Methanol Dehydration to Dimethyl Ether over Modified $\gamma$-Al$_2$O$_3$ with Acid, Base and Zeolite (NaA and NaX)

Maria Ulfah$^{*1}$  
Hendra Suherman$^1$  
Melia Laniwati$^2$  
IGBN Makertihartha$^2$  
Subagjo Subagjo$^2$

$^1$ Department of Chemical Engineering, Bung Hatta University, Jl. Gajahmada No. 19, Nanggalo Olo, Kampus III Bung Hatta University, Padang, Indonesia  
$^2$ Chemical Reaction Engineering & Catalysis Group, Department of Chemical Engineering, Institut Technology Bandung, Jl. Ganesa 10, Bandung, Indonesia  
* e-mail: mariaulfah@bunghatta.ac.id

The effect of acids, bases, zeolite NaA and zeolite NaX impregnation to $\gamma$-Al$_2$O$_3$ on the catalyst characteristics and activity against methanol dehydration reaction were investigated. The catalyst characteristics include N$_2$ physisorption, X-ray diffraction (XRD), and temperature-programmed desorption of ammonia (NH$_3$-TPD) in addition to catalytic dehydration of methanol performed in a micro fixed-bed reactor at 270°C and 1 atm. The results of XRD characterization showed no changes related to the modification of alumina over acids, bases, and zeolite NaA and zeolite NaX. Therefore, the modification did not have any effect on the crystalline structure of alumina. The textural and surface acidity of $\gamma$-Al$_2$O$_3$ changed post addition of acids, bases, zeolite NaA and zeolite NaX. NH$_3$-TPD analysis results demonstrated that synthesized $\gamma$-Al$_2$O$_3$ has three types of acid sites: weak, medium, and strong; however, the weak acid sites were not observed on alumina catalysts modified phosphate, KOH, zeolite NaA, and zeolite NaX. Furthermore, the concentration of strong acid sites increased in the catalyst containing KOH. The catalytic test results showed that the untreated $\gamma$-Al$_2$O$_3$ catalyst gave prominent activity in dehydration of methanol compared to the treated catalyst following the number and strength of acid sites.

Keywords: Dimethyl ether, Methanol dehydration, Modified alumina, Surface acidity, Textural properties

INTRODUCTION

Dimethyl ether (DME) with the molecular formula C$_2$H$_6$O is the simplest non-toxic, non-carcinogenic, and non-corrosive aliphatic ether compound with no carbon-carbon (C-C) bonds. It is environmentally friendly because it has a high cetane number (55-60) and low CO and NO$_x$ emissions in exhaust gases from
Methanol dehydration (MTD) in the presence of a solid acid catalyst offers a potential approach for dimethyl ether production. Among the studied catalysts, gamma type alumina ($\gamma$-$\text{Al}_2\text{O}_3$) and H-form zeolite (H-Y; H-ZSM, H-ZSM-22) have been widely used for commercial production of DME (Zao et al. 2016). The commonly used catalyst in the MTD process, $\gamma$-$\text{Al}_2\text{O}_3$ imposing high selectivity towards DME and high mechanical resistance with lower production costs. However, the strong acid site characteristics of $\gamma$-$\text{Al}_2\text{O}_3$ lead to the production of undesirable hydrocarbons as byproducts and coke deposition. Coke deposition onto the catalytic surface and in catalyst pores will cause rapid deactivation of alumina. DME formation through methanol dehydration over acid sites of $\gamma$-$\text{Al}_2\text{O}_3$ is mainly related to acid sites with weak and medium strength (Fu et al. 2005, Yaripour et al. 2005, Keshavarz et al. 2010). The $\gamma$-$\text{Al}_2\text{O}_3$ structure is considered a cubic defect spinel-type (MgAlO$_4$) in which the Al$^{3+}$ ion substitutes the Mg$^{2+}$ ion. Thus the alumina surface has an excess of positive charge (Saravanan et al., 2017).

Furthermore, $\gamma$-$\text{Al}_2\text{O}_3$ demonstrated lower hydrothermal stability and hydrophobic surface. Water produced in the MTD reaction competes with methanol; both adsorbed onto the catalyst’s surface, with water being adsorbed more strongly. Thus, lowering the selectivity, activity, and stability of the catalyst. Accordingly, several techniques have been employed for this purpose; for instance, modifying alumina with the addition of promoters to enhance $\gamma$-$\text{Al}_2\text{O}_3$ performance in the MTD process (Sun et al., 2014).

