts can be reused without catalyst deactivation. Characterization of the spent catalysts by FT-IR spectroscopy, Raman spectroscopy, and amine titration indicated the formation of P-OH group after methanol dehydration reaction.

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1. Introduction

In present, world energy consumption is continuously increasing together with industrial and transportation expansion. World most important and useful energy reservoirs are crude oil and natural gas. In 1985, there was more than 54 million barrel per day of oil consumption; it increases to 85 million barrel per day in 2005. There is anticipating following by world economic growth and the truth that oil is circumscription energy and will be used up in the future oil consumption will be 75% increase more in 2010 and its price will continuously increase [Semelsberger et al. 2006]. For these reasons, research and development of alternative energy for oil replacement has received much attention continuously in order to find the most suitable alternative energy in the future.

Dimethyl ether (DME) is one of the promising alternative fuels due to their huge reservoir and easy production. Dimethyl ether can be used to substitute for liquefied petroleum gas (LPG) and diesel engine because of their similar properties of LPG and high cetane number. Dimethyl ether can be produced from either synthesis gas or methanol. In this study, production of only dimethyl ether from methanol dehydration is focused.

The most acceptable catalyst for methanol dehydration is gamma alumina (γ-Al_2O_3) due to its suitable acidity in this reaction but still there are studies in the way of modification of γ-Al_2O_3. One of the very interesting catalysts is amorphous aluminum phosphate ($AlPO_4$), modified gamma alumina with phosphate group, because of their ability to reduce coking and by-products. Moreover, $AlPO_4$ give a promising property to resist water that occurs during methanol dehydration reaction.

2. Survey of Related Literature

2.1 Catalysts for methanol dehydration

It is known that in dehydration of hydrocarbon reaction acidity is needed to catalyze reaction. Many solid-acid substances are used as catalyst such as zeolite and alumina. Methanol dehydration reaction also needs acid catalyst but medium acidity is necessary if high methanol conversion and selectivity of dimethyl ether (DME) are desired. Many researchers have established knowledge about suitable acidity in methanol dehydration to dimethyl ether. These reports are very useful to develop better catalysts in the future.

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 $SiO_2/\gamma\text{-}Al_2O_3 > ZrO_2/\gamma\text{-}Al_2O_3 \approx \gamma\text{-}Al_2O_3 > B_2O_3/\gamma\text{-}Al_2O_3$ because $SiO_2/\gamma\text{-}Al_2O_3$ had the highest acidity and became rather hydrophobic resulting in the decrease of sorption capacity of water. Then, vary wt% loading of $SiO_2/\gamma\text{-}Al_2O_3$ 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. [de Farias et al. 2004] evaluated $Al_2O_3{\bullet}B_2O_3$ catalysts which were synthesized by co-precipitation and impregnation methods applying two calcinations temperatures and boria 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.

Vishwanathan et al. [Vishwanathan et al. 2004] studied a series of TiO_2–ZrO_2 mixed oxides with varying molar ratio of TiO_2 to ZrO_2 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 CH_3OH conversion activity are increasing with TiO_2 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%. TiO_2–ZrO_2 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 H_2O) 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 (CMeOH > 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.

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-Al_2O_3, and $Ti(SO_4)_2/\gamma$-Al_2O_3 catalysts for dehydration of methanol to dimethyl ether (DME). The H-ZSM-5 and SDY possessed strong Brønsted acidity and exhibited high activity for conversion of methanol to DME at relatively low temperatures. Coke formation 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 γ-Al_2O_3 by $Ti(SO_4)_2$ 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 $Ti(SO_4)_2/\gamma$-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. This study could be concluded that zeolites were not suitable in this reaction because of their highly acidity that caused coke formation on surface and deactivated the catalyst. Moreover, the appropriate amount of Brønsted acid sites is necessary for this reaction.

A number of studies follow the same trend, Fei et al. [Fei et al. 2006] examined synthesis of dimethyl ether (DME) via methanol dehydration over HY zeolite and 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. Moreover, 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 was ascribed to the adequate dilution of the strong acid sites of ZSM-5 in the γ-Al_2O_3 matrix.

2.2 Modified alumina catalysts for methanol dehydration

Although, γ-Al_2O_3 seems to be suitable catalyst in methanol dehydration, there are studies on modification of γ-Al_2O_3 showing higher catalyst activity. 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 of 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 for these aluminosilicate catalysts.

Khom-In et al. [Khom-In et al. 2008] studied γ-Al_2O_3, χ-Al_2O_3 and mixed γ- and χ-crystalline phases with various ratios as catalyst in methanol dehydration. They found γ-Al_2O_3 catalyst containing 20 wt% of χ-phase which was synthesized by solvothermal method exhibited the highest DME yield. The NH_3-TPD and ion-exchange titration results revealed that the existence of 20 wt% χ-phase in solvothermal synthesized γ-Al_2O_3 with synthesized by solvothermal method increased significantly both the density and the strength of surface acidity of alumina.

Furthermore, Yaripour et al. [Yaripour, Baghaei et al. 2005] also investigated silica–titania and modified γ-Al_2O_3 with phosphorus which were prepared by co-precipitation (sol–gel) method 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 aluminum phosphate catalysts. Also, it was observed that the surface acidity of aluminum phosphate catalysts decreased with increasing 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.

Modified alumina catalyst with phosphate or aluminum phosphate is very interesting because of their abilities to reduce the amounts of coking and by-products. However, aluminum phosphate is strongly dependent on the method of preparation, chemical composition (Al/P molar ratio), and activation temperature. Aluminum phosphate has structure in both crystalline and amorphous structure. Kumar et al. [Kumar et al. 2006] studied activated of aluminum phosphate in methanol dehydration reaction. Co-precipitation and impregnation were chosen method as the preparation method of aluminum phosphate which had ratio of aluminum and phosphorus as 1:1. Aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$) was used as a aluminum precursor but in phosphate precursor, both ammonium hydrogenphosphate ($(NH_4)_2HPO_4$) and phosphoric acid (H_3PO_4) were chosen. The result has shown that all catalysts which were prepared by co-precipitation method had structure in amorphous structure. However, for impregnation method only catalyst that had phosphoric acid as phosphate precursor showed amorphous structure whiles the use of ammonium hydrogenphosphate gave crystalline phase catalyst. Reaction test result has shown that amorphous aluminum phosphate gave higher activity than crystalline one because of their significant different in acidity and surface area. At 350°C, amorphous aluminum phosphate from co-precipitation method gave rapid increase of conversion but decreasing in amorphous aluminum phosphate from impregnation method. Therefore, more experiment pointed that decreasing of activity due to changing in structure from amorphous to crystalline one. This study could be concluded that suitable phase of aluminum phosphate is amorphous structure.

