Characterization and Catalytic Activity of $\gamma$-Al$_2$O$_3$-ITB on Methanol Dehydration

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Abstract. National Plan on Energy of Indonesia 2017 states that dimethyl ether (DME, CH$_3$OCH$_3$) will be used as partial substitution of LPG for household fuel. Methanol dehydration using a solid catalyst is a common technology to produce DME. In this research, a catalyst $\gamma$-Al$_2$O$_3$ prepared in our laboratory has been characterized. This catalyst had a surface area of 194.4 m$^2$/g, a total pore volume of 0.55 mL/g, and an average pore diameter of 112.3 Å. This catalyst had medium and high acidity sites. Activity tests of this catalyst were carried out in a fixed bed reactor at temperatures of 240, 260 and 280°C. The gas flow rates were related to the gas hourly space velocity of 1500, 2142 and 3000 h$^{-1}$. Experimentally, the conversions of methanol were close to that of thermodynamic conversions, i.e about 90% depending on the reaction temperature. The outlet gas was found to contain H$_2$ up to 2% indicating that there were side reactions besides the dehydration of methanol to DME.

1. Introduction
DME synthesis can be carried out with two pathways, i.e. direct synthesis and indirect synthesis (two-stage synthesis). According to economics and thermodynamics limitations, direct synthesis is more interesting than indirect synthesis. The direct synthesis of DME involves two types of catalysts, i.e catalyst for methanol synthesis (Cu based) and catalyst for methanol dehydration catalyst (solid acid catalyst).

It is known that the reaction of methanol dehydration ($2\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$) is the limiting rate in DME production. Therefore, the catalyst for dehydration of methanol to DME must have good activity, high selective for DME and also be resistant to the presence of H$_2$O [1, 2].

Methanol dehydration catalysts include $\gamma$-Al$_2$O$_3$, modified of Al$_2$O$_3$ with silica, TiO$_2$-ZrO$_2$, clay, ion exchange resin, boehmite (AlOOH) and zeolites such as H-ZSM-5, HY, mordenite, SAPO, and ferrierite [3]. Our research has been dealt with the used $\gamma$-Al$_2$O$_3$ which originally prepared as support for various catalysts, such as dehydro-sulphurization of crude oil. This catalyst was prepared by the Laboratory of Chemical Reaction Engineering and Catalysis, ITB, so-called $\gamma$-Al$_2$O$_3$. The objective of this research was to investigate the characteristics and activity of this catalyst $\gamma$-Al$_2$O$_3$-ITB.
2. Methodology

2.1. Material and Experimental Equipment
Methanol for analysis EMSURE (CAS: 67-56-1) was used as a reactant and ultra-high purity (UHP) N₂ was used as a carrier gas. The catalyst γ-Al₂O₃-ITB was produced by the Chemical Reaction and Catalysis Engineering Laboratory-ITB. A fixed bed reactor was made of stainless steel with an ID of 2 cm (Figure 1). The reactor temperature was controlled by a temperature control panel. The condenser in the downstream of the reactor was used to condense methanol and water.

![Experimental setup](image)

**Figure 1.** Experimental setup

2.2. Experimental Procedure and Analysis
The surface characteristics of γ-Al₂O₃-ITB catalyst were analyzed using N₂ adsorption-desorption based on Brunauer-Emmett-Teller (BET) method. The pore characteristic was analyzed using the Barret-Joyner-Halenda method. The elemental composition of the catalyst was analyzed using XRD (X-ray fluorescence). The acidity classification of catalyst γ-Al₂O₃-ITB was analyzed using NH₃-TPD (ammonia temperature-programmed desorption).

Dehydration of methanol to DME was carried out in two steps: (a) purging using N₂, and (b) conversion of methanol to DME. Purging was carried out under N₂ with a flow rate of 100 mL/min (measured at 1 bar, 30°C). This step was intended to remove air or other gases from the inside of the reactor. Purging was carried out for one hour and a temperature of 240 - 260°C.