The performance of $\gamma$-$\text{Al}_2\text{O}_3$ impregnated by phosphoric acid has been investigated by Yaripour et al. (2005) through modifying $\gamma$-$\text{Al}_2\text{O}_3$ over phosphorus (molar ratio aluminum to phosphate = 2), it has been observed that the catalytic activity is positively stimulated. Higher methanol conversion and insignificant byproducts generation were observed in the phosphorus-modified catalyst process.

Mao et al. (2006) have investigated the effect of hybrid catalysts of modified $\gamma$-$\text{Al}_2\text{O}_3$ over ammonium sulfate in the range of 0-15% sulfate content on the direct synthesis process of DME from syngas. The hybrid catalyst containing physically mixed sulfated alumina, $\text{SO}_4^{2-}/\gamma$-$\text{Al}_2\text{O}_3$ with 10 wt.% sulfate content and CuO-ZnO-$\text{Al}_2\text{O}_3$, followed by calcination at 550°C exhibited the highest selectivity and yield on the formation of dimethyl ether.

Wang et al. (2013) prepared the bifunctional catalyst from aluminum and amino acetic acid by using triblock copolymer pluronic F127 as a template via evaporation-induced organic assembly method. The MTD process performed at
high temperature (450°C) catalyzed over the solid acid-base bifunctional catalyst displayed higher methanol conversion and DME selectivity than H-[F] ZSM-5 and H-ZSM-5 catalysts with merely one group of acid site.

On condition throughout the MTD reaction, the water as a byproduct can be selectively removed, according to Le Chatelier’s principle, lead to enhancement of the conversion and selectivity of methanol dehydration to DME. Some researchers have reported hydrophilic membrane performance to remove water in situ during the MTD process. A novel FAU-LTA zeolite dual-layer membrane established by Zhao et al. (2016) has displayed its performance as a catalytic membrane reactor for the MTD process. The reaction was expected to occur in the top H-FAU zeolite layer with moderate acidity. Water as a byproduct is eliminated in situ by the Na-LTA zeolite layer, between the alumina support and the H-FAU zeolite. The combination of moderate acidity and sustainable water removal significantly increases DME production to 90.9% at 310°C and 100% DME selectivity.

Investigation of the correlation between the performance of 8 commercial γ-Al2O3 and 2 self-prepared γ-Al2O3 catalysts in addition to physicochemical characteristics of these catalysts to the dehydration reaction of methanol vapor into DME has been carried out by Akarmazyan et al. (2014). Based on textural properties analysis (BET and BJH methods), acidity (NH3-TPD), crystallinity (XRD), and the catalyst activity tests, it was discovered that textural properties, the number of acid sites, and degree of crystallinity prompting catalysts activity on methanol dehydration reaction into DME. The alumina catalyst with the highest ratio of weak to moderate acid sites showed excellent catalytic activity and stability (Akarmazyan et al., 2014).

Herein, in this study correlation between physicochemical characteristics of modified γ-Al2O3 catalysts over acids, bases, zeolites, and catalytic activity was investigated. The catalyst’s properties were reviewed about the analysis of N2 adsorption, X-ray diffraction (XRD), and temperature-programmed desorption ammonia (NH3-TPD).

MATERIALS AND METHODS

Materials

Potassium hydroxide, NaOH, CH3OH, and Na2SiO3.9H2O were obtained from PT. Bratacem, Bandung-Indonesia. Other chemicals used in this study were (NH4)2SO4, HNO3, H3PO4, NH3 solution (25 wt.%), and NaAlO2. The raw material for gamma-alumina synthesis (boehmite) was obtained from PT. Pertamina, Indonesia.

Preparation of γ-Al2O3 Catalyst

γ-Al2O3 pellets (Al) were prepared according to published compositions and procedures (Ulfah and Subagjo 2012).

Preparation of Modified γ-Al2O3 Over Acids and Bases

Acid. Acid-modified γ-Al2O3 was prepared via impregnation over variations of acid types; (NH4)2SO4 (Al-amm. sulfate) and H3PO4 (Al-phosphate). Each was dissolved in distilled water by mass ratio acid : water of 1:13. The impregnation was conducted for 5 hours, followed by
filtration. The paste was left overnight at room temperature, then dried at 120°C for 2 hours, and calcined at 570°C for 3 hours.

