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Preparation of *Catalyst Cu-ZnO-MgO-Al₂O₃* for Direct Synthesis of DME

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Abstract. Direct synthesis of DME catalyst was prepared using the co-precipitation method. The catalyst contained CuO/ZnO/Al₂O₃ about 40/27/33 (%-wt). Two types of catalyst were prepared, i.e. CZMA0 (Mg 0%-wt) and CZMA20 (Mg 20%-wt). Both of catalysts were activated using reducing gas (5% H₂ and N₂). The activity test was conducted by syngas model which contained (%-mole) 65% H₂, 28% CO and 7% N₂. The reaction was carried out in a fixed bed reactor at 5 bar, and temperature of 240, 250 and 260°C. Synthesis shown CZMA20 catalyst gave the highest catalytic activity with 73% of CO conversion and 66% of H₂ conversion (5 bar and 260°C). Direct synthesis of DME was also carried out using a dual-catalyst, i.e. catalyst for methanol synthesis (M151, the commercial catalyst of methanol synthesis) and methanol dehydration (γ-Al₂O₃-ITB). The activity of dual catalyst shown 93% of CO conversion and 91% of H₂ conversion. This activity was more stable than two other catalysts (CZMA0 and CZMA20).

1. Introduction

In 2017, the Indonesian government has decided to use DME (dimethyl ether) as partial substitution of LPG. DME has been commercially made by dehydrating methanol, including DME plant in Indonesia. DME can be used as household fuel like LPG, propellant, the substitution of diesel and intermediate of chemicals. Application of DME has been a particular concern around the world. Large production capacity of DME will be needed in order to fulfill future demand [1].

DME is generally produced through two steps process. First, natural gas, hydrocarbons, coal, or biomass would be converted to syngas that contains H₂ and CO. Furthermore, syngas would be synthesized into DME. This two steps process can be expressed by the following reactions:

a. synthesis of methanol



b. dehydration of methanol to DME



c. water-gas shift reaction



The third reaction may influence the extent of the other two reactions. Many researchers are interested to develop the direct synthesis of DME. Direct synthesis of DME process can be expressed by the following reaction:



An important factor in direct synthesis of DME is the catalyst. Direct synthesis of DME (reaction 4) can be conducted by using Cu-based catalyst as reported in [1]. Unfortunately, this type of catalyst has low thermal stability, so development is being done to improve the catalyst resistance. Catalyst for direct



synthesis of DME is considered as a bifunctional catalyst: for methanol synthesis and dehydration of methanol. Metal components of bifunctional catalyst generally contain metal oxides such as CuO, ZnO, MgO, and Al₂O₃. Dehydration of methanol to DME was conducted by using solid-acid catalysts such as γ -Al₂O₃, modified silica alumina, TiO₂-ZrO₂, bohemite (AlOOH) and zeolites (H-ZSM-5, HY, mordenite, SAPO, MCM, ferrierite, chabazite, and H-beta).

There are many opportunities to develop Cu-based catalysts with various types of promoters and composition of catalysts to make a bifunctional catalyst of direct synthesis of DME. Addition 20%-wt of MgO has been proved the increases of activity of catalyst compared to those 0%-wt of MgO promoters, such as increases in CO conversion from 19% to 37%, and DME selectivity from 36% to 83% [1]. Therefore, Cu-ZnO-MgO-Al₂O₃ catalyst is interesting to be developed further.

The objective of this research was the preparation of Cu-ZnO-MgO-Al₂O₃ catalyst for the direct synthesis of DME. Activity catalyst was evaluated based on CO and H₂ conversions [1].

2. Experimental section

2.1 Catalyst preparation and characterization

The raw catalyst of CuO-ZnO-MgO-Al₂O₃ was prepared using the coprecipitation method [2]. At first, solutions of Cu(NO₃)₂, Zn(NO₃)₂, Al(NO₃)₃, Mg(NO₃)₂ were mixed with a certain ratio in order to obtain the target of catalyst composition (see Figure 1). The mixed solution of Cu, Zn, Mg, and Al would be precipitated by the solution of Na₂CO₃ simultaneously. Throughout the process temperature and pH were constant at 60°C and 7. The mixture was stirred at 700 rpm to get a homogeneous mixture and assist in the formation of the catalyst crystals. After aging, the catalyst will be wash with demineralized water and drying at 105°C. The raw catalyst that contains CuO, ZnO, MgO, and Al₂O₃ was calcinated and ready to used as a catalyst of direct synthesis of DME.

