Synthesis and characterization of modified γ-Alumina-NaA and γ-Alumina-NaX zeolite composites as methanol dehydration catalysts in synthesis Dimethyl Ether (DME)

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Abstract. Dimethyl ether (DME) is of great interest due to its wide application. It is currently being demonstrated for use as an alternative diesel fuel or substituting LPG for household. DME production via methanol dehydration reaction is affected by textural properties and catalyst surface acidity. The experimental study of textural properties in addition to surface acidity of both γ-Al₂O₃ prepared in this study and modified γ-Al₂O₃ over zeolite A and X mixing were conducted. The catalysts were characterized by N₂ adsorption-desorption, X-ray diffraction (XRD), and temperature programmed desorption of ammonia (NH₃-TPD). Referring to N₂ adsorption/desorption isotherm using the Brunauer-Emmet-Teller (BET) equation, the catalysts were observed possessing high specific surface area (170–279 m²·g⁻¹) and pore diameters of 5.6 – 8.8 nm (mesoporous). The XRD patterns of all catalysts still reveals clear peaks of γ-Al₂O₃ components. The strength of the acid sites of alumina modified with zeolite A is categorized as medium acid sites, whereas by modified by zeolite X varies.

1. Introduction
Alumina (Al₂O₃) has been used widely as a catalyst and heterogeneous catalyst support owing to its lower cost, thermal stability, high specific areas, surface acidity and interaction with transition-metals deposited onto the surface. It exists in α, γ, κ, ρ, η, and θ phases, each exhibits a unique properties [1]. The γ-alumina phase is commonly used in methanol dehydration reaction into dimethyl ether (DME).

Dimethyl ether, also known as methoxymethane (CH₃OCH₃), is the smallest aliphatic ether compound in the absence of a C-C bonds that benefits from being non-toxic, non-carcinogenic and non-corrosive. Due to its high cetane number (55-60), DME can be used in a diesel engine that produce low levels of CO and NOx, thus DME can be counted as an alternative fuels [2]. Furthermore, considering the similarity of its physical properties with those of liquefied petroleum gas (LPG), DME can easily add or replace LPG for home cooking, power generation, and LPG derived engines [3]. DME also used as a CFC aerosol-propellant replacement, raw material for chemical products, and solvent. The rising demand for DME in the near future is attributed to its widespread applications as
precedently reported. Moreover, the well-developed LPG infrastructures can be adapted for DME, thus makes DME formidable for practical use [4].

Methanol dehydration to DME reaction (MTD) carried out over solid acid catalysts is economically and thermodynamically favored [2]. Solid acid catalysts, such as alumina and zeolite, being the most common acid catalysts employed in the dehydration of methanol to produce DME commercially. Alumina and zeolite strong acid sites tend to lead to coke formation or other undesired by-products such as hydrocarbons, thus decreasing DME selectivity. The production of DME through MTD reaction is mainly related to sites with weak and medium acidity [2-10]. Accordingly, the surface acidity of solid acid catalysts, such as alumina and zeolite, is adjusted and modified to increase DME selectivity and catalytic stability. Modifying the catalyst by adding alkaline, alkaline earth, transition, rare earth metals, or other composite oxides is the strategy to adjust the surface acidity [7].

Adjusting the surface acidity of zeolite can be obtained over introduction of Na⁺ ion on zeolite structures. Modified H-form zeolite over Na⁺ exhibits higher MTD performance, high activity, selectivity and stability at temperatures of 230-340 °C [8, 9]. The catalyst surface acid sites display moderate acid strength which is responsible to inhibit hydrocarbon and coke formation.

Wang et al. (2013) observed that the key to MTD reaction is related to sites with weak acids and bases (bi-functional catalysts). Weak acidic sites facilitating the activation of O in methanol, while weak basic sites activating H of hydroxyl group in surrogate methanol molecules [10]. The investigation prepared the bi-functional catalysts over aluminium acid and aminoacetic with triblock copolymer pluronic F127 as a template via and evaporation induced organic assembly method.