**Base.** Base-modified γ-Al₂O₃ was prepared via impregnation over various base types (KOH and NaOH) and solvents (water and methanol) by mass ratio base : solvent of 1:13. Al-K-W samples were synthesized by immersing self-prepared Al₂O₃ in a mixture of KOH and water and Al-K-M samples in a mixture of KOH and methanol. Moreover, different self-prepared alumina was prepared via impregnation in a mix of NaOH-water (Al-Na-W) and NaOH-methanol (Al-Na-M) solutions. The impregnation time, drying conditions, and calcination was following with acid-modified γ-Al₂O₃.

**Preparation of Zeolite-Modified γ-Al₂O₃**

**Zeolite NaA.** Zeolite NaA was synthesized as described by Milton and Buffalo (US Pat. 2882243). The reactant mixture composition was designated Na₂O/SiO₂, SiO₂/Al₂O₃, and H₂O/NaO molar ratio of 1.44, 2.2, and 55, respectively. The catalyst was synthesized by introducing zeolite NaA into boehmite (weight ratio of 1:3), water, HNO₃, and NH₃ solution (25 wt.%). The mixture was extruded and kept at room temperature overnight, followed by oven-drying at 120°C for 2 hours and calcined at 570°C afterward. The sample is denoted as Al-NaA.

**Zeolite NaX.** Al-NaX catalyst was synthesized by mixing one part of zeolite NaX and three-part boehmite (weight ratio). Zeolite NaX was synthesized as described by Milton and Buffalo (US Pat. 2882244). The homogeneous solid mixture was added with water, HNO₃, and NH₃ solution (25 wt.%), then extruded, left overnight, dried and calcined.

**Characterization of catalysts**

The BET surface area, the total pore volume, and the average pore diameter were measured using a N₂ adsorption-desorption isotherm method by NOVA 2200 instrument (Quantachrome, USA). X-ray diffraction patterns were obtained to determine the particle crystallite size and component identification (X’Pert PRO, PW Model 3040/60 console) using CuKα monochromatized source and Ni filters over the 2θ interval 10-80°. The modified catalysts’ total acidity measurements were determined by temperature-programmed desorption of ammonia (NH₃-TPD) on a Quantachrome TPR Win v4.0 instrument.

**Catalytic Activity**

Methanol dehydration to dimethyl ether (DME), using the synthesized catalysts, at atmospheric pressure and temperature of 270°C was studied in a glass reactor (Dₐ of 20 mm). Before use, the catalysts were crushed and sieved to 60-80 mesh. During the evaluation, 1 gram of catalyst was loaded to the reactor by packing glass wool pads at both the catalyst bed ends. Before any experiments, the catalyst was activated in situ at atmospheric pressure from room temperature to 200°C at a heating rate of 5°C/min under a continuous nitrogen flow rate of 150 ml/min. The activated mixture of methanol and nitrogen was introduced to the reactor at a flow rate of 130 ml/min (GHSV = 156000/hour), and the reactor temperature was elevated to 270°C. Product analysis was carried out for 6
The concentration of methanol (MeOH) was determined using a Gas Chromatography 14-B Shimadzu. Porapak Q was used as a separating column equipped with a TCD detector, injector temperature of 120°C, column temperature of 180°C, and temperature detector of 200°C. Methanol conversion was calculated based on the chromatogram area using the following Equation (1).

$$X_{\text{MeOH}} = \frac{A_{\text{MeOH}}/A_{N2}}{A_{\text{MeOH}}/A_{N2}}_\text{air}$$

(1)

**RESULTS AND DISCUSSION**

**Catalyst Characterization**

**Table 1. Pore Properties of Catalysts**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>$P_v$ (cc/g)</th>
<th>$D_p$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$-Al</td>
<td>249.21</td>
<td>0.42</td>
<td>6.86</td>
</tr>
<tr>
<td>Al-S</td>
<td>210.06</td>
<td>0.37</td>
<td>7.06</td>
</tr>
<tr>
<td>Al-P</td>
<td>191.11</td>
<td>0.37</td>
<td>7.74</td>
</tr>
<tr>
<td>Al-K-W</td>
<td>225.89</td>
<td>0.41</td>
<td>7.32</td>
</tr>
<tr>
<td>Al-K-W</td>
<td>263.71</td>
<td>0.48</td>
<td>7.34</td>
</tr>
<tr>
<td>Al-N-W</td>
<td>226.04</td>
<td>0.41</td>
<td>7.20</td>
</tr>
<tr>
<td>Al-N-M</td>
<td>192.63</td>
<td>0.35</td>
<td>7.36</td>
</tr>
<tr>
<td>Al-NaA</td>
<td>278.88</td>
<td>0.39</td>
<td>5.66</td>
</tr>
<tr>
<td>Al-NaX</td>
<td>239.37</td>
<td>0.37</td>
<td>6.26</td>
</tr>
</tbody>
</table>

Table 1 summarizes the textural properties of modified $\gamma$-Al$_2$O$_3$ catalysts over acids, bases, and two types of zeolite (A and X). The textural properties were obtained in reference to nitrogen adsorption-desorption data through Brunauer-Emmett-Teller (BET) method to compute the specific surface area ($S_{\text{BET}}$), total pore volume ($P_v$, cc/g), and average pore diameter ($D_p$, nm).