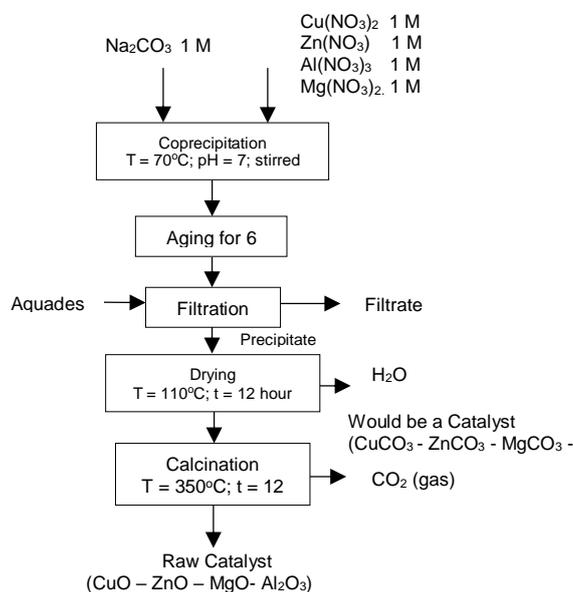


Figure 1. Preparation of catalyst by coprecipitation method

2.2 Activation of catalyst, or reduction of CuO catalyst to Cu

Pore property of raw catalyst was carried out using *Quantochrome Instruments Nova 300e*, in Laboratory of Analytical Instrument, Department of Chemical Engineering ITB. Activation of raw catalyst must be conducted to convert CuO to Cu in the same reactor before being used for the synthesis of DME. This reduction of CuO was done using 5% H₂ and N₂. The reduction process was carried out at 1.5 bar, and the temperature was increased step by step.

- Purging reactor using N_2 at 80 mL/min (measured at 27°C), 1.5 bar and 150°C for 2 hours.
- Gas reduction (5% H_2 and N_2) into the reactor at 80 mL/min, 1.5 bar and 150°C for 1 hour.
- Increasing reactor temperature up to 180°C, and hold for 1 h.
- Increasing reactor temperature up to 210°C, and hold for 1 h.
- Increasing reactor temperature up to 240°C, and hold for 1 h.
- Increasing reactor temperature up to 270°C, and hold for 3 h.

Started from the reactor temperature of 180°C, the progress of reduction from CuO to Cu was observed by measuring the consumption of H_2 . The activation process or reduction of CuO was stopped when the H_2 concentration in the reactor effluent was the same as influent. This process was very critical related to the catalyst activity in the synthesis process. The activation and activity test of catalyst was carried out in a fixed bed tubular reactor with 1.3 cm diameter and 38 cm length. This reactor was heated using an electric heater and provided with a temperature controller. Schematic diagram of activation and activity test of catalyst are presented in Figure 2.

2.3 Catalyst activity test of direct synthesis of DME process in a fixed bed reactor.

Without opening the reactor, the reactor temperature was decreased to the desired temperature of synthesis, which is: 240, 250, and 260°C. The gas reduction flow was changed with the syngas (65% H_2 , 28% CO and 7% N_2). Operating pressure 5 bar and temperature 240, 250, and 260°C. The flow rate of the syngas was 50 mL/min. In this study, the synthesis process was carried out for 10 hours.

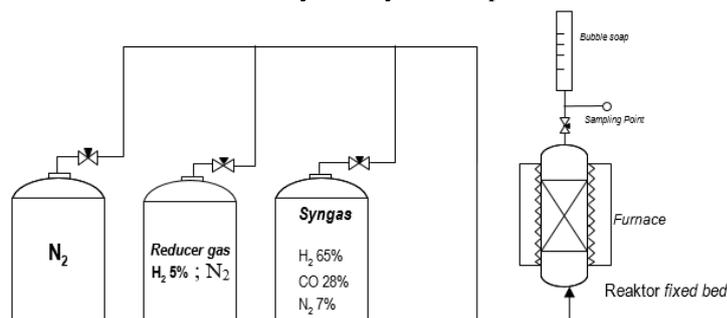


Figure 2. The experimental device of direct synthesis of DME process

The gas compositions were analyzed using two types of gas chromatography:

- Shimadzu GC-14B, with separation column of Porapak-Q: CH_3OH and CH_3OCH_3 analysis
- Shimadzu GC-2014, with separation column of Porapak-Q and Molsieve: H_2 , CO, CO_2 , and N_2 analysis

Inlet gas compositions were analyzed at the beginning of experiments on catalyst activation and activity test. Outlet gas compositions during activation of catalyst were analyzed every 15 min. This data was necessary to evaluate CuO reduction. During activity tests, outlet gas sample was taken every 15 or 30 min. The samples were analyzed for gaseous composition, methanol and DME compositions.