2.3 Effect of operating conditions on methanol dehydration

The effect of water in methanol dehydration has been reported. It is shown that water is poison of catalyst in this reaction. Xu et al. [Xu et al. 1997] report that most of solid-acid catalyst deactivated during reaction when water was existed. They proposed that water would block active site and impede methanol from adsorption on active site.

Jun et al. [Jun et al. 2002] studied the effect of water on activity of γ-Al_2O_3 in methanol dehydration by addition of 65 torr vapor pressure of water in substance. The result showed that activity of catalyst at temperature 523 K was significant decreased from 70% to 37% conversion of methanol after 40 hour of vapor stream. They pointed that water in reaction decreased activity of the catalyst because molecule of water adsorbed on active sites of catalyst. Although, Lewis acid sites could change to Brønsted acid if there was water in reaction but Brønsted acid sites of γ-Al_2O_3 is very weak acid. Moreover, kinetic data confirm that increasing of activated energy of dimethyl ether synthesis is equal to the increasing of energy by added water that came from heat of adsorption of water (about 16 kcal/mol) when water covered most of surface of catalyst. In addition, water that exists in reaction would reverse equilibrium of reaction and decrease activity of methanol dehydration also.

However, there are some studies reported an opposite result that water in reaction could increase activity of catalyst instead of deactivate catalyst. One of the explanations is that Lewis acid sites could be changed to Brønsted acid sites and gave more activity to catalyst. Ramos et al. [Ramos et al. 2005] studied the role of Brønsted and Lewis acid sites in synthesis of DME and concluded that either Brønsted acid sites or Lewis acid–base pair sites are play a role in such reaction and, generally, the stronger the acid sites the more active the catalysts.

However, it should be recalled that as far as Brønsted sites are involved, their strength and the reaction temperature should be controlled to avoid hydrocarbons formation. The mechanism based on Lewis acidity, on the other hand, requires an adjacent acid–base pair sites to provide the reaction between the adsorbed alcohol molecule on an acidic site and an adsorbed alkoxide anion on a basic site. These interesting phenomena have been found on the catalysts with phosphate group.

András Ludmány et al. [Ludmany et al. 2004] studied physical and catalytic properties of amorphous titanium hydrogenphosphate ($Ti(HPO_4)_2$) and proved that it could be an active catalyst in alcohol dehydration also; cyclohexanol, methanol and pentanol were chosen as substances. Main part of study focused on cyclohexanol dehydration, 100% conversion of cyclohexanol was reached at temperature of 350°C and the conversion was still the same even temperature was decreased to 300°C. Two further experiments were carried out to explain this interesting phenomenon. One titanium hydrogen phosphate was activated by argon atmosphere and another one in vapor pressure at 280°C before they were tested in cyclohexanol dehydration until 50% conversion at 280°C and step temperature down to 250°C. The first catalyst that activated with argon was almost ineffective but the second one was highly active in a short time. It could be concluded that water is a major cause of conversion increasing of alcohol dehydration reaction. From DTA results (differential thermal analysis) and TG (thermo gravimetric) of amorphous titanium hydrogenphosphate showed that catalyst has similar structure with crystalline alpha phase more than gamma phase of titanium hydrogenphosphate. Moreover, the literature data said that alpha phase of titanium hydrogenphosphate could be changed to gamma phase by heating in 10M of phosphoric acid and inter layer of titanium hydrogenphosphate were also increasing (7.6 Å and 10.6 Å for alpha and gamma phase respectively) because of insertion of hydration water, This swollen molecule could bring some inserted alcohol in catalyst with water and give more activity of catalyst. The swollen catalyst with water and alcohol inside the layers retains its high activity until it loses the alcohol and water by evaporation.

In addition, Fu et al. [Fu, Hong et al. 2005] reported that when they regenerated coke form SDY zeolite after methanol dehydration reaction at 773 K for 2 hour, the activity of regenerated catalyst increase from 86.5% of fresh catalyst to 87.5% conversion of methanol at 503 K. Although, regeneration might recovered the activity completely, clearly indicating that the de-activation was indeed due to the coking. But it could be an effect of water that increased activity of catalyst also.

There are several studies of catalysts characterization and analysis of the reactant product. These reports are very useful and guideline for this works. 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 GC for on-line analysis. The catalytic activity was calculated based on CH_3OH conversion or CH_3OCH_3 yield. Other compounds in the effluent stream (CO, CO_2, H_2O, CH_3OH and CH_3OCH_3) were analysed on-line with a Shimadzu 14B gas chromatograph with a TCD detector and a Porapak-Q column operating at 110 °C.

3. Procedure

3.1 Preparation of amorphous aluminum phosphate catalyst by precipitation method

In this study, the modified Bautista's aqueous solution precipitation method [Bautista, 2005] was chosen as catalyst preparation method. The details of chemicals and method for preparation of amorphous aluminum phosphate have shown as follows:

• Aluminum nitrate, ($Al(NO_3)_3 \cdot 9H_2O$)	analytical grade, Aldrich
• Phosphoric acid, (85% H_3PO_4)	analytical grade, Aldrich
• Aqueous ammonia solution, (25% NH_4OH)	analytical grade, Merck
• 2-Propanol, (C_3H_5OH)	analytical grade, Fisher Scientific

Preparation of 6 grams of amorphous aluminum phosphate, 18.45 grams of aluminum nitrate was diluted in 30 ml of deionization water to prepared aluminum precursor solution. Mixing and stirring this aqueous solution at controlled temperature of 0°C, equal molar amount of phosphate precursor, 1.68 ml of phosphoric acid was added to form amorphous aluminum phosphate with have Al/P ratio =1. Aqueous ammonia solution was added dropwise to precipitation of aluminum phosphate until pH of solution = 7. The solution would changed from homogenous to gelled mass meanwhile pH adjustment and rapidly viscous when pH closed to 7. Notice that neutralization of acid-base has generated amount of heat, make sure that controlled temperature was constant. Filtration and wash catalyst gel with vacuum filter and deionization water to remove excess substance and contaminant. Wash again with 2-propanol and dried at 100°C for 24 hour. The resulting catalyst would be calcined at 650°C in air for 3 hours to air atmosphere.