When a stable condition in the reactor had been achieved, methanol was injected into the reactor. The flow rate of N₂ was about 50 mL/min. The total flow rate (N₂ and methanol vapor) through the reactor was adjusted to get a GHSV (gas hourly space velocity) 1500-3000/h. The reaction was carried out for 7 hours. In the downstream of the reactor, the gas passed through the condenser to condensed out water (a reaction product, and un-reacted methanol). Gas samples were analyzed using Shimadzu GC 2014 having parallel separating column of Molecular Sieve and Porapak-Q. Composition of liquid product was analyzed using GC Shimadzu 14-B with Porapak-Q as separating column.
3. Result and Discussion

3.1. Characteristic of catalysts

The catalyst $\gamma$-Al$_2$O$_3$-ITB has a large surface area of 194.4 m$^2$/g and a pore diameter of 112.3 Å (the result of BET analysis is presented in Table 1). This pore surface area may be classified as large and hopefully could facilitate the dehydration reaction. XRF characterization showed that the main component of $\gamma$-Al$_2$O$_3$-ITB was Al$_2$O$_3$ with a concentration up to 99.3%. The presence of MgO on the catalyst could be expected to reduce the potential of formation of carbon deposits on the surface of the catalyst [4]. And the presence of TiO$_2$ was considered for regulating the acidity of the catalyst [5]. For comparison, the characteristics of two commercial catalysts for production of DME are presented also in Table 1. Having a pore surface area between the two commercials catalyst, the catalyst $\gamma$-Al$_2$O$_3$-ITB could be expected to have good catalytic activity.

| No | Characteristic       | $\gamma$-Al$_2$O$_3$-ITB | Commercial J-xx | Commercial K-xx |
|----|----------------------|--------------------------|-----------------|-----------------|
| 1  | Surface area (m$^2$/g) | 194.4                    | 128.3           | 370.9           |
| 2  | Pore volume (mL/g)   | 0.55                     | 0.72            | 0.24            |
| 3  | Pore diameter (Å)    | 112.3                    | 225.8           | 26.1            |
| 4  | Bulk density (kg/m$^3$) | 2030                    | 3300            | 2600            |

Composition (%-weight)

|   | Al$_2$O$_3$ | SO$_3$ | Na$_2$O | MgO | SiO$_2$ | Fe$_2$O$_3$ | TiO$_2$ | CuO |
|---|-------------|--------|---------|-----|---------|-------------|---------|-----|
| 5 | 99.35%      | 0.01%  | 0.03%   | 0.17%| 0.09%   | 0.01%       | 0.21%   | 0.04%|
| 6 | 97.36%      | 1.27%  | 0.47%   | 0.26%| 0.21%   | 0.03%       | 0.95%   |      |
| 7 | 94.51%      | 1.58%  | 0.23%   | 0.26%| 1.73%   | 0.95%       |         |      |

Figure 2. Pore size distribution using the BJH method
Based on the adsorption-desorption N\textsubscript{2} analysis using BJH method, the pore size of \(\gamma\text{-Al}_2\text{O}_3\)-ITB (\textit{Table 1, Figure 2}) might be classified as a mesopore (pore size in the range of 20-500 Å) [6]. This was also confirmed using an N\textsubscript{2} adsorption-desorption isotherm analysis (\textit{Figure 3}).

\begin{center}
\includegraphics[width=\textwidth]{figure3.png}
\end{center}

\textbf{Figure 3.} N\textsubscript{2} adsorption-desorption isotherm of \(\gamma\text{-Al}_2\text{O}_3\)-ITB

Based on the N\textsubscript{2} adsorption-desorption isotherm, the catalyst \(\gamma\text{-Al}_2\text{O}_3\)-ITB could also be classified as a type of V (\textit{Figure 3}). Adsorption on mesopore solids takes place through multi-layer adsorption, resulting in Type V desorption adsorption curves (\textit{Figure 3}). A catalyst having a Type V could be used for adsorption of water in Ordered Organic-Inorganic Nanocomposite (OOINs) with hydrophobic surfaces [6, 7]. This capability of \(\gamma\text{-Al}_2\text{O}_3\)-ITB might be used as a catalyst for methanol dehydration to DME.