3. Result And Discussion

The scopes of this study were catalyst characterization, activation of raw catalyst, the effect of temperature and pressure on CO and H_2 conversion from CZMA0, CZMA20, and dual catalyst.

3.1 Catalyst Characterization

The surface area of catalyst was considered as the most important catalyst character. This pore surface area was measured on the raw catalyst (before activation or reduction of CuO). Catalyst CZMA0, Cu-ZnO- Al_2O_3 with 0%-wt MgO, had a surface area of 285 m^2/g . While catalyst CZMA20 with 20%-wt MgO had a surface area of 125 m^2/g . Decreasing the surface area of the catalyst occurs because of the

increase in Mg concentration in the catalyst. This will cause changes in activities of the catalyst but increase the selectivity of DME products.

3.2 Activation of Raw Catalyst

CZMA0 and CZMA20 catalyst had similar progress in CuO reduction that indicated of H₂ conversion (Figure 3). Based on the progress of H₂ conversion, H₂ consumption of activation of CZMA20 was clearly more than CZMA0, as indicated by a higher H₂ conversion for CZMA20. The activation process was done completely after 400 min.

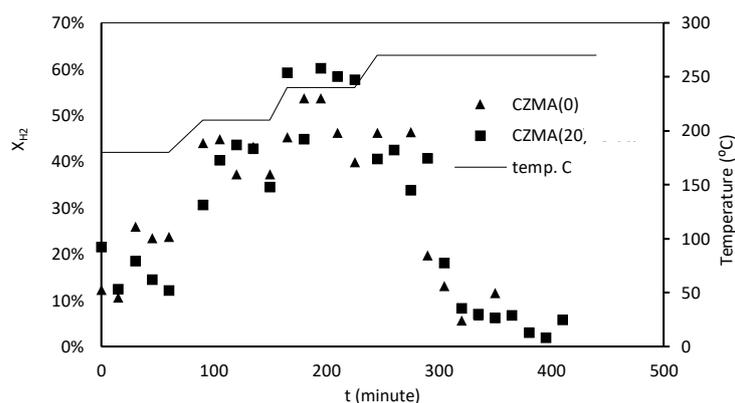


Figure 3. H₂ conversion during activation process

3.3 Effect of Temperature

The fresh catalyst was used in each condition in the activity tests. CO conversion of CZMA0 increased until 300 min, at three different reaction temperatures (Figure 4.a). The activity of CZMA0 indicate the active site of catalyst works well but after that decreased because of deactivation of the catalyst. For CZMA0 at 240°C, its activity decreased significantly after 200 min. The best activity of CZMA0 catalyst was shown 51% of CO conversion at 260°C and there was no indication of deactivation of the catalyst. Meanwhile, catalytic activity CZMA20 catalyst was lower than CZMA0. The activity of CZMA0 at 250°C was the best until 500 min, even it dropped drastically afterward. Thus, the quality of this catalyst was not homogeneous or the reproducibility in preparation of catalyst was not good. Discussion of this aspect was also applicable for catalyst CZMA20.

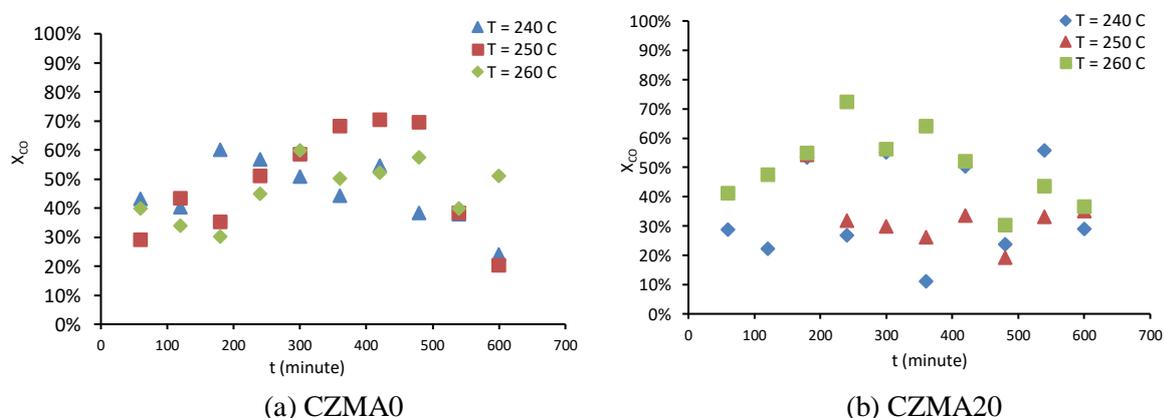


Figure 4. CO conversion in during activity test of direct synthesis of DME
P = 5 bar; Q = 50 mL/min

Despite data fluctuation as shown in Figure 4, CO conversions on this study (60%) were relatively higher than reported by Asthana et.al (35%), with a pressure of 30 bar [1]. According to the thermodynamic of reaction equilibrium (calculated using *Aspen*), CO conversion might be as high as 90% at those reaction temperatures. Thus, there was a large chance to improve the catalyst.