3.2 Preparation of gamma alumina catalyst by solvothermal method

Synthesis gamma alumina method was using preparation method of various phases of alumina supports (gamma phase, chi phase and their mixed-phase) by solvothermal [Khom-in, 2007]. The details of chemicals, equipment (autoclave reactor line) and method for preparation of pure gamma alumina by solvothermal method have shown as follows:

• Alumina Isopropoxide: AIP, ($[(CH_3)_2CHO]_3Al$)	analytical grade, Aldrich
• 1-Buthanol, (C_4H_9OH)	analytical grade, Fluka
• Methanol, (CH_3OH)	commercial grade, Merck
• Nitrogen gas, (N_2)	ultra high purity, TIG

In this study, stainless steel autoclave reactor was connected to pressure gauge with relief valve to prevent runaway reaction. Test tube was used to contain the reagent and solvent inside autoclave reactor. In condition of 15 grams of amount of starting material and100 ml of organic solvent was contained in the test tube with another 30 ml of organic solvent in the gap between test tube and autoclave wall. Thermocouple is attached to the reagent in the autoclave. Autoclave reactor used for the experiment is shown in Figure 1.

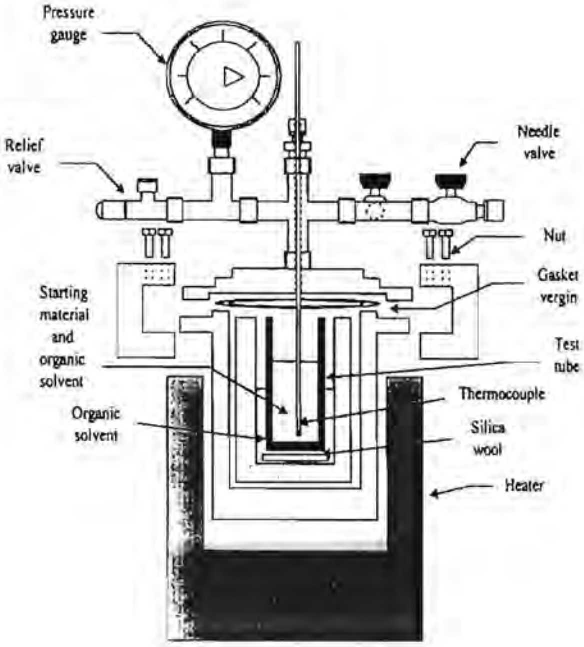

Figure 1 Autoclave reactor

Moreover, temperature program controller was connected to a thermocouple attached to the autoclave with electrical furnace supplied the required heat to the autoclave for the reaction. 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 2

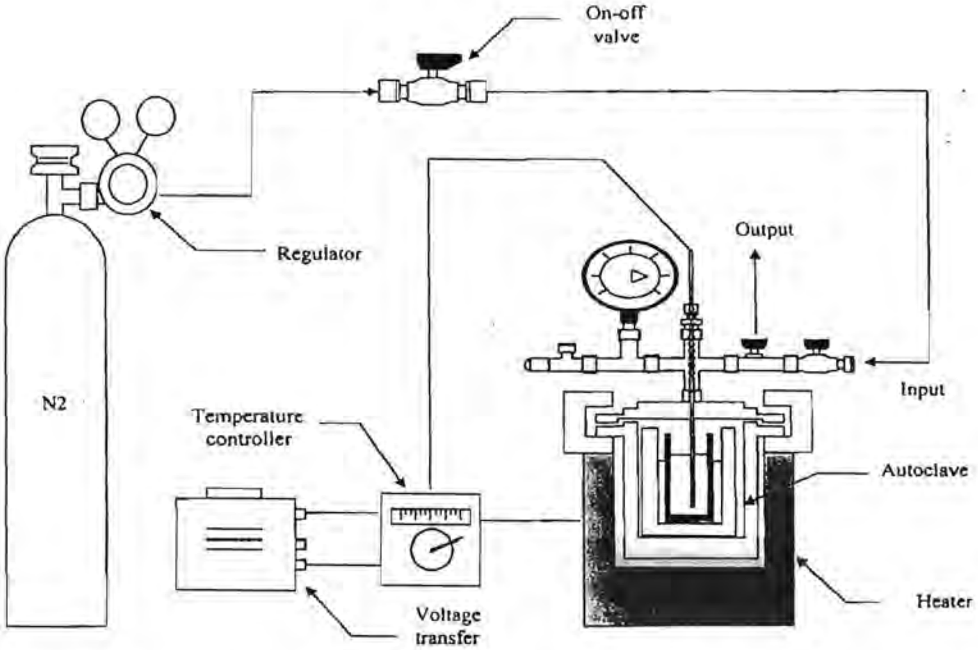

Figure 2 Diagram of the reaction equipment for the synthesis of catalyst.

The equipment for the synthesis of alumina by solvothermal method consisted of: 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 addition 30 ml of same solvent was placed in the gab 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. [J.Khom-in, 2007]

3.3 Catalyst Characterization

3.3.1 X-ray diffraction

The crystallinity of the prepared catalysts was identified using powder X-ray diffraction (XRD) by an X-ray diffractometer SIEMENS D 5000 connected with a personal computer with Diffract AT version 3.3 program for fully control of the XRD analyzer. The experiments were carried out by using Ni-filtered Cu K_{α} radiations with a generator voltage and current of 30 kV and 30 mA, respectively. A scan step of 0.04° was applied during a continuous run in the 20 – 70° range.

3.3.2 Nitrogen physorption

The catalyst 0.2 gram was study BET 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.

3.3.3 Temperature Programmed Desorption of Ammonia (NH_3-TPD)

The acid properties of prepared catalysts were observed by temperature programmed adsorption of ammonia (NH_3-TPD) by using Micromeritics chemisorp 2750 pulse chemisorption system. In an experiment, about 0.10 g of the catalyst sample was placed in a quartz tube and pretreated at 200°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 1.0 h. Then the sample was heated from 40 to 800°C at a heating rate 10°C /min. The amount of ammonia in effluent was measured via TCD signal as a function of temperature.

3.3.4 Fourier transform infrared (FT-IR)

Fourier transform infrared (FT-IR) were performed to identify the hydroxyl groups of catalysts. Infrared survey was recorded by using Nicolet 6700^{TM} spectrometer in the range of 4000-400 cm^{-1} at a resolution of 2.0 cm^{-1}.