Zhou et al. (2016) employed a sandwich FAU-LTA zeolite with dual-layer membranes as a catalytic membrane reactor of dimethyl ether synthesis (DME). Methanol dehydration into DME conducted on the upper layer of H-FAU zeolite with moderate acidity, and water as the by-product of MTD reaction was removed in situ on Na-LTA zeolite layer that possessed hydrophilic properties [11]. Na-LTA zeolite layer was located between porous alumina supporter and H-FAU. The combination provide 90.9% methanol conversion at 310 °C and DME selectivity of 100%. The dual-layer membrane of FAU-LTA zeolite was prepared on a porous α-Al₂O₃ tube over 3-aminopropyltriethoxysilane (APTES) as a covalent linker between the zeolite LTA layer and the α-Al₂O₃ support.

This research aims to develop and characterize of the γ-Al₂O₃-Zeolite NaA (Al-Zeo-Ao and Al-ZeoA-33) and γ-Al₂O₃-Zeolite NaX (Al-Zeo-Xo and Al-ZeoX-33) catalysts. The catalysts were prepared by mixing A or X zeolite with boehmite at ratio of 1:3, dried and calcinated at 570 °C for 3 hours. The effect of zeolite type and Na content on catalysts properties was investigated and compared with self-prepared γ-Al₂O₃ derived from boehmite. The catalysts produced in this studied were characterized by BET, XRD and NH₃-TPD.

2. Method

2.1. Catalyst preparation

2.1.1 γ-Al₂O₃ catalyst. Gamma alumina catalysts were prepared by using sol-gel method; the boehmite (AIOOH) was weighed and added to water, nitric acid 3 wt. % and sodium hydroxide 25 wt. %. After mixing, the mixture was extruded and stored at room temperature for 48 hours. The mixture was dried at 120 °C for 3 hours and calcinated at 570 °C for 2 hours [12].

2.1.2 Al-ZeoA0 catalyst. Zeolite A (4Å) was synthesized as described in US Patents Document 2882243 [13]. The reactant mixture has a composition expressed in terms of molar ratio of:

\[
\begin{align*}
\text{Na}_2\text{O}/\text{SiO}_2 & = 1.44 \\
\text{SiO}_2/\text{Al}_2\text{O}_3 & = 2.2 \\
\text{H}_2\text{O}/\text{Na}_2\text{O} & = 55
\end{align*}
\]
Al-ZeoA catalyst was prepared by adding zeolite 4Å into boehmite (weight ratio of 1:3), water, nitric acid 3 wt. % and sodium hydroxide 25 wt. %. The mixture was extruded and stored at room temperature for 24 hours, then dried at 120 °C for 2 hours and calcinated at 570 °C for 3 hours.

2.1.3 Al-ZeoXo catalyst. Zeolite X was synthesized as described in US Patents Document 2882244 [14]. The mixture of reagents were prepared with the Na2O/SiO2, SiO2/Al2O3, and H2O/Na2O molar ratio of 1.3, 3.4 and 38, respectively. Al-ZeoX catalyst was prepared by adding zeolite X into boehmite (weight ratio of 1:3), water, nitric acid 3 wt. % and sodium hydroxide 25 wt. %. The paste was formed into shapes and stored at room temperature for 24 hours. The shaped paste then dried at 120 °C for 2 hours and calcinated at 570 °C for 3 hours.

2.1.4 Al-ZeoA33 catalyst. ZeoA-33 catalyst was prepared by homogenizing zeolite 4Å and metakaolin (from Lampung, Indonesia) with weight ratio of 4:3. Sodium hydroxide 33 wt. % was added into the mixture and homogenized to form paste. The shaped paste was inserted into sealed HDPE container and stored at room temperature for 4 days. After 4 days, the paste was crystallized at 100 °C for 17 hours in an oil batch. ZeoA33 pellets were washed then dried and calcinated at 570 °C for 2 hours. The pellets were crushed and added into boehmite, water, nitric acid 3 wt. % and sodium hydroxide 25 wt. %. The paste was shaped into pellets and stored at room temperatures for 24 hours. After 24 hours, the pellets were dried and calcinated.

2.1.5. Al-ZeoX33 catalyst. ZeoX-33 catalyst was prepared by homogenizing zeolite NaX and metakaolin with the ratio weight of 4:1. Sodium hydroxide 33 wt. % was added into the mixture and homogenized to form paste. The paste was shaped into pellets, inserted into sealed HDPE container and stored at room temperature for 4 days then crystallized. ZeoX33 pellets were washed then dried and calcinated at 570 °C for 2 hours. The next procedure is similar with ZeoA33 preparation as described previously.