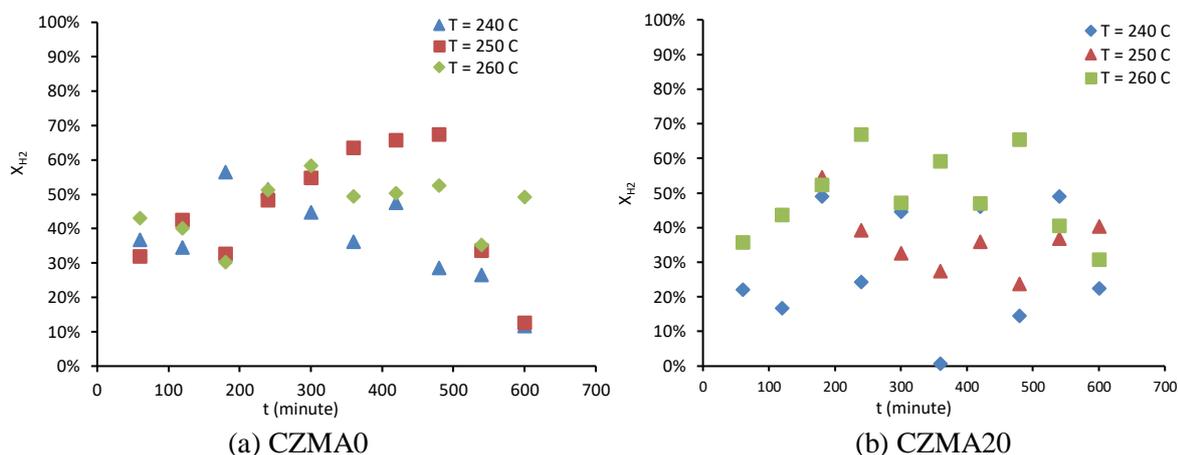
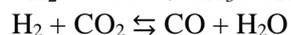


Figure 5. H₂ conversion in during activity test of catalyst
P = 5 bar; Q = 50 mL/min

Based on H₂ conversion (Figure 5), the stability of the catalyst was apparently very low. Progress in H₂ conversions was quite the same as CO conversion. The highest H₂ conversion was about 60%, but surprisingly it was higher than the thermodynamic equilibrium of 40% for direct synthesis of DME (equation 4). Probably, there were other reactions consuming H₂ beside direct synthesis of DME according to equation (4).



Reaction (5) was the overall reaction of methanol synthesis (equation 1), methanol dehydration (equation 2) and homogeneous water shift (equation 6). Reaction (6) might be possible if: (a) the catalyst activation step was not yet completed or (b) catalyst was exposed to air so there was re-oxidation of Cu to CuO.

A series of experiments using two bed of catalysts was done by a commercial catalyst of methanol synthesis (Topsøe M151) and a methanol dehydration catalyst ($\gamma\text{-Al}_2\text{O}_3$). The ratio of those catalysts was about 1:4 respectively. The reaction was carried at 240°C and 5 bar. As expected, CO and H₂ conversions were significantly higher than CZMA0 and CZMA20 catalysts. A more stable activity of the dual catalyst was also observed (Figure 6). Unfortunately, the experiments were not yet carried out for sufficiently long time.