3.3.5 Fourier transform Raman (FT-Raman)

Fourier transform Raman (FT-Raman) were performed to identify the phosphate groups of catalysts using Perkin Elmer, spectrum GX in the Raman shift range of 200-3600 cm^{-1} at a resolution of 4.0 cm^{-1}

3.3.6 Amine titration using Hammett indicators [Yurdakoc, 1999]

The acid strength of a solid surface is defined as the ability of the surface to convert an adsorbed neutral base into its conjugate acid. If the reaction proceeds by means of proton transfer from the surface to the adsorbate, the acid strength is quantitatively expressed by Hammett and Deyrup's H^0 acidity equation 1.

$$H^0 = pK_a + \log[B]/[BH^+] \qquad (1)$$

where [B] and $[BH^+]$ are the concentrations of the neutral base and its conjugate acid respectively, and pK_a is $pK_{BH}{}^+$. If the reaction takes place by means of the electron pair transfer from the adsorbate to the surface, H^0 is expressed by equation 2.

$$H^0 = pK_a + \log[B]/[AB] \qquad (2)$$

where [AB] is the concentration of the neutral base which reacted with the Lewis acid or electronpair acceptor, A. The amount of acid on a solid is usually expressed as the number or mmol of acid sites per unit weight or per unit surface area of the solid. In the amine titration method using indicators, the color of suitable indicators adsorbed on the surface will give a measure of its acid strength. If the color is that of the acid form of the indicator, then the value of the H^0 function of the solid is equal to or lowers than the pK_a of the conjugate acid of the indicator.

The Hammett indicators used in the present study are listed in Table 1, together with color changes and pK_a's. Moreover, to give some idea of the acid strength range, corresponding sulfuric acid compositions are also listed.

Acid Amount Determination, samples should be freshly dried at 393K before carrying out the indicator tests, and were subjected to color immediately after drying, or if this was not convenient, were stored in screw cap test tubes in a desiccators until color tests were performed. Since water is a base, the effect of water adsorption changed the color intensities of the adsorbed indicators or caused a shift to lower acid strengths.

Amine titration using Hammett indicators carried out. 0.1 g of catalyst was suspended in 9 ml of benzene with 3 dropwise of Hammett indicators; indicator solution was prepared by diluted 0.1 g of indicator in 100 ml of non-polar organic solvent. If suspension catalyst solution has color of acid form of indicators, the catalyst had more acid strength than pK_a of indicators, titrated to measured the acid amount with 0.01 M of n-butylamine in benzene solution until color of solution changed to base form, than the solution was shacked for at least 2 hour, if color changed to acid form, titrated again with same procedure until color turned to base form permanently. Strength and amount of acid sites reported in range depending on amount and type of used Hammett indicators.

Table 1 Basic indicators used for the measurement of acid strength

Indicator	Color Base Form	Color Acid Form	pK_a
Neutral Red	yellow	red	+6.8
Methyl Red	yellow	red	+4.8
Methyl Orange	yellow	orange	+3.7
Phenylazonaphtylamine	yellow	red	+4.0
p-Dimethylaminoazobenzene (Methyl Yellow)	yellow	red	+3.3
2-Amino-5-azotuluene	yellow	red	+2.0
Benzeneazodiphylamine	yellow	purple	+1.5
Crystal Violet	blue	yellow	+0.8
p-Nitrobenzeneazo-(p'-nitro-dipehylamine)	orange	purple	+0.43
Dicinnamalacetone	yellow	red	-3.0
Benzaacetophenone	colorless	yellow	-5.6
Anthraquinone	colorless	yellow	-8.2
2,4,6-Trinitroaniline	colorless	yellow	-10.1

* The indicator is liquid at room temperature and acid strength corresponding to the indicator is higher than the acid strength of 100 percent H_2SO_4.

3.4 Reaction study in dehydration of methanol

3.4.1 Chemical and Reagents

- UHP Helium Gas, 99.999% as carrier gas of reaction test
- Methanol, (CH_3OH) from Merck as reactant
- Distillation water, (H_2O)

3.4.2 Instrument and Apparatus

The equipment for the reaction of aluminum phosphate and gamma alumina consisted of: The flow diagram of the reaction that is methanol dehydration to dimethyl ether is shown in Figure 3

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

(b) Saturator: Saturator was made from glass and set to bubble methanol and control pressure of methanol. Moreover, saturator was set to feed water vapor to pretreatment catalysts before reaction test.

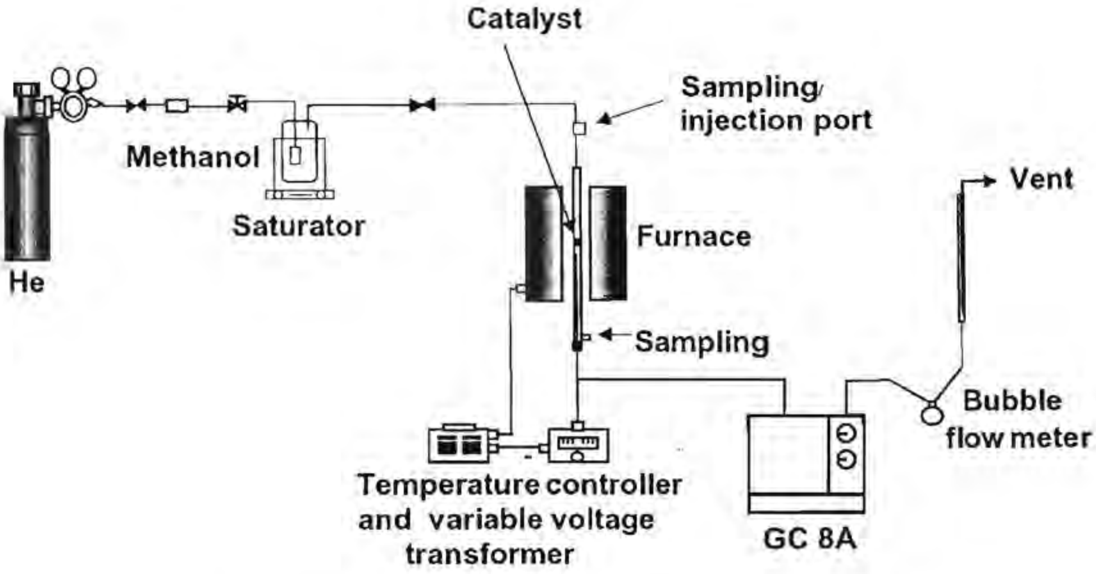

Figure 3 A schematic of methanol dehydration system

(c) 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.

