Activity Test of CuO/γ-Al₂O₃ as Catalyst of Methanol Dehydration to Dimethyl Ether at Atmospheric Pressure

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Abstract. Dimethyl ether (DME) is already used as a propellant and intermediate chemicals. Now, Indonesia will use DME as alternative energy for Liquid Petroleum Gas (LPG), as a result of the continued increase in LPG imports. In this study, DME was synthesized by dehydration of methanol process. The γ-Al₂O₃ and modified CuO/γ-Al₂O₃ ITB use as catalysts for the process. The objective of this research was to compare of catalytic activity of two catalysts at methanol dehydration to DME. The catalyst activity test was carried out in a tubular fixed-bed reactor (ID 1 cm and length 21 cm). Methanol dehydration was carried out at 1 bar, GHSV 1,100-2,200/h, methanol 1.9-4 mL/h, N₂ 10-30 mL/min (27.5°C and 0.93 bar). The downstream gas of the reactor was analyzed using gas chromatography and the condensate was analyzed using a refractometer. The γ-Al₂O₃-ITB catalyst gives the highest performance with 89.6% of methanol conversion, 6.6% of DME yield, and 16.6% of DME selectivity. Whereas CuO/γ-Al₂O₃ catalyst has a lower performance by 85.5% of methanol conversion, 1.4% of DME yield, and 3.7% of DME selectivity.

1. Introduction

Dimethyl Ether (DME) is environmentally friendly energy that is low in emissions of CO, NOX, SOX, and other harmful pollutants. DME can be produced from coal or biomass so that it is following the National Plan on Energy of Indonesia (RUEN 2017) and the National Energy Policy (KEN). The Synthesis of DME could be done by two methods, namely direct synthesis, and indirect synthesis. Direct synthesis of DME was conducted by the conversion of syngas (a mixture of H₂ and CO) using a bifunctional catalyst. Meanwhile, the indirect synthesis of DME was conducted by dehydration of methanol using an acid solid catalyst. The reaction of the dehydration of methanol to DME was as follows:

\[ 2\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \]  

(1)

Currently, DME was synthesized by dehydration of methanol using solid acid catalysts such as γ-Al₂O₃, modified Al₂O₃, and zeolites. Dehydration of methanol to DME using the γ-Al₂O₃ catalyst was carried out at a temperature of 150-340°C and a pressure of 1-10 bar (1, 2). The results have shown that the increase in temperature could reduce the yield of DME (an exothermic reaction).

The increase of synthesis temperature increased methanol conversion approaching equilibrium conversion, and an increase of the methanol flow rate causes decreased methanol conversion. Meanwhile, the pressure did not change the methanol conversion. The methanol conversion was 84% at a temperature of 290°C and a pressure of 1 bar (2). The HZSM-5 catalyst could be used in the
dehydration of methanol to DME, and the activity of this catalyst was 78% of methanol conversion and 100% of selectivity of DME at 190℃ (1). However, the HZSM-5 catalyst formed light hydrocarbons as a by-product of methanol dehydration.

Dehydration of methanol to DME also carried out by 3% CuO/γ-Al₂O₃, 2% Fe₂O₃/γ-Al₂O₃, and CuO-Fe₂O₃/γ-Al₂O₃ at temperatures of 250°C-290°C and pressure atmospheric. The highest methanol conversion was 70% by CuO-Fe₂O₃/γ-Al₂O₃ catalyst at a temperature of 290°C and 100% of DME selectivity (3). The objective of this research was to compare the activity of γ-Al₂O₃ and modified the γ-Al₂O₃ catalyst (CuO/γ-Al₂O₃) produced by the Chemical Reaction and Catalysis Engineering Laboratory-ITB.

2. Methodology
This research was carried out by two steps process: (1) Modified of γ-Al₂O₃ the catalyst used impregnation method, and (2) activity test of the catalyst before and after modified.

2.1. Modification of Catalyst
The γ-Al₂O₃ catalyst was modified with CuO using 0.1 M of Cu(NO₃)₂·3H₂O solution. The CuO/γ-Al₂O₃ catalyst with 3% weight of CuO was prepared by mixing 49 ml of 0.1 M Cu(NO₃)₂·3H₂O solution and 10 grams of γ-Al₂O₃ catalyst that produce by the Chemical Reaction and Catalysis Engineering Laboratory-ITB. Then stirred at 27.5 ℃ and atmosferic pressure for 4 hours. After the impregnation process, the catalyst was drying at a temperature of 80 ℃ for 10 hours and calcined at a temperature of 650℃ for 6 hours (Figure 1).

![Figure 1. Modification of γ-Al₂O₃ using the impregnation method.](image)

2.2. Activity Test.
The dehydration of methanol to DME was carried out in a fixed bed tubular reactor with a 15 mm of ID, 50 mm of bed height, and 2 grams of catalyst (Figure 2). In the first step, the reactor was purging using N₂ gas. The flow rate of N₂ gas was 100 mL/minute at 27.5℃ and 1 bar. At the same time, the reactor heated to an operating temperature of 260-300℃. The purging process was carried out for 1 hour.
The next step was the activity test of catalyst. The flow rate of N\textsubscript{2} gas was 10-30 mL/min at 27.5°C and 1 bar. Liquid methanol was injected into the reactor at 1.9-4 mL/h, before entering the reactor the methanol is heated to vapor phase. The methanol dehydration process was done at a temperature of 260-300 °C, a pressure of 1 bar, and Gas Hourly Space Velocity (GHSV) of 1,100-2,200/h.