2.2. Characterization catalysts
The BET surface area (SBET), total pore volume (Vp), and pore diameter (Dp) were measured using a NOVA 2200 instrument (Quantachrome, USA). The XRD patterns of all the calcined samples were recorded on a Bruker dB advance (40 kV, 30 mA) X-Ray diffractometer, using a Cu-Kα radiation source (λ=1.5406 Å) and a nickel filter in the 2θ range of 0–80°. The acidity of the samples was measured via NH3-TPD, using a Quantachrome TPR Win v4.0 instrument, which included on-line thermal conductivity detection (TCD).

3. Results and Discussion
3.1. Textural properties
Table 1 summarizes the textural properties of modified γ-Al2O3 catalyst over two types of zeolite (A and X). The textural properties were derived attributed to nitrogen adsorption-desorption data using Brunauer, Emmett and Teller (BET) method to elaborate the specific surface area (SBET), total pore volume (Pv, cc/g) and average diameter pore (Dp, nm). The crystallite size of alumina was determined over XRD results using Scherrer equation.

Methanol dehydration into DME is strongly attribute to the textural properties, degree of crystallinity and total amount of Al2O3 acid sites [15]. The study suggested that materials with higher porosity (larger than 1 cm3 g−1) or smaller crystallite size (lesser than 3.5 nm) are less active, most probably attributed to its highly amorphous nature. Furthermore, the investigation reported that higher conversion of methanol was presented by catalyst with average cylindrical pores of about 9-10 nm, total pore volume of 0.60-0.80 cm3 g−1 and crystallite size of 5-5.5 nm. In particular, such materials possess specific surface area of about 195-240 m2 g−1.
The textural, acidic properties and catalytic activity of γ-alumina are greatly influenced by the preparation method. Nano crystalline γ-alumina prepared by sol-gel method via sucrose as template shows the highest catalytic activity. Concerning the NH₃-TPD analysis, Keshavarz et al. (2011) confirmed that smaller crystallite size and moderate acidic sites showed higher catalytic activity. Such catalyst have specific surface area of 294 m² g⁻¹, pore volume of 0.54 cm³ g⁻¹, cylindrical pores of 7.4 nm and crystallite size of 4.2 nm [6].

Considering the extensive number of nanostructured gamma alumina application in different areas, the preparation of such materials with interesting morphology and high specific surface area over simpler methods has gained significant importance [16]. Potter et al. developed a nano sized gamma alumina via room temperature precipitation/digestion method and subsequent calcination of boehmite at 550 °C for 5 hours. The study investigated that the product surface area and average pore volume were 133.90 m² g⁻¹ and 1.02 cm³ g⁻¹, respectively [17]. Prida et al. (2009) have prepared nano gamma alumina using sodium hydrogen carbonate, sodium carbonate and ammonium bicarbonate. The spherical nano sized particle with a surface area of 190 m² g⁻¹ and pore volume of nearly 0.467 cm³ g⁻¹ was obtained over ammonium carbonate [18].

In the present study, it is focused on gamma alumina preparation based on sol-gel method and calcination at 570 °C with boehmite as raw material. The surface area of self prepared gamma alumina was about (249.209 m²/g) while pore volume was about 0.421 cm³/g. This value of surface area is greater than 125 m²/g and it indicates that synthetic nano gamma alumina is very stable [17]. The physicochemical parameters of developed catalysts were expressed in Table 1.