(d) Temperature program controller: A temperature program controller was connected to a thermocouple attached to the reactor and variable voltage transformer and controlled the temperature.

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

(f) 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 were Porapak Q and Porapak N (3 m×3 mmØ) for analyzing the concentration of methanol (CH_3OH), water (H_2O) and dimethyl ether (CH_3OCH_3) with different by-production, Porapak Q for CH_4 CO_2 and light olefins, Porapak N for CO and CH_4. Operating conditions were shown in Table 4.3.

As shown in Figure 3, 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 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 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: 150-300◦C under atmospheric pressure. The reaction products were analyzed with a gas chromatograph with a TCD detector and a Porapak-Q and Porapak-N column were operating at 110°C and 100°C [Ng 2002].

Table 2 Operating condition gas chromatograph for methanol dehydration reaction

Gas Chromatograph	**Shimazu, GC 8A**	**Shimazu, GC 8A**
Detector	TCD	TCD
Column	Porapak-Q	Porapak-N
Carrier gas	Helium (UHP)	Helium (UHP)
Carrier gas flow	50 ml/min	30 ml/min
Column Temperature		
- Initial	110°C	100°C
- Final	110°C	100°C
Detector temperature	110°C	100°C
Injector Temperature	110°C	100°C
Analyzed gas	CH_3OH, H_2O, DME, CO_2 and light olefins	CH_3OH, H_2O, DME, CO and CH_4

The product gas composition was analyzed 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 both Porapak column. Porapak Q and Porapak N were used to analyze feed reactant and major product; CH_3OH, H_2O and DME with different by-production, Porapak Q for CH_4 CO_2 and light olefins, Porapak N for CO and CH_4. The calibration curves for calculation of composition of reactant and products in methanol dehydration were shown in Appendix A.

4. Results and Discussion

4.1 Crystal structure

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. In addition, if material has structure of amorphous, the X-ray beam would scattered and gave a little diffraction quantity of X-ray beam from material which showed very low intensity of XRD Diffraction pattern. The measurements were carried out at the diffraction angles (2θ) between 20 and 70 degrees.

The XRD Diffraction patterns for amorphous $AlPO_4$, solvothermal γ-Al_2O_3, and commercial γ-Al_2O_3 has shown in Figure 4. The patterns indicated that the nature structure of $AlPO_4$ was amorphous and both commercial and synthetic γ-Al_2O_3 were crystal structure of which indicated obviously at degree 2θ of 32°, 37°, 39°, 45°, 61° and 66° indicating the pure γ- phase of alumina [Khom-In, 2008].

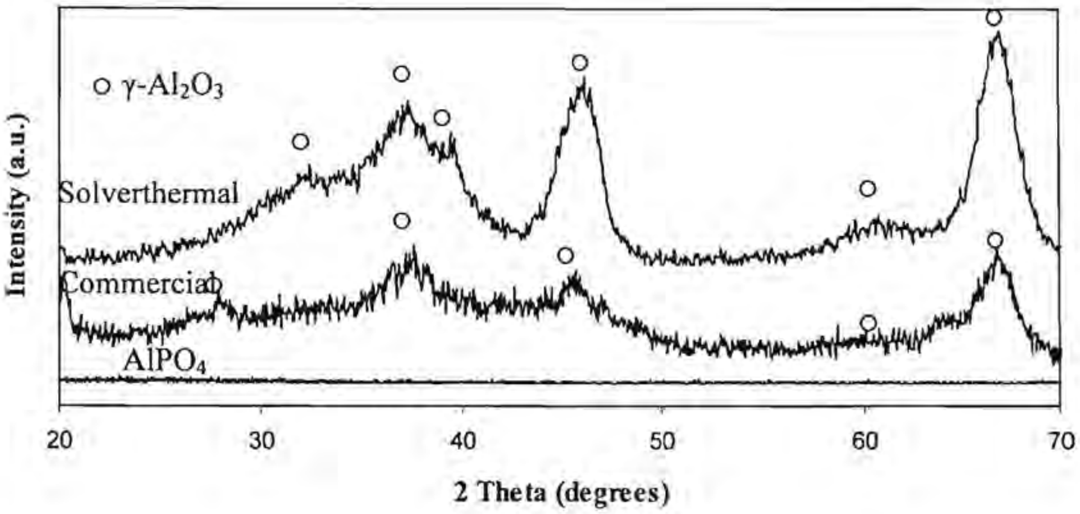

Figure 4 XRD patterns of amorphous $AlPO_4$, solvothermal γ-Al_2O_3, and commercial γ-Al_2O_3

4.2 Surface area and pore structure

The most common procedure for determining specific surface area, pore size and pore volume of solid material are based on adsorption and condensation of nitrogen at liquid phase temperature. The specific surface area was calculated by BET (Brunauer Emmett Teller) equation method.

The physical properties of amorphous $AlPO_4$, solvothermal γ-Al_2O_3, and commercial γ-Al_2O_3 such as BET surface areas, pore volume and pore radius were collected in Table 3. The solvothermal γ-Al_2O_3 showed higher surface area than the commercial one while $AlPO_4$ showed the highest surface area and the largest pore size and pore volume.

Table 3 Physical properties of amorphous $AlPO_4$, synthesis and commercial Al_2O_3

Catalyst	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore radius (Å)
Amorphous $AlPO_4$	171	0.76	177.1
Solvothermal γ- Al_2O_3	159	0.44	81.4
Commercial γ- Al_2O_3	149	0.23	37.0

4.3 Amount of acidity

Acidity of catalyst was indicated by adsorption of saturated NH_3 on the the catalyst surface. Amount of NH_3 desorption determined from peak area shows number of acid sites and desorption temperature shows bonding strength or strength of acidity of the catalyst. The NH_3-TPD profiles for amorphous $AlPO_4$, solvothermal γ-Al_2O_3, and commercial γ-Al_2O_3 have shown in Figure 5. The result shows that $AlPO_4$ had large broad peak at temperature of 50°C to 250°C, representing weak acid sites which were much higher than strong acid sites at high temperature. Solvothermal γ-Al_2O_3 showed 3 broad peaks during the temperature range of 50 to 240°C, 240 to 450°C, and 480 to 600°C, respectively. The profile was referred to strong acid sites with larger peaks at higher temperature above 400°C. The commercial γ-Al_2O_3 shows only 2 broad peaks during the temperature range of 50 to 240°C and 240 to 450°C, indicating the acid strength between $AlPO_4$ and solvothermal γ-Al_2O_3. The acid properties of catalysts are also reported in Table 4. The calculation of the acidity is shown in Appendix C. The total amount of acidity of the catalysts were increased in the order of amorphous $AlPO_4$ (35.82 mmol H^+/g catalyst) > solvothermal γ-Al_2O_3 (21.56 mmol H^+/g catalyst) > commercial γ-Al_2O_3 (10.14 mmol H^+/g catalyst), respectively.

