Hybrid Catalyst Cu-Zno/Al_2O_3-HZSM-5 for Direct Synthesis Dimethyl Ether from CO and H_2 (Syngas)

P R Tyas[1], S D S Murti[1,*], S D Nanda[2]

[1]*Center of Technology for Energy Resources and Chemical Industry, Agency for Assessment and Application of Technology, Serpong, Tangerang Selatan, Banten, Indonesia*
[2]*Departement of Chemistry, Syarif Hidayatullah State Islamic University, Jakarta, Indonesia*
[*]*Corresponding author. Email: sd.sumbogo@bppt.go.id*

ABSTRACT
Dimethyl Ether (DME) is an alternatives energy that can be synthesized through a direct process from syngas (CO and H2) with utilizing Cu-ZnO/Al2O3-HZSM-5 as a hybrid catalyst. Direct synthesis DME technology is relatively new technology by utilizing syngas that can be derived from gasification of biomass and coal. The purpose of this study is to obtain the catalyst composition with the most optimal performance. Catalyst is prepared with co-precipitation method through variation ratio of the catalyst Cu-ZnO-Al2O3 that be mixed with HZSM-5. The component Cu-ZnO-Al2O3 catalysts were characterized using XRD, EDX, BET, and FE-SEM. Test of catalyst activity carried out with fixed bed reactor at temperature 260ºC and pressure 20 bar using ratio syngas (H2: CO = 2). The products of reaction were analyzed with GC-FID (Product DME) and GC TCD (CO conversion). From the result of catalyst characterization were identified that hybrid catalyst CZA A shown better characteristic compared other catalyst. In the catalyst activity testing, the highest yield was obtained for hybrid catalyst CZA A the value is 15.03%and CO conversion is 28.15%.

Keywords: *Hybrid Catalyst, Dimethyl Ether, Syngas, Optimization*

1. INTRODUCTION

Increasing technology and society activities will also increase energy demands in various sectors. One of them is the household sector where the total final energy consumption in 2014 was 106 million SBM (Equivalent Oil Barrel) with a contribution of electricity as much as 48%, followed by LPG for cooking by 47%. National LPG demands will increase with the presence of kerosene substitution program with LPG. The increase of LPG consumption is recorded have growth by 1.86% per year. LPG demands cannot be fulfilled from domestic production, where data in 2014 for LPG supply mostly (41%) is obtained from imports[1]. Increasing of energy demands significantly can impact the scarcity of LPG in the market so that imports of LPG are increasingly high. Therefore, to reduce dependence on fossil fuels and the amount of LPG imports, the government intends to use DME as an alternative of LPG.

Dimethyl ether (DME) is non-toxic gas, environmental friendly and has an economical price compared to LPG[2]. DME has the same properties as propane and butane (LPG forming compounds), so DME can be distributed using LPG handling technology[3]. Production of DME can be done through direct and indirect process. Direct DME synthesis process is more economical than the indirect process because it takes place in one reactor [4]. The most common raw material for DME production is syngas which consists of a mixture of mainly hydrogen and carbon monoxide. Syngas can be produced from the gasification process of biomass and / or coal, where biomass and / or coal is a potential energy source in Indonesia [5,6]. Therefore, the use of syngas from the gasification process of biomass and / or coal to produce DME is one of the effective pathways for the supply of alternative fuels.

Technology of direct synthesis DME from syngas is an interesting research topic and is still being developed. One focus of developing direct synthesis DME is to obtain the optimal type and composition of the catalyst. The catalyst is expected to have high activity and is not easily deactivated. The catalyst for direct synthesis DME must have a multiple function, which is as a catalyst for methanol synthesis (from syngas) and a methanol dehydration catalyst into DME. The commonly used methanol synthesis catalyst is Cu based catalyst as the active side. While the catalyst components for dehydration of methanol are acidic solids, which include γ-Alumina, zeolite, silica, and alumina. Cu-based catalysts have high activity for CO conversion in DME synthesis, but this catalyst is easy to deactivate because of sintering of the Cu active side on the surface of the catalyst[3,7].

Some research has studied the optimal catalyst composition for direct synthesis of DME from syngas. In 2012, Abu-dahrieh et al.[7]investigated the deactivation of Cu-ZnO-Al2O3 (CZA) catalysts with various acidic solid catalysts (γ- Al2O3, NH4ZSM-5, HZSM-5) and found that CZA-HZSM-5 catalysts had the best activity and stability for direct DME synthesis from syngas. Higher acidity levels on the HZSM-5 make it more active as a methanol dehydration catalyst. In 2006, Fei et al.[8]studied the effect of Cu in Cu-Mn-Zn / Zeolite-Y catalysts and found that increasing of Cu could increase catalyst activity for DME synthesis. Then in 2010, Hermansyah et al.[3]have studied several ratios of Cu: Zn with γ- Al2O3 as acidic solids and concluded that the optimal Zn amount can reduce sintering of Cu, if the Zn content is too slight the catalyst will deactivate faster.

