Dehydration of Methanol to Dimethyl Ether (DME): Performance of Three Types of Catalyst At Atmospheric Pressure

Aisyah Ardy [a], Herri Susanto [b], Rahmad Dennie Agustin Pohan, Jenny Rizkiana, and Melia Laniwati

Department of Chemical Engineering, Institut Teknologi Bandung, 40132 Bandung, Indonesia

corresponding authors: [a] aisyahardy@student.itb.ac.id
[b] herri@che.itb.ac.id

Abstract. A research on the production of dimethyl ether (DME) at lower pressure has been conducted in related to the national program on partial substitution of LPG with DME in the near future (*RUEN 2017*). DME may be liquefied at a pressure of about 6 atm (25°C), or a temperature of -25°C (1 bar). Burning of DME may produce a cleaner flue gas than LPG. Experiments on dehydration of methanol to produce DME were carried out at a atmospheric pressure (1 bar) and a temperature of 240°C. The experiment was conducted in a tubular reactor with a diameter of 20 mm. and three types of catalyst, i.e. γ-Al_2O_3 (from our laboratory), and two commercial catalysts namely catalyst A and catalyst B. The γ-Al_2O_3 catalyst had a surface area of 194.4 m^2/gram, an average pore diameter of 11.2 nm, and a total pore volume of 0.546 mL/gram. Methanol concentration in the influent of the reactor were 0.02 mol/L, 0.05 or 0.07 mol/L. It was found that γ-Al_2O_3 catalyst had a better activity than the two commercial catalysts. A stable conversion of methanol of 72% was obtained on γ-Al_2O_3 catalyst for on stream time of 6 to 10 hour. Kinetics of dehydration of methanol to DME on γ-Al_2O_3 catalyst could be represented as a first order reaction with an activation energy Ea of 256.6 kJ/mol and a frequency factor k_o of $8 \cdot 10^{+28}$.

INTRODUCTION

The increase in energy demand is not in balance with the national energy production. Currently more than 60%. of LPG demand in Indonesia is imported. A reduction of LPG import has been planned by the government through partial substitution of LPG with dimethyl ether (*General Plan of National Energy in Indonesia*, RUEN 2017). DME (dimethyl ether, CH_3OCH_3) has more less physical properties with LPG, particularly the boiling point or vapor pressure. Although the heating value of DME is about 70% of LPG, the burning characteristics of DME is more or less similar to LPG. Many experimental studies on the use of mixtures of DME and LPG for cooking stove have been done. A trial market has also been carried out in a part of Jakarta. Moreover, DME has a high cetane number of 55-60, so it may be a more environmentally friendly fuel for diesel engine.

At this moment, DME is used mostly for propellant, and produced using the catalytic dehydration of methanol. Similar to methanol, DME may directly be synthesized from synthesis gas, a mixture of H_2 and CO. Direct synthesis of DME actually passes two reaction steps: methanol synthesis and followed by methanol dehydration. Based on the kinetics studies, the direct synthesis of DME is dictated by the dehydration of methanol to DME [1, 2]. Thus, a development of catalysts for dehydration of methanol is very challenging to get a good selectivity to DME and resistant to the presence of H_2O.

Catalysts of methanol dehydration may be γ-Al_2O_3 and its modification with silica, and TiO_2-ZrO_2, also clay, ion exchange resin, H-ZSM5, HY, mordenite, SAPO, MCM, ferrierite, chabazite, and H-Beta [3]. Of those catalysts, γ-Al_2O_3 has been known as a catalyst with almost 100% selectivity to DME. Catalyst γ-Al_2O_3 prepared in our *Laboratory of Chemical Reaction Engineering and Catalysis, ITB* has been used in this study. This γ-Al_2O_3 has been prepared originally as a support of catalyst for various purposes, such as for catalyst of FT-fuel, catalyst of hydrotreating, catalyst of fluid catalytic cracking and other else. The catalytic performance of this catalyst was then compared to those of commercial catalysts from a DME plant in Indonesia. Results of this experimental study will be used to prepare a dual bed reactor composting of two catalysts for methanol synthesis and that for methanol dehydration. These results will also be used to prepare a bi-functional catalyst containing two active sites: Cu for methanol synthesis and Al_2O_3 for methanol dehydration.