Table 4 Acidity of amorphous $AlPO_4$, synthesis and commercial Al_2O_3

Catalyst	Adsorbed volume of ammonia, (ml)	Total acid site, (mmol H^+/g)
Amorphous $AlPO_4$	87.6	35.82
Solvothermal γ-Al_2O_3	52.71	21.56
Commercial γ-Al_2O_3	24.8	10.14

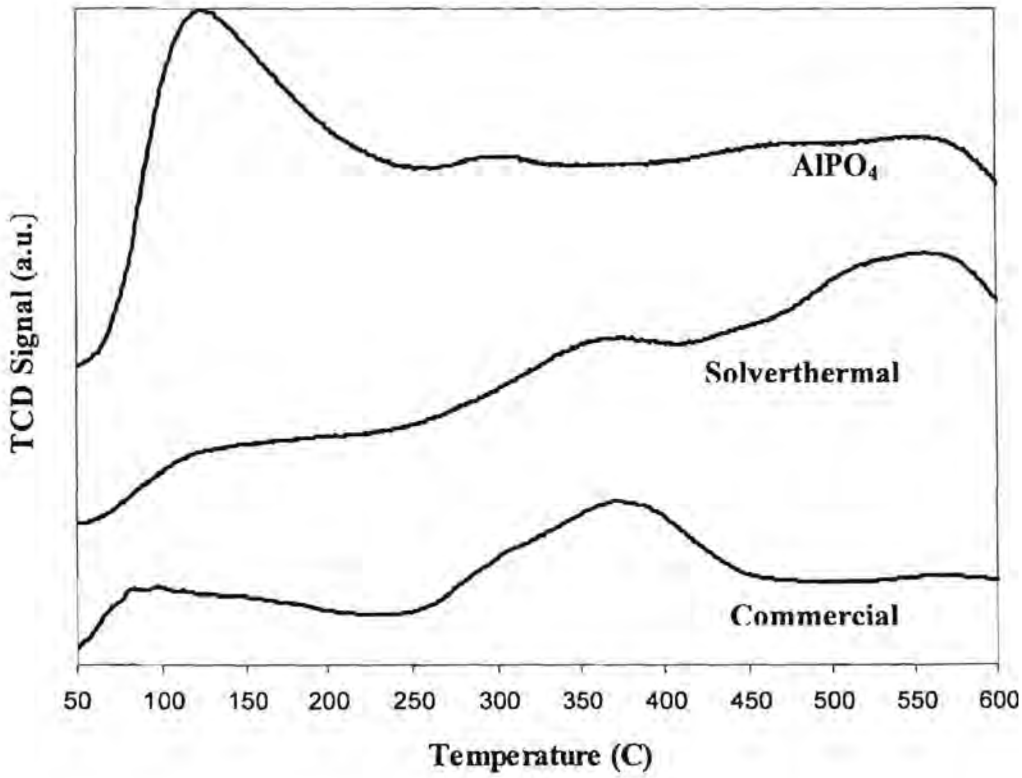

Figure 5 NH_3-TPD Profiles of amorphous $AlPO_4$, commercial γ-Al_2O_3 and synthetic solvothermal γ-Al_2O_3 catalysts.

4.4 Reaction Study

Results of reaction test have shown that amorphous $AlPO_4$ and solvothermal synthesized γ-Al_2O_3 have significantly higher activity than the commercial catalyst as illustrated in Figure 6. Activity of catalysts directly increased with rising temperature as the kinetic energy of the system increased with increasing temperature. Both of the synthesized catalysts ($AlPO_4$ and solvothermal γ-Al_2O_3), the reaction started to occur at 200°C and had a sharp increasing of methanol conversion at 250°C. However, activity of amorphous $AlPO_4$ was slightly decreased at 300°C due to decreasing of equilibrium conversion of methanol dehydration reaction, exothermic reaction, at high temperature after reaction has reached equilibrium conversion at 250°C. The trend of activity of $AlPO_4$ synthesis and commercial γ-Al_2O_3 were followed their amount of acidity and surface area as determined from NH_3-TPD and N_2 adsorption respectively. Moreover, all the three catalysts gave almost 100% selectivity of DME with less than 1% of by product such as carbon monoxide and methane.

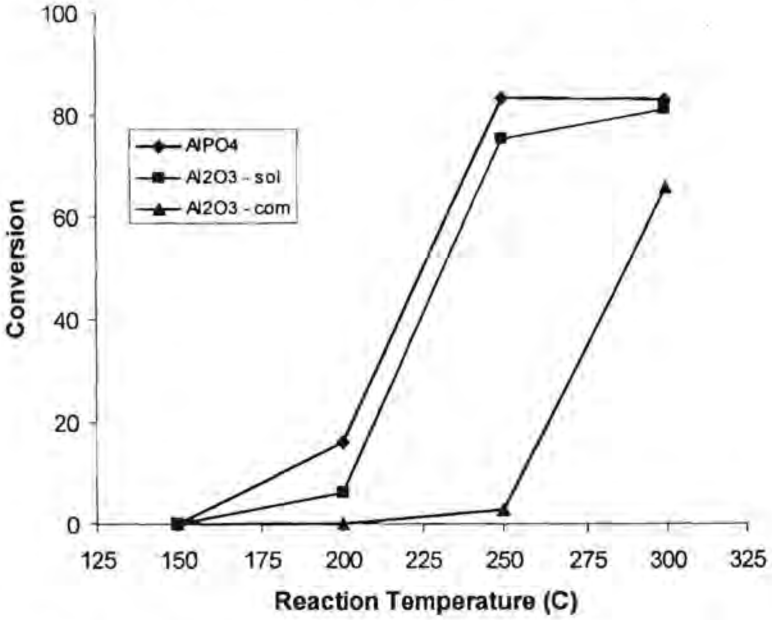

Figure 6 Methanol conversion profiles of fresh catalysts (reaction temperature 150-300°C, 0.2 g catalyst, and GHSV=5,300 h^{-1})