A gas sample was taken downstream of the reactor at sampling point 2 every one hour and analyzed using Gas Chromatography. Meanwhile, the condensate sample (sampling point 1) was analyzed using a refractometer (Figure 2).

2.3. Evaluation of Data

The performance of the γ-Al\textsubscript{2}O\textsubscript{3} catalyst and 3% CuO/γ-Al\textsubscript{2}O\textsubscript{3} catalyst for the dehydration reaction of methanol to DME showed by the methanol conversion (X), the yield of DME (Y), and the DME selectivity (S) which can be calculated as follows.

\[
X_{\text{MeOH}} (%) = \frac{\text{Mole of upstream methanol} - \text{Mole of downstream methanol}}{\text{Mole of upstream methanol}} \times 100\%
\]

(2)

\[
Y_{\text{DME}} (%) = \frac{\text{mole of DME}}{\text{Mole of upstream methanol}} \times 100\%
\]

(3)

\[
S_{\text{DME}} (%) = \frac{\text{mole of DME}}{2(\text{Mole of upstream methanol} - \text{Mole of downstream methanol})} \times 100\%
\]

(4)

3. Results and Discussion

3.1. The comparison of catalyst activity

Methanol conversion on the γ-Al\textsubscript{2}O\textsubscript{3}-ITB catalyst was constant at 82% for 4 hours with GHSV 2,142/hour, and 80% of methanol conversion at GHSV 1,100/hour for 12 hours (Figure 3). While the highest activity of CuO/γ-Al\textsubscript{2}O\textsubscript{3} catalyst shown 90% of methanol conversion that exceeds the equilibrium conversion. The CuO/γ-Al\textsubscript{2}O\textsubscript{3} catalyst decreased its activity after 4 hours at a temperature of 280 °C, but at a temperature of 300 °C the results obtained were quite constant (Figure 4). The uneven CuO dispersion on the surface of γ-Al\textsubscript{2}O\textsubscript{3} during impregnation made the fluctuate of the catalyst activity.
Figure 3. Comparison of catalytic activity of the γ-Al₂O₃ catalyst and the CuO/γ-Al₂O₃ catalyst at a temperature of 280°C.

Water was produced during the process of methanol dehydration, which could make water and methanol to compete to adsorb on the catalyst surface (Xu et al., 1997). Cu metal can partially cover the active site of the γ-Al₂O₃ catalyst which decreased the acidity of the catalyst. The experiment of Armenta et al. (2018) shown 45% of methanol conversion using the CuO/γ-Al₂O₃ catalyst. But even so, the addition of CuO to the γ-Al₂O₃ ITB catalyst also showed an increase in the methanol conversion, such as 90% of the methanol conversion synthesis obtained at 3 hours experiment process.

Figure 4. Comparison of catalytic activity of the γ-Al₂O₃ catalyst and the CuO/γ-Al₂O₃ catalyst at a temperature of 300°C.

This shows that the addition of CuO given an effect on increasing the methanol conversion which was closer to the equilibrium conversion. These results were in line with the statement from Armenta et al. (2018) that the addition of CuO to a commercial γ-Al₂O₃ catalyst can increase methanol conversion.

3.2. DME Yield

The experiments that have been carried out using γ-Al₂O₃ ITB catalyst and CuO/γ-Al₂O₃ catalyst at the variation of GHSV at a temperature of 280°C and a pressure of 1 bar (Figure 5). The highest yield of DME was 6.6% at GHSV 2142/hour using the γ-Al₂O₃ ITB catalyst, and the lowest was around 0.2%.
Dehydration reaction using CuO/γ-Al₂O₃ catalyst was given a lower DME yield than γ-Al₂O₃. The highest DME yield was 3% at GHSV 1,200/hour which lasted for 8 hours, and the lowest was about 0.5%. This relatively low yield was thought to be due to side reactions such as the formation of H₂ and light hydrocarbons, and also because the addition of CuO masks the active site of the catalyst.

4. Conclusion
The effect of the addition of CuO increased the methanol conversion. The methanol conversion was 79% on the γ-Al₂O₃ ITB catalyst and increased to 86% on the CuO/γ-Al₂O₃ catalyst, under the same conditions at 300 °C and GHSV 1,200/hour. But the yield of DME that formed of the γ-Al₂O₃ ITB catalyst was better than the CuO/γ-Al₂O₃ catalyst. The yield of DME was 6.55% at 280°C and GHSV 1,100/ hour using the γ-Al₂O₃ catalyst. Whereas 1.4% of the yield of DME using the CuO/γ-Al₂O₃ catalyst at 280°C and GHSV 1200/hour. The low of the yield of DME was thought to be due to side reactions.

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