MATERIAL AND METHODS

Materials

Methanol (Merck Co.) was used as feedstock. Ultra high purity of N_2 was used as inert gas for purging the reactor and also as an internal standard mixed with methanol. The methanol concentration in the influent of the dehydration reactor was in the range of 0.02 – 0.07 mol/L (30-76 %-vol, mixed with N_2). The catalysts for methanol dehydration were γ-Al_2O_3, catalyst A and catalyst B from a DME plant in Indonesia.

Methods

The experiments were conducted in a tubular reactor having a diameter of 20 mm, heated electrically to get a desired and controlled temperature. Catalyst charge in the reactor was about 2 g, giving a bed height of about 1.5 cm. The whole apparatus consisted of the tubular reactor, N_2 bottle and piping, a bubbling bottle to get a mixture methanol in N_2, gas sampling points and a bubble soap meter for flow measurement (Figure 1).

Firstly, purging was applied to remove gases from the reactor before the catalytic methanol dehydration. This purging was carried out using N_2 with a flow rate of 100 mL/min and the ambient temperature, for 1 hour. After purging, the catalytic methanol dehydration was then carried out to evaluate the performance of catalyst. The methanol dehydration was carried out at the atmospheric pressure and a temperature varied from 240°C-290°C. Reactor feed was a mixture of methanol vapor in N_2 obtained from bubbling of N_2 at a rate of 85 mL/min through methanol in a bubbling bottle. Reaction might be represented as follows:

$$2CH_3OH \rightleftarrows CH_3OCH_3 + H_2O \qquad \Delta H_{298} = -23.5 \text{ kJ/mol} \qquad (1)$$
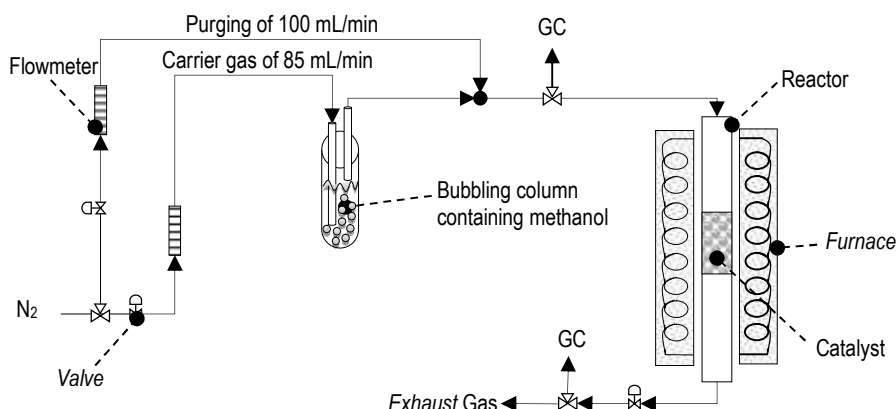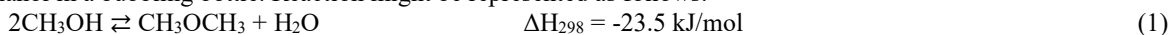

FIGURE 1. Equipment set up

Analysis of gas composition and conversion of methanol

Gas samples were taken at the inlet and at the outlet of the reactor. The concentration of MeOH was analyzed using a *Gas Chromatography 14-B Shimadzu*, having the following conditions: (i) Porapack Q for separating

column, (ii) TCD detector, (iii) injector temperature of 120°C, (iv) column temperature of 180°C, and (v) detector temperature of 200°C. Conversion of methanol was calculated based chromatogram using the following equation.

$$X_{MeOH} = \frac{\left(A_{MeOH} \big/ A_{N2} \right)_{in} - \left(A_{MeOH} \big/ A_{N2} \right)_{out}}{\left(A_{MeOH} \big/ A_{N2} \right)_{in}}$$
(2)

Where:
a. X_{MeOH} = conversion of methanol
b. A_{MeOH} = area of methanol in chromatogram.
c. A_{N2} = area of methanol in chromatogram
d.   subscripts *in* and *out*   = sampling points: at inlet or outlet of reactor.