4.5 Catalyst Reusability

4.5.1 Catalyst activity of the spent catalysts

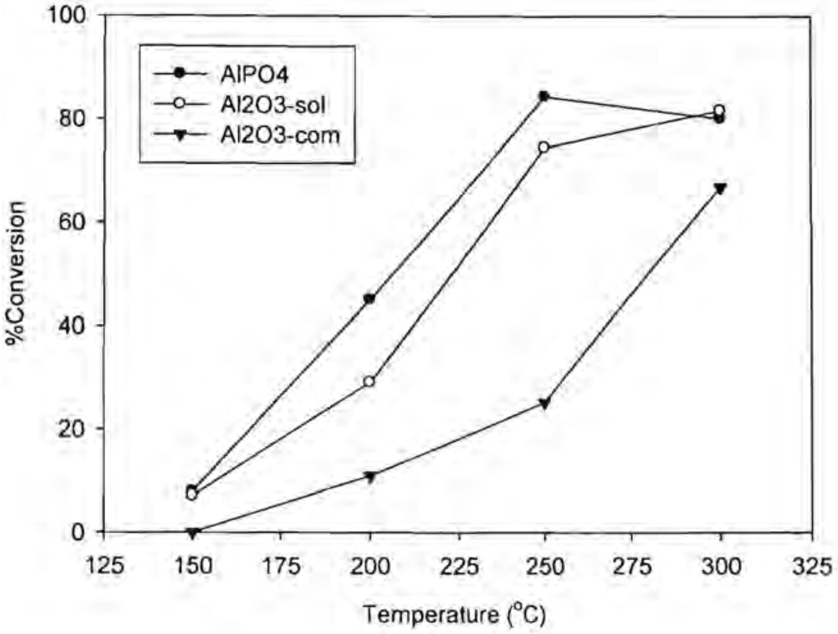

Figure 7 The activity profile of spent catalysts (reaction temperature 150-300°C, 0.2 g catalyst, and GHSV=5,300 h^{-1})

As shown in Figure 7, all the catalysts can be re-used in the methanol dehydration without catalyst deactivation. The same trend of activity was found in which $AlPO_4$ > Al_2O_3-sol > Al_2O_3-com. At the temperature of 200°C, the methanol conversions were significantly increased from 15.3% to 45.1% for the amorphous $AlPO_4$ and 6.0% to 29.1% for the solvothermal synthesized γ-Al_2O_3. The commercial γ-Al_2O_3 also showed an increasing of methanol conversion from 3% to 25% at temperature of 250°C and up to 11% at 200°C. The DME selectivity remained the same as those of the fresh catalysts.

4.5.2 Characterization of spent catalysts

4.5.2.1 Thermal Gravimetric Analysis (TGA)

Thermogravimetric analysis or TGA is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. The results of TGA are shown in Figure 8. The fresh $AlPO_4$ showed more percent weight loss than the spent $AlPO_4$. The excess water which may be the weak bond chemisorption water could not accelerate reaction and became a poison of catalyst. According to study of Xu et al. [Xu, 1997], the presence of water in this reaction has a strong inhibiting effect on the activity of γ-Al_2O_3, whereas the effect is less significant over zeolite (H-ZSM-5).

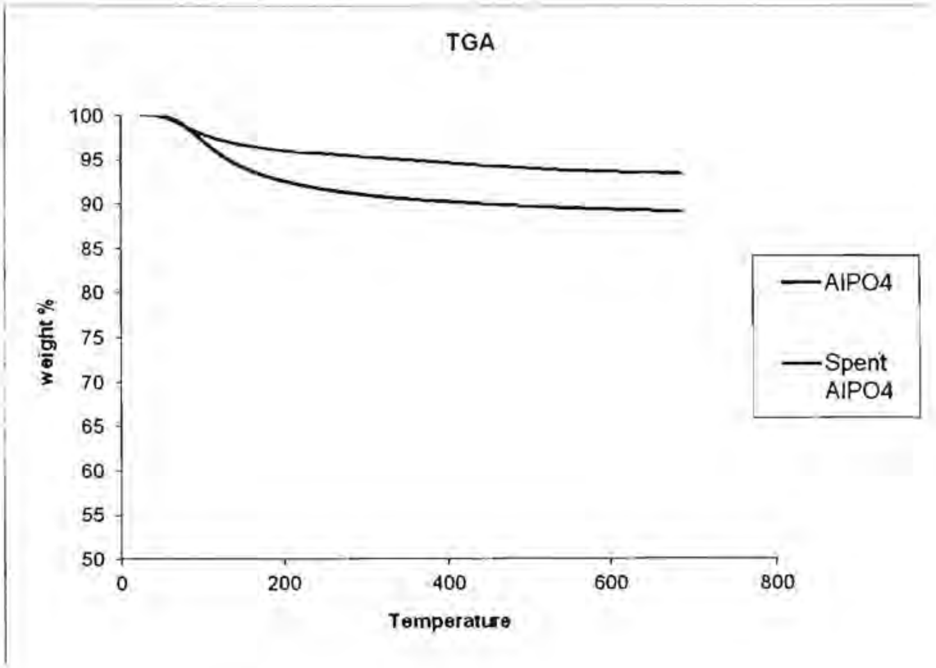

Figure 8 TGA profile of fresh and spent $AlPO_4$

4.5.2.2 Fourier transformed Infrared Spectroscopy (FT-IR)

The results show that spent catalyst had more amount of hydroxyl group than fresh one, due to their significant higher intensity of FI-TR at wavelengths of 2950, 3600 and 3750 cm^{-1}. The strong sharp band around 3750 cm^{-1} which was also accompanied by a broad band around 3400 cm^{-1}, could be assigned to the hydroxyl stretching mode of surface phosphate or pyrophosphate species as reported by Armaroli et al., [Sun, 2007]. The shoulders that appeared around 2900 cm^{-1} of pretreatment catalysts probably indicated the presence of hydroxyl groups of carious strengths attached to phosphorous in these samples [Kumar, 2006]. The results of both 2950 cm^{-1} and 3750 cm^{-1} band indicated that there was an increase of hydroxyl on phosphate group in catalyst after reaction. In the other words, molecules of water were adsorbed and bonded with phosphorous atoms in catalyst in the form of P-OH group.

