

Modification of acid properties and catalytic properties of AlPO_4 by hydrothermal pretreatment for methanol dehydration to dimethyl ether

Krit Lertjiamratn^a, Piyasan Prasertthdam^a, Masahiko Arai^b, Joongjai Panpranot^{a,*}

^a Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

^b Division of Chemical Process Engineering, Graduate School of Engineering, Hokkaido University, Sapporo, 060-8628, Japan

ARTICLE INFO

Article history:

Received 26 November 2009

Received in revised form 5 February 2010

Accepted 9 February 2010

Available online 17 February 2010

Keywords:

Dimethyl ether

Methanol dehydration

AlPO_4

Hydrothermal treatment

Acid properties

ABSTRACT

An amorphous AlPO_4 catalyst prepared by precipitation method was subjected to pretreatment with 10 mol% water vapor at 100–300 °C for 15 min prior to activity tests in the dehydration of methanol to dimethyl ether (DME). The catalysts pretreated at 200–300 °C exhibited higher methanol conversion than the non-treated catalyst while the one treated at a lower temperature of 100 °C showed lower activity. As revealed by FT-IR and FT-Raman results, there was an increase of lattice hydroxyls on the hydrothermally treated catalysts in the form of P-OH group (weak Brønsted acid sites). Amine titration using Hammett indicators confirmed the increase of both strength and number of acid sites on these catalysts. However, hydrothermal pretreatment at 100 °C may result in catalyst poisoning by weakly bonded water molecules instead so that lower catalyst activity was obtained. More than 99% selectivity to DME was achieved on both non-treated and hydrothermally treated AlPO_4 catalysts in this study.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Dimethyl ether (DME) is one of the promising alternative fuels that can be used to replace liquefied petroleum gas (LPG) and diesel fuels because of their similar properties to those of LPG and their high cetane number [1–3]. Moreover, DME was identified as the ultraclean alternative fuel for diesel engines with emission levels meeting the California ULEV standards [4]. DME could be produced from either synthesis gas or methanol. The production of DME via methanol dehydration is more favorable as regards thermodynamics and economy [2,5].

Methanol dehydration to DME is usually carried out over solid-acid catalysts such as H-ZSM-5, steam de-aluminated H-Y zeolite (SDY), and $\gamma\text{-Al}_2\text{O}_3$. The most widely used material is probably $\gamma\text{-Al}_2\text{O}_3$, due to its suitable acidity for this reaction that yields good performance in terms of methanol conversion and DME selectivity. Aluminum phosphate (AlPO_4) is also one of the promising catalysts in this reaction, because of its lower amounts of coking and by-products and water resistant property [3,4]. The catalytic activity of AlPO_4 in methanol dehydration was found to be dependent on

the preparation method, chemical composition (Al/P molar ratio), and activation temperature [3,6].

Water may be a poison in methanol dehydration reactions because it could block active sites and impede methanol from adsorption on the catalyst surface [7,8]. Nevertheless, there are a number of studies reporting opposite results. For example, Ludmány et al. [4] have shown that the presence of water in a reaction can increase the catalytic activity of amorphous titanium hydrogenphosphate ($\text{Ti}(\text{HPO}_4)_2$) in alcohol dehydration due to swollen effect resulting in an increase of the inter layer of $\text{Ti}(\text{HPO}_4)_2$. The swollen catalyst with water and alcohol inside the layers retains its high activity until it loses the alcohol and water by evaporation. Fu et al. [9] also reported a slight increase of activity of SDY zeolite catalyst in methanol dehydration after regeneration under hydrothermal conditions at 500 °C for 2 h. Another hypothesis about why water could increase the activity of alumina-based catalyst is that the Lewis acid sites could change to weak Brønsted acid sites upon contact with humidity [7].

In the present work, an amorphous AlPO_4 catalyst was pretreated under various hydrothermal conditions prior to activity test in the dehydration of methanol. The catalysts were characterized by X-ray diffraction (XRD), N_2 physisorption, Fourier transform infrared spectroscopy (FT-IR), Fourier transform Raman spectroscopy (FT-Raman), and amine titration with Hammett indicators. The catalyst activities were correlated with their surface characteristics and acid properties.