RESULTS AND DISCUSSION

The performance test of γ-Al₂O₃ catalyst were carried out at atmospheric pressure and a temperature between 220° up to 290°C. Methanol concentrations in the feed were about 0.02 mol/L (30%-vol) and the gas velocity, GHSV was about 2,936 h⁻¹. Catalyst characterization indicated that γ-Al₂O₃ has a comparable surface area to the two commercial catalysts A and B, and also to that reported in a literature (Table 1). The conversion of methanol from the use of γ-Al₂O₃ may be higher than that from Catalyst A, and lower than that from Catalyst B.

TABLE 1. Pore properties of catalyst

| No | Characteristic | γ-Al₂O₃ | Commercial Catalyst | | γ-Al₂O₃ [4] |
			Catalyst A	Catalyst B	
1	Surface area (m²/g)	194.40	128.30	370.90	168.10
2	Pore Volume (mL/g)	0.55	0.72	0.24	0.50
3	Pore Diameter (Å)	112.30	225.80	26.10	116.50

Indeed, experimental results indicated that γ-Al₂O₃ catalyst had a better activity than Catalyst A and even than Catalyst B after the on stream time above 400 min (Figure 2). Between starting up until the on stream time of 400 min, catalyst γ-Al₂O₃ and Catalyst A seemed to undergo a activation period. The performance of catalyst B appeared the least one. This lowest performance of catalyst B was due probably its pore diameter of only 26.1 Å, while the concentration of methanol in the feet of 0.02 mol/L (30%-vol) was too high resulting a blockage in the pore and subsequently deactivation of catalyst.
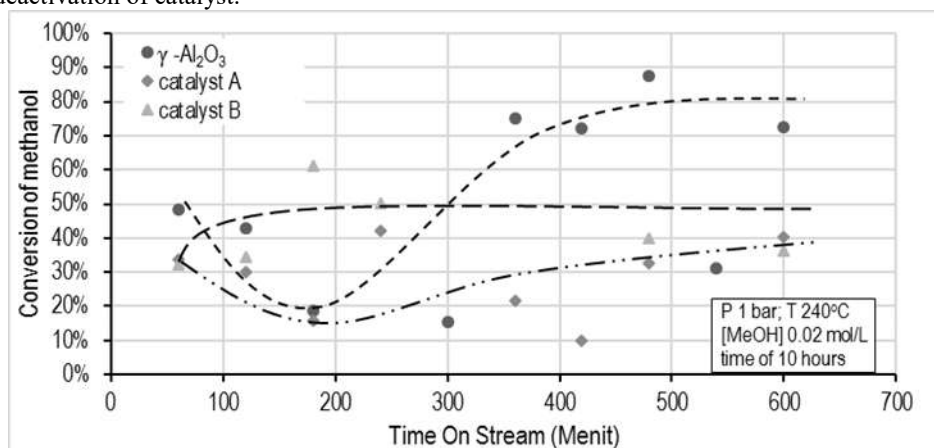

Figure 2. Comparison of activity of catalyst of dehydration of methanol

The conversion of methanol in γ-Al₂O₃ was stable at 72% after 400 min (± 6 hour) on stream time, while the conversions in Catalyst A and Catalyst B decreased after 4 hours. These might indicate that the catalysts had been deactivated due probably to the presence of H₂O as a by-product of methanol. In this case, methanol would compete with water in the adsorption on the pore surface [5, 6].