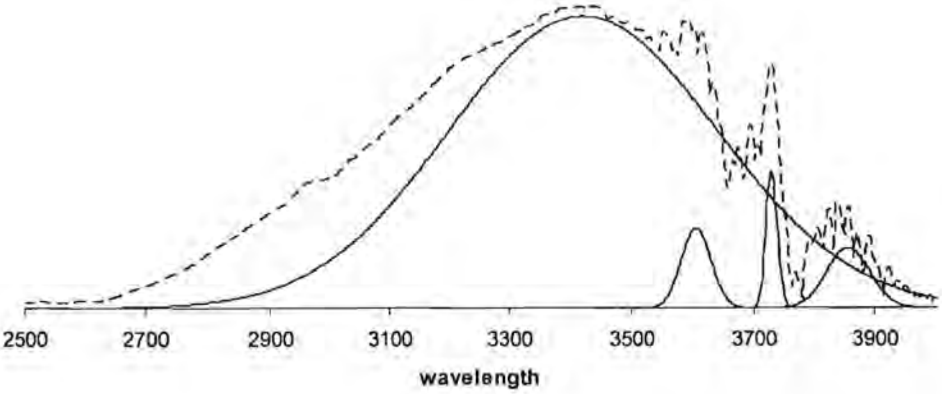

Figure 9 De-convolution FT-IR spectra of hydroxyl group of fresh $AlPO_4$

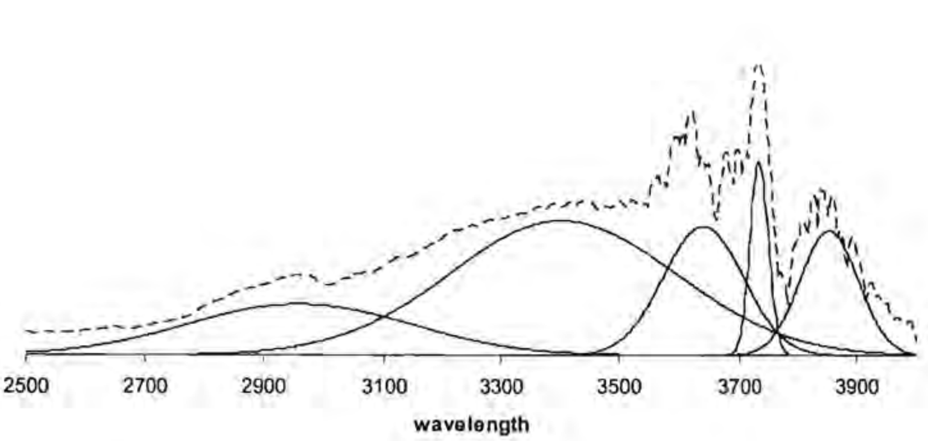

Figure 10 De-convolution FT-IR spectra of hydroxyl group of spent $AlPO_4$

4.5.2.3 Fourier transformed Raman Spectroscopy (FT-Raman)

To investigate and confirm the result of phosphate group from FT-IR, FT-Raman spectroscopy analysis was carried out. According to phosphate Raman bands, Figure 5.15 shows Raman spectra from Raman shift of 900-1500 cm^{-1} of fresh $AlPO_4$ and 100-300°C pretreated $AlPO_4$ catalyst. The Raman band at 1050 and 1200 cm^{-1} indicate the presence of PO_3^{2-} and PO_2^{1-} compounds, respectively [Hernandez, 2006]. Moreover, Raman study of phosphate groups by de Jager and Prinsloo indicated that Raman shift of 876-992 cm^{-1} could be P-OH band in several structure, according to Raman-shift due to matrix effect and phosphate functional groups formula such as PO_2^{1-},PO_3^{2-} ,PO_4^{3-} and $P_2O_7^{2-}$ [de Jager, 2001]. Raman shift of 985 cm^{-1} that occurred after water pretreatment could be attributed to P-OH band and confirmed the result of FT-IR that water could adsorbed and chemical bonding with phosphate groups.

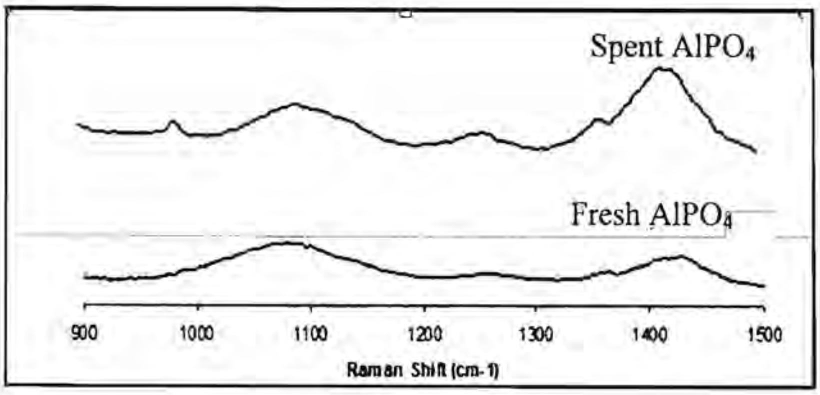

Figure 11 FT-Raman spectra of fresh and spent $AlPO_4$

4.6 Conclusions

Three types of alumina-based catalysts (γ-Al_2O_3 prepared by solvothermal method, commercial γ-Al_2O_3, and amorphous $AlPO_4$ prepared by precipitation method) have been studied in the dehydration of methanol for DME production. The catalyst activity was in the order: amorphous $AlPO_4$ > solvothermal γ-Al_2O_3 > commercial γ-Al_2O_3. The activity in the dehydration of methanol depends on the amount of acidity and surface area of the catalysts. Aluminium phosphate ($AlPO_4$) has shown to be a potential catalyst for the production of DME via methanol dehydration. It gave considerably high activity (40% conversion) at much lower reaction temperature (150-200°C) than γ-Al_2O_3 catalysts thus became more appropriate for a practical use. There was no catalyst deactivation under the conditions used and all the catalysts can be reused in the methanol dehydration with high activity.

4.7 References

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