\begin{center}
\includegraphics[width=\textwidth]{figure4.png}
\end{center}

\textbf{Figure 4.} TPD analysis of catalyst \(\gamma\text{-Al}_2\text{O}_3\)-ITB
The dehydration reaction of methanol to DME should take place with the help of a weak to medium acidity catalyst. This acidity might be contributed by Al$_2$O$_3$ component of the catalyst. Based on the results of acidity analysis using NH$_3$-TPD, the catalyst γ-Al$_2$O$_3$-ITB was found to have medium and strong acid sides (Figure 4). So, it might be inevitable that this catalyst caused a generation of various side products such as H$_2$, C$_2$-C$_4$, and other hydrocarbons. The possible side reactions in dehydration of methanol are reported in many research, such as [8-10].

### 3.2. Activity Test

This research is one part of comprehensive research on direct synthesis of dimethyl ether (DME) using dual bed catalyst conducted by the Chemical Engineering Department of Institut Teknologi Bandung. The catalyst that plays a role in this process was Cu-based catalyst for methanol synthesis and γ-Al$_2$O$_3$ catalyst for dehydration methanol to DME. Direct synthesis of DME operated at below 300°C because the Cu-based catalyst was easily deactivated at high temperature. Thus, the activity test of the catalyst of dehydration methanol was tested at below 300°C.

The activity test of the γ-Al$_2$O$_3$-ITB catalyst was carried out at atmospheric pressure, and temperature of 240, 260 and 280°C. The gas flow rate was adjusted to get a GHSV in the range of 1500 - 3000 h$^{-1}$. Dehydration at 240°C clearly gave conversions of methanol lower than those according to the thermodynamic equilibrium reaction (Figure 5). These were understandable since the reaction rates were relatively low, so the residence times were not sufficient to achieve the equilibrium conversion of methanol.

![Figure 5. Activity test of γ-Al$_2$O$_3$-ITB](image)

Using ASPEN software, simulations were conducted using R-Equil and compare to experiment (Table 2). The simulation was done with assumption that only one reaction occurs, namely dehydration of methanol to DME. The experiment shown although the methanol conversion was high and the H$_2$O production was high, but there was no DME detected in the product. The liquid composition was dominated by residual methanol and H$_2$O.
At temperatures of 260° and 300°C, some experimental conversions of methanol clearly higher than those of thermodynamic equilibrium. This might indicate that there were side reactions of methanol to H₂, C₂-C₄, and hydrocarbons. The formation of by-products had been confirmed using the measurement of H₂ content in the outlet gas leaving the reactor (Figure 6). H₂ concentration was as high as 2% at a reaction temperature of 240°C and GHSV of 1500 h⁻¹ (a relatively low gas flow rate). But surprisingly, the presence of H₂ in the outlet gas was significantly low in reaction temperature of 280°C.

The possibility of generation of side products was also checked based on thermodynamic using Aspen Plus process simulator. Possible all products of methanol decomposition were as follows: CH₃OCH₃ (DME), H₂O, CO, CO₂, H₂, C₂H₆ (ethane), C₂H₄ (ethene), and C₂H₂O₂ (methyl formate). The simulation results showed that the possibility of products generation is presented in Table 3.

At all temperatures of 240, 260 and 280°C, methanol and DME were not the stable compounds. Thermodynamically, conversion of methanol ended to H₂O, C₂H₆, and H₂ (Table 3, left columns). The gas composition in dry basis was presented in Table 2, right columns. Since the experimental H₂ content in the gas was about 2%, the formations of side products were not as much as that of thermodynamic prediction. Thus, the catalyst γ-Al₂O₃-ITB might already indicate its selectivity in directing the dehydration of methanol to DME rather than thermodynamic conversions. From this point, modifications of γ-Al₂O₃ still needed to improve its selectivity. Possible improvement is additions of Si and P to avoid the formation of hydrocarbon products, and the addition of Ti(SO₄)₂ to increase DME formation [11].