As γ-Al₂O₃ catalyst was better compared to the other two catalysts, tests on stability and resistance of γ-Al$_2$O$_3$ catalyst had been conducted for higher concentrations of methanol, i.e.: 30%, 66%, and 76% or 0.02, 0.05 and 0.07 mol/L respectively. The activity test of this catalyst was carried out at atmospheric pressure and temperature of 240°C. As understandable, a higher concentration of methanol in the inlet stream gave a higher conversion of methanol (Figure 3). This was understandable from the kinetic view point. It might also conclude that γ-Al$_2$O$_3$ catalyst could handle an inlet stream with higher concentrations.
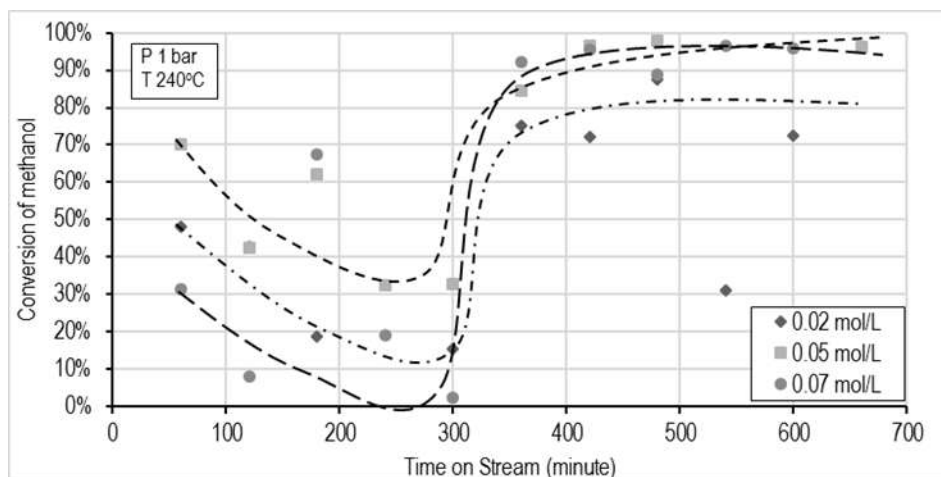

FIGURE 3. Catalytic activity of γ-Al$_2$O$_3$

As the methanol dehydration is an equilibrium reaction with slightly exothermic, an increase in reaction temperature would decrease in the conversion of methanol. Measured conversion of methanol decreased with an increase in reaction temperature (Figure 4). A conversion of methanol up to 70% was observed at a reaction temperature of 290°C. Of course, the reaction rate still depended on many factors, such as the pore properties of catalyst.
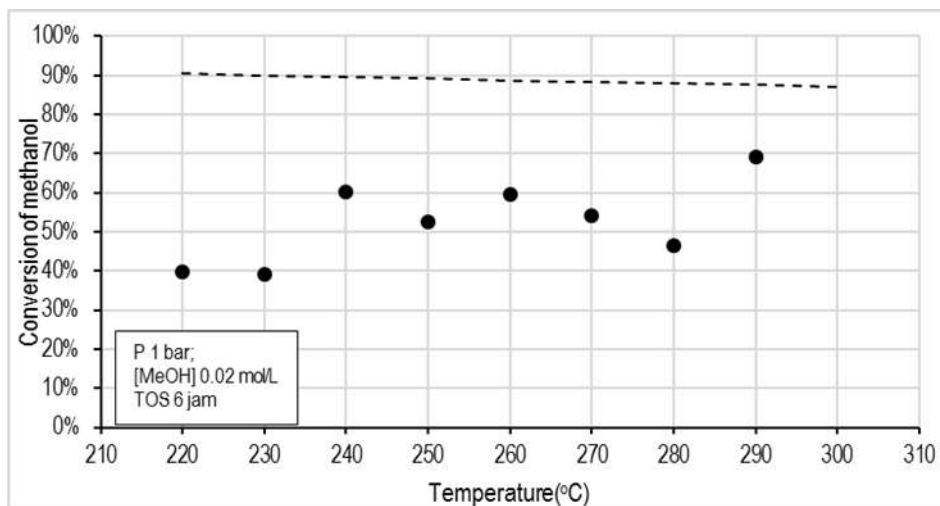

FIGURE 4. Catalytic activity of γ-Al$_2$O$_3$ at various of reaction temperature

With assumption of ideal gas in the reaction system in the methanol dehydration, the pressure has no effect on the reaction rate as represented in equation (1). Then, the equilibrium conversion of methanol dehydration as a function was clearly a weak function of temperature (Figure 4). Here, the measured conversion of methanol was clearly far below the equilibrium one. In other words, the dehydration of methanol to DME had a very slow reaction rate. Many other reactions might also take place to yield various by-products, based on equations (3) and (4).

$$2\ CH_3OH \quad \rightleftarrows CH_3OCH_3 + H_2O \tag{1}$$
$$CH_3OH \quad \rightleftarrows CO + 2\ H_2 \tag{3}$$
$$CO + H_2O \quad \rightleftarrows CO_2 + H_2 \tag{4}$$

As the equilibrium conversion of methanol was a weak function of temperature, an increase in reaction temperature might speed up to achieve the equilibrium conversion. Having experimental data on reaction rate (eq.5) [2] at various temperature, kinetic parameter of reaction from Arrhenius equation (6), could be calculated (Figure 5).