* Corresponding author. Tel.: +66 2218 6869; fax: +66 2218 6877.

E-mail address: joongjai.p@chula.ac.th (J. Panpranot).

2. Experimental

2.1. Catalyst preparation

An amorphous AlPO_4 catalyst with Al/P molar ratio = 1 was prepared by a modified version of the aqueous solution precipitation method of Bautista et al. [10]. Firstly, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (analytical grade, Aldrich) was diluted in deionized water and mixed with H_3PO_4 (85%, v/v Aldrich) by stirring at a controlled temperature of 0°C . Then aqueous ammonia solution was added drop-wise until the precipitation occurred at pH of solution ca. 7. The precipitate was filtered out and washed with distilled water to remove excess substances and any contaminants, and then washed again with 2-propanol. The filtrated mass was dried at 110°C overnight and calcined at 650°C in air flow for 3 h.

The AlPO_4 so prepared was subjected to hydrothermal pretreatments at different temperatures. It was exposed to a stream of 10 mol% water vapor in helium at a GHSV $5300\text{ h}^{-1}\text{ cm}^3/\text{min}$ and at temperatures of $100\text{--}300^\circ\text{C}$ for 15 min.

2.2. Catalyst characterization

The XRD patterns of the prepared catalysts were measured from 10° to $80^\circ 2\theta$ using a SIEMENS D5000 X-ray diffractometer and $\text{Cu K}\alpha$ radiation with a Ni filter. Surface area, pore volume, and average pore diameter were measured by N_2 physisorption using a Micromeritics ASAP 2020. FT-IR was performed using a Nicolet 6700 spectrometer in the range of $4000\text{--}400\text{ cm}^{-1}$ at a resolution of 2.0 cm^{-1} . FT-Raman was performed using a PerkinElmer, spectrum GX in the Raman shift range of $200\text{--}3600\text{ cm}^{-1}$ at a resolution of 4.0 cm^{-1} . The acidity of the catalyst samples was determined by amine titration method using Hammett indicators according to Ref. [11]. The NH_3 -TPD was performed in a Micromeritic Chemisorb 2750 automated system. Before adsorption, the sample was pretreated in high purity N_2 ($50\text{ cm}^3/\text{min}$) at 200°C for 1 h. Then, it was saturated with 15% NH_3 -He at 80°C for 1 h ($50\text{ cm}^3/\text{min}$) and subsequently flushed with flowing He at 100°C for 1 h ($50\text{ cm}^3/\text{min}$) to remove physisorbed NH_3 . The temperature-programmed desorption was carried out from 35 to 600°C at a constant heating rate of $10^\circ\text{C}/\text{min}$.

2.3. Catalytic activity test

The dehydration of methanol over non-treated and hydrothermally treated AlPO_4 was carried out in a fixed-bed reactor (i.d. 6 mm) using 0.2 g of catalyst and a gas hourly space velocity (GHSV) of 5300 h^{-1} . Methanol was bubbled by helium through a glass saturator maintained at 29°C . The reaction was conducted at $150\text{--}300^\circ\text{C}$ under atmospheric pressure. The reactant and products were analyzed using a gas chromatograph with a TCD detector and Porapak-Q and Porapak-N columns at 110°C and 100°C , respectively.

3. Results and discussion

3.1. Catalytic activity in the dehydration of methanol

The AlPO_4 synthesized by a modified precipitation method in this work had amorphous structure as determined by XRD (not shown) and possessed a BET surface area of $171.2\text{ m}^2/\text{g}$, a pore volume of $0.758\text{ cm}^3/\text{g}$, and an average pore radius of 17.7 nm. The non-treated AlPO_4 catalyst was tested in the dehydration of methanol to DME at the temperature range $150\text{--}300^\circ\text{C}$ and the results are shown in Fig. 1. As compared to a commercial $\gamma\text{-Al}_2\text{O}_3$ (Aldrich) that possessed BET surface area $149\text{ m}^2/\text{g}$, pore volume $0.23\text{ cm}^3/\text{g}$, and average pore radius 3.7 nm, the catalytic activity