**Table 2.** Comparison simulation using Aspen R-Equil and Experiment

| No | Component | Simulation Aspen R-Equil | Experiment |
|----|-----------|--------------------------|------------|
| 1  | CH₃OH     | 12% 12% 14% 46% 33% 23% | 12% 12% 14% 46% 33% 23% |
| 2  | CH₃OCH₃   | 44% 44% 43% 0% 0% 0%     | 44% 44% 43% 0% 0% 0%     |
| 3  | H₂O       | 44% 44% 43% 54% 67% 77% | 44% 44% 43% 54% 67% 77% |
|    | X_CH3OH   | 89% 88% 87% 83% 88% 95% | 89% 88% 87% 83% 88% 95% |

**Figure 6.** Hydrogen concentration at the outlet of the reactor

![Graph showing hydrogen concentration over time](image-url)
Table 3. Distribution of product prediction using Aspen Plus using R-GIBBS

| Conversion of Methanol | Reaction Temperature (°C) | Reaction Temperature (°C) |
|-----------------------|---------------------------|---------------------------|
|                       | 240 | 260 | 280 | 240 | 260 | 280 |
| CH₃OH                 | 100.00% | 99.99% | 99.99% | 100.00% | 99.99% | 99.99% |
| CH₃OCH₃               | 0.00% | 0.00% | 0.01% | 0.00% | 0.00% | 0.00% |
| H₂O                   | 43.83% | 40.08% | 36.20% | 43.83% | 40.08% | 36.20% |
| CO                    | 0.04% | 0.08% | 0.17% | 0.07% | 0.14% | 0.27% |
| CO₂                   | 13.96% | 14.79% | 15.79% | 24.86% | 24.69% | 24.75% |
| C₂H₄                  | 0.21% | 0.51% | 0.12% | 0.37% | 0.84% | 0.18% |
| C₂H₂O₂                | 0.00% | 0.00% | 0.00% | 0.00% | 0.00% | 0.00% |
| C₂H₆                  | 28.89% | 27.43% | 26.00% | 51.44% | 45.78% | 40.76% |
| H₂                    | 13.07% | 17.11% | 21.71% | 23.27% | 28.55% | 34.04% |
| Sum                   | 100.00% | 100.00% | 100.00% | 100.00% | 100.00% | 100.00% |

This research was an initial study using γ-Al₂O₃-ITB as a catalyst for dehydration methanol to DME. The γ-Al₂O₃ catalyst was originally made with good characteristics as support of catalyst. The research proved that γ-Al₂O₃-ITB can be used as a solid acid catalyst with a category of high acidity catalyst. These characteristics of catalyst provide a final product was gas of short-chain hydrocarbons, aromatics, and also have a tendency for form of carbon deposits. Therefore, it is necessary to modify the γ-Al₂O₃-ITB catalyst to reduce its acidity to the weak and medium category with the desired final product being DME.

4. Conclusions

Characterization of catalyst γ-Al₂O₃ prepared in ITB indicated that this catalyst had properties in between two commercial catalysts obtained from a DME plant in Indonesia. The catalyst γ-Al₂O₃-ITB had good characteristics with surface area (194.4 m²/g), pore diameter (112.3 Å), and was classified as a material with the pore of the multilayer mesopore level. Unfortunately, the γ-Al₂O₃-ITB catalyst has medium and high acidity characteristics, is causes a side reaction to the formation of H₂ and various hydrocarbons. Therefore, this catalyst γ-Al₂O₃ was still needed to be modified to increase its selectivity for the conversion of methanol to DME. The treatment that can be given to the γ-Al₂O₃-ITB catalyst was modification with the addition of Si or P so that the acidity level of the catalyst decreased to low and moderate level. This acidity level was the ideal criteria which were needed for the process of dehydrating methanol to DME.

5. References

[1] Ng, K.L., D. Chadwick, and B.A. Toseland 1999 Kinetics and modelling of dimethyl ether synthesis from synthesis gas Chemical Engineering Science 54(15) p. 3587-3592.
[2] Ratamanalaya, P., L. Sunun, V. Terdthai, and R. Palghat A. 2011 Kinetics Study of Direct Dimethyl Ether Synthesis IChE International Conference 2011 (Hatyai, Thailand).
[3] Azizi, Z., M. Rezaeimanesh, T. Tohidian, and M.R. Rahimpour 2014 Dimethyl ether: A review of technologies and production challenges Chemical Engineering and Processing: Process Intensification 82 p. 150-172.
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