From Table 1 it can be seen that the catalyst samples may differ in textural properties. The decrease in the specific surface area of $\gamma$-Al was observed over the samples with S, P, Na, and zeolite NaX. Similar results were also displayed by Limlathong et al. (2019) and Malkov et al. (2017); the specific surface area and total pore volume of alumina were decreased with an increase of P loading. It may be due to P particles’ blocking of alumina pores (Limlathong et al., 2019).

The alumina catalyst’s textural properties impregnated over ammonium sulfate (SO$_4$/$\gamma$-Al$_2$O$_3$) solution have been reported by Mao D et al. (2006). The surface area of impregnated $\gamma$-Al$_2$O$_3$ over 5 wt.% sulfate content and calcined at 550°C was reduced from 297.7 m$^2$/g to 281.5 m$^2$/g. It is attributed to the evolution of SO$_3$ disintegrated from the sulfate ion bonded to the alumina surfaces. As the sulfate content increased to 10 wt.% and calcined at 750°C, the observed catalysts’ surface area decreased, affected by the collapse of pores. In this study, the surface area of impregnated $\gamma$-Al$_2$O$_3$ over SO$_3$ 2.4 wt.% (analyzed by XRF PANalytical Epsilon 3) and calcined at 570°C was reduced from 249.21 m$^2$/g to 210.06 m$^2$/g, attributed to the decomposition of SO$_3$ on the surface of $\gamma$-Al$_2$O$_3$.

Based on Table 1, it can be seen that a decrease in BET surface area and pore volume of the buffer observed over the samples post impregnation with a mixture of aqueous solution and NaOH or methanol and NaOH on $\gamma$-Al. The decrease was attributed to the possible formation of
Na compounds deposits on the alumina support surface, which is considered to be similar to previous publications (Limlathong et al. 2019, Malkov et al. 2017). The significant reduction in the surface area of the Al-N-M catalyst sample compared to Al-N-W was observed due to different Na species generated on the gamma-alumina surface between the two aluminas. During the evaluation, it was observed that the NaOH and methanol mixture was more turbid than NaOH and water mixture. Moreover, NaOH exhibits lower solubility in polar solvents such as methanol despite the weight ratio of NaOH : water was 1:13.

Figure 1a, 1b, and 1c illustrate the nitrogen adsorption-desorption isotherm of pure gamma-alumina, modified alumina over acids, bases, and zeolites (NaA and NaX), respectively. All the nitrogen adsorption-desorption isotherm showed typical reversible Type IV adsorption isotherms defined by IUPAC, reprinted from Sing et al. (1985). The hysteresis loops were formed due to capillary condensation of nitrogen in mesopores. The hysteresis loop for all catalysts is very similar to the H1 type, which is often connected with porous materials consisting of either agglomerates or compacts of relatively homogeneous spheres in a moderately regular array, and hence narrow distributions of pore size (Hajimirzaee et al. 2014).

Figure 2 displayed the obtained XRD pattern of γ-Al2O3, alumina modified with acids, bases, and zeolites. All catalysts displayed sharp peaks toward γ-Al2O3, which was specifically observed at 2θ = 37°, 46° and 67°. The XRD pattern of modified alumina over sulfate, phosphate, Na, and K was in accordance with pure γ-Al2O3. This similar pattern confirms that the modification did not have any effect on the crystalline structure of alumina. Furthermore, the XRD pattern of SO3, P, Na, and K ions was not detected due to their small crystalline size (below 0.2 μm), disorder, absorption, and divergent sample packing density (Hajimirzaee et al. 2014).