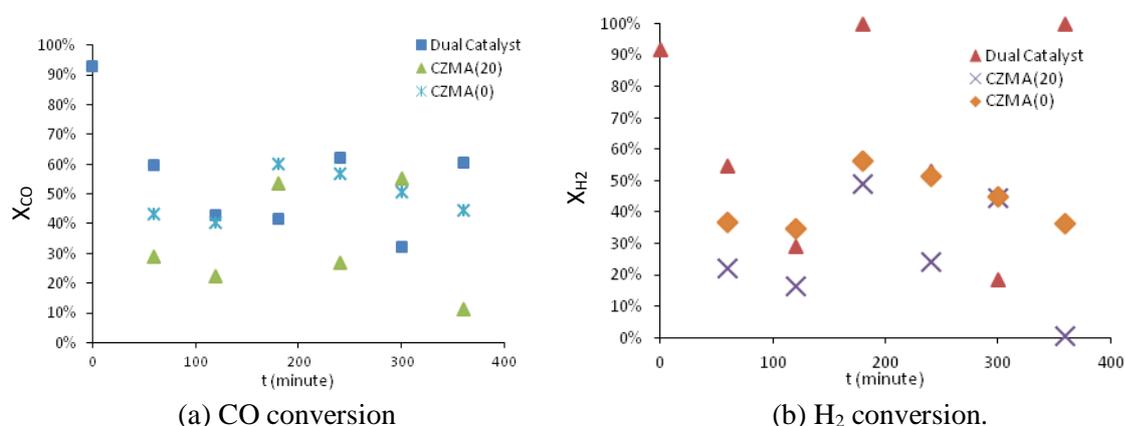


Figure 6. Comparison of the activity of CZMA(0) CZMA(20) and dual catalyst

3.4 Effect of Pressure

Based on equation (4), a higher pressure would give a higher conversion. Indeed, our experiments with a pressure of 7 bar resulted in higher CO conversion (Figure 7), as well as H₂ conversion. Surprisingly, the catalyst activity at a reaction pressure of 7 bar appeared more stable than that of 5 bar, for both CZMA0 and CZMA20. Furthermore, the activity of both catalysts also looked the same, based on CO conversion.

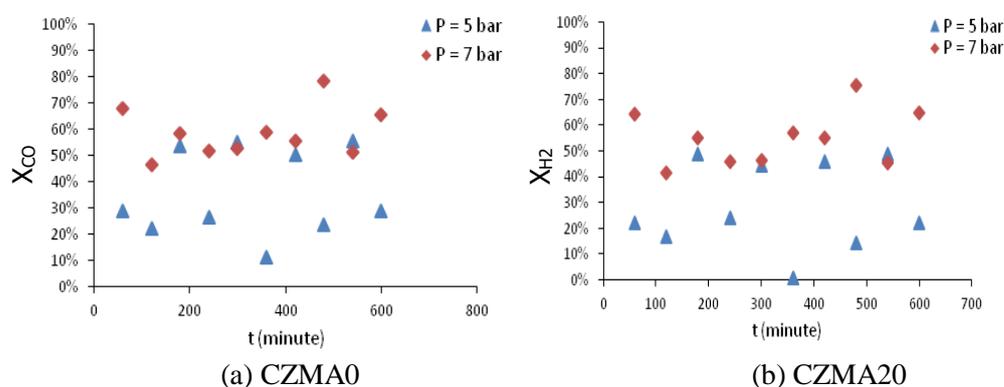


Figure 7. Effect of pressure on CO conversion $T = 240^{\circ}C$

Effect of pressure would be more significant on methanol synthesis (equation 1) than on methanol dehydration reaction (reaction 2). Thus, the formation of methanol would be more than that of DME. As a result, increased reaction pressure would give a higher concentration in the product. This phenomenon was reported by Prasad, et.al. [6]. So, in a dual catalyst system, the amount of catalyst for dehydration should be larger than the amount of catalyst for methanol synthesis.

3.5 Yield of DME

The yield of DME was defined as a molar fraction of inlet syngas (CO and H₂) converted into DME. Absolutely, the yield of DME was not good enough and still require a lot of improvement. In this study, the yield of DME was less than 0.01%. The yield of DME from the experiment using dual catalyst was also very low. The yields of methanol as an intermediate product of synthesis using CZMA0, CZMA20 and dual catalyst were also very low. It was suspected that the gas chromatography was not yet calibrated properly.

4. Conclusion

The catalyst for direct synthesis of DME has been prepared using the co-precipitation method several times successfully. CZMA0 without MgO had a good pore surface area of 285 m²/g, while that of CZMA20 with 20% MgO had relatively low pore surface area of 125 m²/g. CZMA20 consumed more H₂ and took a long time for activation. The advantage of adding MgO on the main catalyst Cu-ZnO-Al₂O₃ was not yet observed in this experimental study.

CO and H₂ conversions were found significantly high, even higher than those reported in the literature. But they were still below the thermodynamic equilibrium conversions of direct synthesis of DME. Effect of reaction pressure was also studied experimentally at 5 and 7 bar. At a higher reaction pressure, CO and H₂ conversion increased accordingly. At a higher reaction pressure of 7 bar, the activity of the catalyst was more constant during the activity test. Dual bed catalyst of direct synthesis of DME consisted catalyst for methanol synthesis and dehydration gave a slightly higher CO and H₂ conversions. This dual catalyst also gave a more stable activity of the catalyst.

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