### Table 1. Physicochemical parameters of developed catalysts

|          | S_{BET} (m²/g) | Pv (cm³/g) | Dp (nm) | Crist. size (Nm) |
|----------|----------------|------------|---------|------------------|
| γ-Al₂O₃ | 249.209        | 0.421      | 6.860   | 15.888           |
| Al-ZeoA0 | 278.877        | 0.395      | 5.660   | 11.935           |
| Al-ZeoA33 | 239.371       | 0.375      | 6.264   | 24.043           |
| Al-ZeoX0 | 215.439        | 0.458      | 8.497   | 19.160           |
| Al-ZeoX33 | 170.365       | 0.372      | 8.743   | 30.470           |

Alumina features a range of advantages including excellent thermal stability, relatively high surface area, high mechanical strength and appropriate acidity concerning MTD reaction exhibited by higher methanol conversion and 100% of selectivity towards DME [7]. However, the ability to absorb water (hydrophilic properties) better than methanol gave a disadvantage to alumina application. Zhou et al. (2016) developed alumina combined with NaA zeolite (LTA) and H-Y zeolite to enhance the reduced activity by water presence on methanol dehydration [11].

NaA zeolite is one of the foremost zeolite in chemical industry due to its hydrophilic properties. Nano-sized and uniform pores of NaA zeolite received great attention that has been reported to be very attractive catalyst in dehydration process [19]. With regard to increase the MTD catalytic activity, self-developed alumina over NaA zeolite were investigated in this study. NaA zeolite preparation was in accordance with US Patents Document 2882244 [14] that was successfully produce zeolite A with pores of 0.4 nm (4Å). Al-ZeoAo catalyst textural properties prepared by mixing boehmite and zeolite 4Å crystalline powder with ratio of 3:1 followed by calcination at 570 °C is shown in Table 1. Zeolite 4Å added will increase alumina specific surface area. On the contrary, pore volume, pore diameter and crystallite size of Al-ZeoAo is smaller than non-modified γ-alumina.

Aliphatic alcohol compound with carbon atoms of C1, C2 and C3 can be adsorbed onto zeolite 4Å [14], but not on zeolite 3Å. In this study, zeolite 3Å was also prepared with preparation method refers to US Patents Documents 3679604 [20]. Firtsly prepared zeolite 3Å was assorted with boehmite, water, HNO₃ (3 wt. %) and NH₄OH (25 wt. %) followed by calcination at 570 °C (Al-ZeoA33). Al-
ZeoA33 specific surface area was smaller than γ-alumina. However, pore volume, pore diameter and crystallite size is greater. Physicochemical properties of Al-ZeoA33 catalyst is shown in Table 1.

Another zeolite type that received great attention in chemical industry as catalysts or adsorbent is faujasite. Zeolite X and Y is classified as faujasite zeolite. Both were distinguished based on Si/Al molar ratio; zeolite X have Si/Al molar ratio of 1-3 and zeolite Y of 4-6. This molar ratio is a deciding factor of surface acidity properties, higher Si/Al ratio resulted in higher surface acidity. In this study, zeolite NaX was developed as reported in US Patents Documents 2,882,244 [13]. Al-ZeoX0 catalyst was prepared by mixing zeolite NaX crystalline powder with boehmite, homogenized, introduced to water, diluted nitric acid and concentrated ammonium hydroxide. Al-ZeoX0 catalyst developed in this study possessed physicochemical properties as displayed in Table 1. Surface area, total pore volume and average pore diameter of γ-Al₂O₃ is decrease with zeolite NaX powder mixed, however the crystallite size is enhanced. Similar trends were also displayed by AlZeoX-33 catalyst; surface area, total pore volume and average pore diameter of γ-Al₂O₃ is decrease with zeolite X-33 pellet added.

According to International Union of Pure and Applied Chemistry (IUPAC) notation, microporous materials have pore diameters of less than 2 nm and macroporous materials have pore diameters of greater than 50 nm; the mesoporous category thus lies in the middle [21]. Pore diameters of catalysts developed in this study were in a range of 2-50 nm, thus categorized as mesoporous. Highly ordered mesoporous Al₂O₃ has excellent thermal stability, high mechanical resistance, as well as high activity and DME selectivity as a result of its weak and moderate acid strength [22].

3.2. Analysis XRD

Figure 1 displays the XRD pattern of catalysts prepared in this study. All the peaks belonging to γ-Al₂O₃ at 2θ = 37.6°, 45.5° and 67.0° can be discriminated from the XRD pattern. Simultaneously, the new diffraction peak attributed to zeolite A appeared at 2θ = 24°, 27.2°, 30°; and 34.3° on Al-ZeoAo and Al-ZeoA33 catalysts as also reported by Milton and Buffalo [13]. The diffraction attributed to zeolite X peak appeared at 2θ = 23.3°, 26.7°, 31° and 33.6° on the XRD pattern of Al-ZeoXo and Al-ZeoX33 catalysts [14]. However, the peaks intensities of γ-Al₂O₃ were not significantly enhanced.