**Fig. 1:** Nitrogen adsorption-desorption isotherms of (a) pure γ-Al2O3 and acid-modified γ-Al2O3, (b) base-modified γ-Al2O3, and (c) zeolite-modified γ-Al2O3.
Figure 2: XRD pattern of pure alumina and modified alumina

Figure 2 shows that new peaks were observed on the XRD pattern of alumina modified with zeolite A (A-NaA) and X(Al-NaX). The presence of peaks observed at values $\theta = 24^\circ; 27.2^\circ$ and $30^\circ$ indicating the presence of zeolite NaA [Somderam et al., 2019] and at $\theta = 23.3^\circ; 26.7^\circ$ and $31^\circ$ for zeolite X (Iftitahiyah et al. 2018).

Temperature programmed desorption of ammonia (NH$_3$-TPD) is one technique for characterizing the density and strength of acid sites. Ammonia molecule is appropriate for this purpose because it can be adsorbed at sites with different strengths and small kinetic diameter (0.26 nm). Thus, allowing the detection of acid sites located in very confined pores (Akarmazyan et al. 2014). The surface acidity values of the modified alumina and pure alumina catalyst as comparison are presented in Table 2. The acidity strength shown in Table 2a was determined by the temperature at which NH$_3$ desorbed. NH$_3$ desorption temperatures lower than 150°C, in the range of 150 - 400°C and above 400°C correspond to weak, medium and, strong acidity, respectively. Table 2b showed the acid concentration, calculated by multiplying the height of the peak with time. In this study, the acidity of pure $\gamma$-Al$_2$O$_3$, modified alumina by phosphorus, KOH (in methanol), zeolite NaA or zeolite NaX were observed.

| Peak NH$_3$ desorption temperature, °C |
|---|---|---|
| Weak | Medium | Strong |
| $\gamma$-Al | 148.79 | 252.98 | 472.10 |
| Al-P | 314.09 | | |
| Al-K-M | 270.48 | 506.14 | |
| Al-NaA | 324.88 | | |
| Al-NaX | 308.21 | 518.83 | |

Table 2a shows that three NH$_3$ desorption peaks of pure $\gamma$-Al$_2$O$_3$ were observed; however, the weak acid sites were not recorded post modification over phosphorus, KOH (in methanol), zeolite A and zeolite X. Surprisingly, the NH$_3$ desorption profile of alumina impregnated with KOH still contains strong acid sites but not found on the alumina catalyst impregnated with phosphoric acid. Medium and strong acid sites were obtained on modified alumina over zeolite NaX, but alumina impregnated with zeolite NaA only displayed medium acid sites. Hajimirzaee et al. (2014) reported that acid distribution altered by changing the ratio of Si/Al in the zeolite. The Si/Al ratio of zeolite NaX ranges from 2.5 ± 0.5 (Milton and Buffalo, 1959a) and for zeolite A ranges...
from 1.85 ± 0.5 (Milton and Buffalo, 1959b). The γ-Al2O3 catalyst contains mainly medium acid sites (94.52%), a small number of weak acid sites (2.23%) as well as strong acid sites (3.25%). Modification of γ-Al2O3 over phosphorus, zeolite Na-A, and zeolite NaX increase the medium acid sites; conversely, the concentration of acid sites increase on Al-K-M catalysts (16.52%).

**Table 2b. Acid Sites Concentration**

<table>
<thead>
<tr>
<th></th>
<th>Weak (% area)</th>
<th>Medium (% area)</th>
<th>Strong (% area)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al</td>
<td>23.53</td>
<td>999.32</td>
<td>34.37</td>
</tr>
<tr>
<td></td>
<td>(2.23)</td>
<td>(94.52)</td>
<td>(3.25)</td>
</tr>
<tr>
<td>Al-P</td>
<td>2251.45</td>
<td>(100)</td>
<td></td>
</tr>
<tr>
<td>Al-K-M</td>
<td>283.52</td>
<td>56.13</td>
<td>(16.52)</td>
</tr>
<tr>
<td></td>
<td>(83.48)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al-NaA</td>
<td>3079.30</td>
<td>(100)</td>
<td></td>
</tr>
<tr>
<td>Al-NaX</td>
<td>1458.18</td>
<td>27.84</td>
<td>(1.87)</td>
</tr>
<tr>
<td></td>
<td>(98.13)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Catalytic Activity**