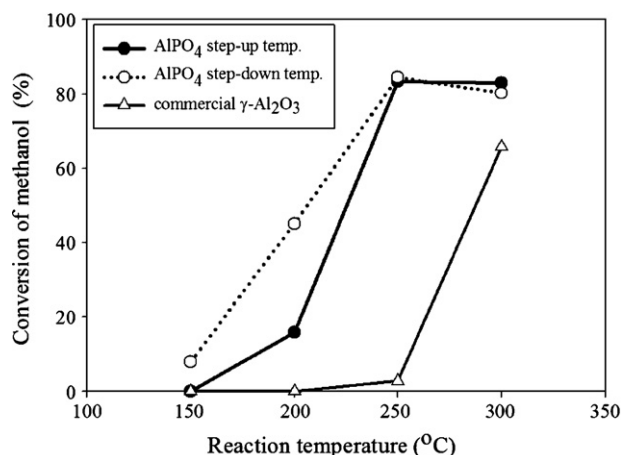


Fig. 1. Methanol conversion profiles of step-up and step-down reaction temperature experiments for the non-treated AlPO_4 catalyst as compared to a commercial $\gamma\text{-Al}_2\text{O}_3$ catalyst (reaction conditions were 0.2 g catalyst, 1 atm, and GHSV = 5300 h^{-1}).

of our synthesized AlPO_4 catalysts in the dehydration of methanol was much higher. Based on the NH_3 -TPD results (Fig. 2), the lower activity of $\gamma\text{-Al}_2\text{O}_3$ was attributed to the lower number of acid sites present. Moreover, while the AlPO_4 catalyst exhibited a large broad peak with the highest peak intensity at ca. 125°C , the commercial $\gamma\text{-Al}_2\text{O}_3$ showed two desorption peaks at ca. 80 and 360°C , indicating the presence of both relatively weak and strong acid sites on $\gamma\text{-Al}_2\text{O}_3$.

The catalytic activities of AlPO_4 catalyst were further investigated in the dehydration of methanol using step-up and step-down reaction temperature tests. For a step-up reaction temperature experiment (increasing temperature from $150 \rightarrow 200 \rightarrow 250 \rightarrow 300^\circ\text{C}$), methanol conversion occurred at 200°C and increased with increasing reaction temperature. Equilibrium conversion ($\sim 82\%$) was reached at 300°C . The AlPO_4 catalyst gave $>99\%$ selectivity to DME with less than 1% of by products such as carbon monoxide and methane. For a step-down reaction temperature experiment using a new catalyst sample (decreasing temperature from $300 \rightarrow 250 \rightarrow 200 \rightarrow 150^\circ\text{C}$), methanol conversion at 200°C increased to 45.1% as compared to 15.3% for the step-up temperature one. The AlPO_4 catalyst also showed some conversion of methanol of ca. 8% at 150°C . It is hypothesized that there was an effect of water vapor and/or initial

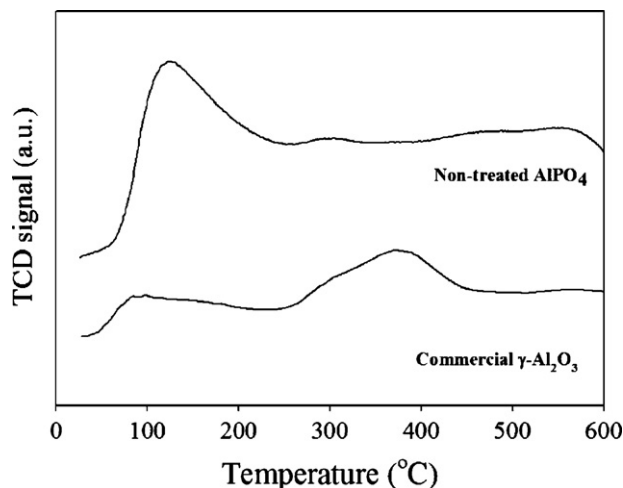


Fig. 2. NH_3 -TPD results of the synthesized- AlPO_4 and the commercial $\gamma\text{-Al}_2\text{O}_3$ catalysts.

Download English Version:

<https://daneshyari.com/en/article/42219>

Download Persian Version:

<https://daneshyari.com/article/42219>

[Daneshyari.com](https://daneshyari.com)