Figure 1 displays the XRD pattern of Al-ZeoA33 and Al-ZeoX33, giving higher zeolite ZeoA0 intensities as compared with ZeoA33, leading to better ZeoA0 crystallinity. Zeolite ZeoA33 prepared by mixing zeolite NaA powder with metakaolin and NaOH solution 33 %-wt. Kaolin was added as a binder to form crystalline powder of NaA, then NaOH solution was added [23]. According to XRD patterns displayed in Figure 1, the specific diffraction peaks of metakaolin at 2θ = 21° and 27° was not observed, suggesting metakaolin was completely converted into zeolite, however low intensities. The aforementioned result was demonstrated by ZeoX33 prepared through resembling method, resulting in lower intensity peaks than ZeoXo.

Degree of crystallinity was in accordance with crystallite size that generally correlates with MTD reaction catalytic activity [4, 7, 15]. The catalyst crystallite size was calculated using equation 1.

\[ B = \frac{K\lambda}{\beta \cos \theta} \]  

(1)

Akarmazyan et al. (2014) reported that reducing crystallite size can further enhance methanol adsorption site, thus increasing methanol conversion [15]. However, further reduction will give opposite results due to excessively small crystallite size will turn into inactive amorphous phase. Crystallite size of developed catalysts were displayed in Table 1. Al-ZeoA33 crystallite was observed bigger than Al-ZeoA0, and so does mixture of γ-Al₂O₃ and zeolite type X.
3.3. **Analysis ammonia temperature programmed desorption (NH3-TPD)**

The acid site concentration and strength were determined by ammonia temperature programmed desorption (Table 2). The total volume of ammonia desorbed, represented by the area in Table 2, equals the total acid site concentration. The temperature at which desorption takes place, relates to the strength of the acid site. The stronger the acid site, the stronger ammonia is bound and the higher the temperature that is required to desorb the ammonia from the acid site.

**Table 2.** Acid site concentration and acid strength distribution determined by ammonia temperature programmed desorption

|                  | Area (signal* time) | Peak NH$_3$ desorption temperature, °C |
|------------------|---------------------|---------------------------------------|
|                  | Peak 1 | Peak 2 | Peak 3 | weak | medium | strong     |
| $\gamma$-Al$_2$O$_3$ | 23.527 | 999.319 | 34.370  | 148.795 | 252.980 | 472.096   |
| Al-ZeoA0         | 3079.302 |         |         | 324.876 |         |           |
| Al-ZeoA33        | 1889.928 |         |         | 306.397 |         |           |
| Al-ZeoX0         | 1458.184 | 27.837  |         | 308.212 | 518.832 |           |
| Al-ZeoX33        | 559.140  |         |         | 259.638 |         |           |

Some researchers have reported that MTD reaction requires high concentration of acidic sites with weak or medium acid strength [2-8].

4. **Conclusion**

The textural properties and acidity of modified alumina catalyst over zeolite A and X has been investigated. Referring to N$_2$ adsorption/desorption isotherm by using the Brunauer-Emmerr-Teller (BET) equation, the catalysts were observed possessing specific surface area of 170–279 m$^2$ g$^{-1}$, pore volumes of 0.35-0.46 cm$^3$ g$^{-1}$, and mesoporous pore diameters of 5.6 – 8.8 nm. The crystallite size of
developed catalyst determined by X-ray diffraction technique was found to be in a range of 11.5-30.5 nm. Modifying alumina over zeolite A and X were not significantly enhancing the specific diffraction intensities with respect to XRD pattern. Self-developed gamma alumina catalyst expressed by the temperature of ammonia desorption possessed weak, medium and strong acid strength. Acid strength distribution of Al-ZeoA0, Al-ZeoA33 and Al-ZeoX33 catalysts was only at medium temperature of 259-325 °C. Al-ZeoXo catalyst possessed medium and strong acid strength; ammonia desorption was at temperature of 308.212 °C and 518.832 °C.

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