Figure 3 represents the catalytic activity of methanol dehydration on γ-Al, Al-P, Al-K-M, Al-NaA, and Al-NaX catalysts performed in a fixed-bed reactor at atmospheric pressure, 270°C, and 99% methanol concentration. As shown in Figure 3, Al catalyst with a surface area of 249.21 m²/g exhibits the highest methanol conversion compared to Al-K-M and Al-NaA catalysts despite greater S_{BET} than gamma-alumina. Akarmazyan et al. (2014) reported that the MTD reaction’s catalytic activity was not solely attributed to the surface area of the catalyst but also to other parameters, e.g., crystallinity and the number of acid sites. According to Wang et al. (2013), the MTD reaction requires an acid-base bifunctional catalyst to activate both nucleophilic and electrophilic methanol molecules. Thus, it can be explained that the lower activity of Al-NaA catalyst compared to Al was attributed to the single type of acid center (see Table 2a). The remarkable increase of strong acid sites concentration in the Al-K-M catalyst (16.52%) compared to γ-Al (3.25%) might lower the first catalyst’s performance. It referred with several investigation reported that MTD reaction demands the presence of weak and medium strength acid sites in high concentration (Fu et al. 2005, Kim et al. 2008, Tokay et al. 2012).

Ardi et al. (2019) reported that the activity of self-prepared γ-Al2O3 catalyst up to 5 hours-time on stream (TOS) obeyed low methanol conversion and increased after 5 hours. This activity was stable at TOS of 72 hours. The same trend was encountered in this study; methanol conversion decreased at 5 hours of TOS and increased subsequently.

As described in the introduction, modifying alumina with phosphorus, zeolite A, X, and activating both acid-base sites can improve the performance of an alumina-based catalyst against the catalytic reaction of methanol dehydration. However, out of the 5 catalyst types studied, unmodified alumina provided the highest conversion. It is correlated with acid sites of weak and medium strength exhibited by pure γ-Al2O3. Yaripour et al. (2005) investigated that aluminum phosphate catalyst with molar ratio Al / P = 2 (DME-AlP2) gave the highest conversion with no byproducts present. Furthermore, DME-AlP1 catalyst (molar ratio Al / P = 1)
gave lower methanol conversion, and DME-AlP3 catalyst generated hydrocarbons (such as methane) as byproducts. The investigation claimed that DME production is associated with weak and medium acid sites. AlP catalyst activity decrease if only weak acid sites present, and the selectivity towards DME decreases if the concentration of the strong acid sites increases. Thus, phosphorus’s appropriate addition \( \gamma \)-Al\(_2\)O\(_3\) will result in maximum catalyst activity, selectivity, and stability to MTD catalytic reaction.

Mao et al. (2006) previously had reported the DME from syngas using a modified \( \gamma \)-Al\(_2\)O\(_3\) catalyst with varied sulfate content (0-15 wt.%). The results showed that the selectivity of DME increased with increasing sulfate content in \( \gamma \)-Al\(_2\)O\(_3\) to 10 wt. % and then decreased with sulfate content above 10 wt.%. These results correlate with an increase in the number and strength of the acid sites.

![Graph](image)

**Fig. 3:** Profile of methanol conversion over \( \gamma \)-Al, Al-P, Al-K-M, Al-NaA, and Al-NaX

This result was attributed to the increasing number and strength of acid sites.

Thus, this study was in agreement with previous reports (Fu et al. 2005, Yaripour et al. 2005, Mao et al. 2006, Kim et al. 2008, Tokay et al. 2012), i.e., the number and distribution of acid sites strength of the catalyst play a significant aspect in the MTD reaction.

**CONCLUSIONS**

Phosphoric acid, KOH, zeolite NaA, and zeolite NaX addition to \( \gamma \)-Al\(_2\)O\(_3\) surrogates the textural properties and surface acidity of the gamma-alumina catalyst. The surface area of modified \( \gamma \)-Al\(_2\)O\(_3\) over KOH and zeolite NaA is greater than untreated \( \gamma \)-Al\(_2\)O\(_3\) but exhibited lower catalytic performance. It is following previous research that surface acidity determines the performance of the methanol dehydration reaction. Based on the results of TPD-NH\(_3\) analysis, weak acid sites were not observed in modified alumina catalysts over phosphate, KOH, zeolite NaA, and zeolite NaX. Furthermore, the concentration of strong acid sites was the greatest on catalyst containing KOH. Self-prepared \( \gamma \)-Al\(_2\)O\(_3\) with a surface area of 249.21 m\(^2\)/g and contains mainly medium acid sites (94.52%), small amounts of a weak acid (2.23%), and strong acid (3.25%) sites provides maximum methanol conversion.

**ACKNOWLEDGEMENT**

The authors would like to thank The Ministry of Technology Research and Higher Education Indonesia for the financial supports (8/EI/KPT/2020). Moreover, the authors would also thank...
Tasnia, Altop, Shifa and Setiawan for their help during the research.

REFERENCES