$$r_{MeOHdehydration} = k \cdot K_{MeOH}^2 \cdot \left[\frac{C_{MeOH}^2 - \left((C_{H2O} \cdot C_{DME})/K_{eqm} \right)}{\left(1 + 2\sqrt{K_{MeOH} \cdot C_{MeOH}} + K_{H2O} \cdot C_{H2O} \right)^4} \right] \tag{5}$$

$$k = k_o \cdot e^{\frac{-Ea}{R \cdot T}} \tag{6}$$

The kinetic parameters are: (i) activation energy, Ea of 256.6 kJ/mol and frequency factor, k_o of $8.0 \times 10^{+28}$. From the value of the activation energy, the dehydration of methanol over γ-Al_2O_3 might be classified as a reaction in mass transfer regime. Compare to literature data (Table 2), methanol dehydration reaction over our γ-Al_2O_3 needed a higher temperature to start, but then it was faster.
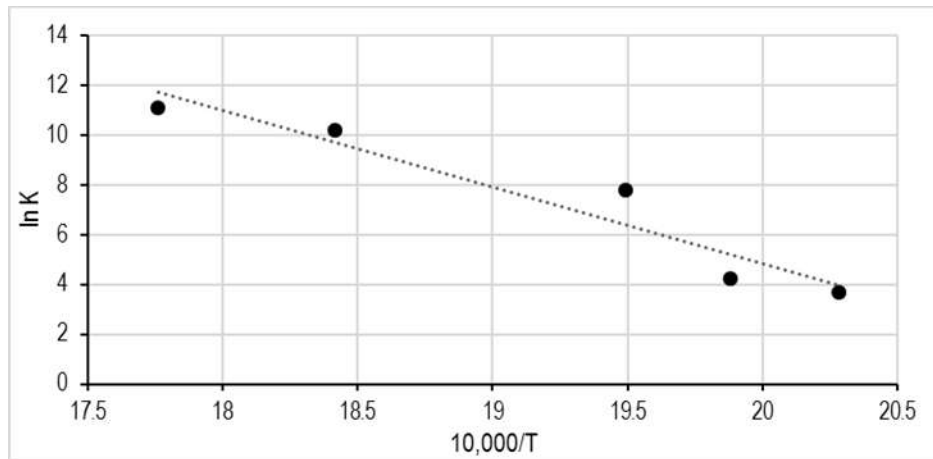

FIGURE 5 Kinetic data of methanol dehydration over γ-Al_2O_3 catalyst

TABLE 2. Parameter kinetic of dehydration of methanol

No	Parameter Kinetic	This Study	[1]	[2]	[7]	[8]	[5]	[9]	[10]
1	Ea, kJ/mol	256.6	69.8	105.0	136.7	125.2	105.0	69.2	62.4
2	k_o, mol/(kg$_{cat}$·s)	$8.0 \times 10^{+28}$	$1.7 \times 10^{+8}$	$3.7 \times 10^{+10}$					

CONCLUSIONS

A catalyst γ-Al_2O_3 prepared in our *Laboratory of Chemical Reaction Engineering and Catalysis* originally for support of catalyst had been tested satisfactorily for the dehydration of methanol to produce DME. This γ-Al_2O_3 showed a promising result based on the conversion of methanol point of view. The catalyst γ-Al_2O_3 had a comparable of pore properties, and gave a better conversion of methanol compared to the two commercial catalysts. Further tests on γ-Al_2O_3 catalyst were conducted with several reaction temperatures and methanol concentrations in the inlet stream of the reactor. The γ-Al_2O_3 catalyst gave a stable conversion of methanol of 72% in the period of 6 to 10 hour on stream time. The kinetic parameters of reaction for dehydration of methanol over γ-Al_2O_3 had been drawn from experiments at different temperature, the activation energy (Ea) 256.6 kJ/mol and frequency factor (k_o)

8.0x10^{+28} mol/(kg$_{cat}$·s). Results in this experiment on the performance of γ-Al$_2$O$_3$ for methanol dehydration would be used as a guide for preparation of a bi-functional catalyst for direct synthesis of DME from bio-syngas obtained from steam gasification of biomass.

ACKNOWLEDGMENTS

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