Research to study the optimal catalyst composition needs to be further investigated. Therefore, in this study optimization of the catalyst ratio was carried out in order to obtain the optimal catalyst composition and reduce the sintering of the Cu active side (catalyst deactivation). The catalyst used in this study was Cu-ZnO/Al2O3 as a methanol synthesis catalyst mixed with HZSM-5 (Si / Al 25) as a methanol dehydration catalyst. The independent variable in this study is the variation of the ratio of Cu-ZnO / Al2O3 catalyst prepared bycoprecipitation method, molar ratio of catalyst is varied inCu:Zn:Al (4:3:1 (CZA A) ; 5:3:1(CZA B); dan 6:3:1 (CZA C)).

2. MATERIALS AND METHODS

2.1 Materials

The materials used in this study is CO UHP (Ultra High Purity), Hidrogen UHP, Nitrogen UHP, Argon UHP, compressed air, standard mixed gas (CO, H2, CO2, CH4), standard gas DME, methanol standard pa, HZSM-5(Si/Al25), Al(NO3)3.9H2O pa, Na2CO3, Cu(NO3)2.3H¬2O pa, Zn(NO3)2.6H2O pa, distilled water, aseton, and Na2CO3.

2.2 Preparation of Cu-ZnO/Al2O3-HZSM-5 catalyst

[(Cu(NO3)2, Zn(NO3)3, Al(NO3)3] solution for each ratio (6: 3: 1 (CZA A), 5: 3: 1 (CZA B), and 4 : 3: 1 (CZA C)) mixed into one solution and put in the burette (precursor solution) .100 mL of distilled water is prepared in a beaker glass and placed over a water bath. The precursor solution is dripped simultaneously with 1 M Na2CO3solution into 100 mL distilled water where the pH is kept neutral and the temperature is around 60 oC. The precipitate in the form of carbonate metal salt is left to stand for 30 minutes at 50 oC. Then filtering and washing with water up to pH 6. The precipitate is dried at 80 oC for 18 hours. hydroxy carbonate precursors (hydrotalcite crystals) calcined at 350 oC for 5 hours to produced oxide Cu-ZnO/Al2O3catalyst. HZSM-5 catalyst with Si / Al 25 ratio calcined at 550oC for 5 hours. Oxide Cu-ZnO/Al2O3catalyst on each type of catalyst (CZA A, B, and C) mixed with HZSM-5 at a ratio of 5: 3 (w / w).

2.3 Catalyst Activity Testing

The catalyst activated in the reactor with reduced at 270oC in atmospheric conditions using 10% hydrogen (10 mL hydrogen in 90 mL nitrogen) for 4 hours. The DME synthesis reaction is carried out using a continuous fixed tubular reactor. The reaction is carried out at a pressure of 20 bar and temperature of 260 °C. The flow rate of the reactant gas is controlled by the mass flow controller with the ratio of the syngas reactant H2: CO (30:15) mL/min. The reaction products are analyzed with GC-FID (DME products) and GC-TCD (CO conversion)

2.4 Catalyst Characterization

Characterization of the catalyst was carried out for Cu-ZnO/Al2O3(CZA) components. In the Cu-ZnO/Al2O3catalyst the characterization method was carried out including crystallinity with XRD, catalyst composition with EDX, surface area with BET, and visual conditions of the catalyst surface with FE-SEM

3. RESULTS AND DISCUSSION

3.1. Synthesis and characterization of Cu-ZnO/Al2O3- HZSM-5

Variation of the ratio of Cu-ZnO/Al2O3catalyst was made by co-precipitation method, the catalyst molar ratio was varied in the molar ratio as follows Cu:Zn:Al (4:3:1 (CZA A) ; 5:3:1(CZA B); and 6:3:1 (CZA C)). Cu-ZnO/Al2O3(CZA) catalyst which is characterized is a catalyst that has passed the calcination and reduction stages

3.2 Characterization of Cu-ZnO/Al2O3-HZSM-5 catalyst

3.2.1 XRD Analysis

Based on the results of XRD analysis in fig 1, it is known that the crystal components formed on each catalyst are Cu, ZnO, and CuO crystals, identification of each crystal is known by comparison with the standard diffractogram of each component. Cu crystalare on 2θ= 43° and 50° (JCPDS 04-0836), ZnO crystalon 2θ= 32°, 34°, 36°, 47°, and 56° (JCPDS 36-1451), while CuO crystal are on 2θ = 35.8°, 39°, 49°, and 62° (JCPDS 05-0661). One of the main crystal components in the catalyst is Cu crystals which are the active side of the catalyst. The diffractogram pattern of Cu components indicates that the CuO to Cu reduction process has succeeded. The ZnO crystal component acts as a promoter which functions to prevent sintering of the active side of Cu[3].

This template, modified in MS Word 2007 and saved as a “Word 97-2003 Document” for the PC, provides authors with most of the formatting specifications needed for preparing electronic versions of their papers. All standard paper components have been specified for three reasons: (1) ease of use when formatting individual papers, (2) automatic compliance to electronic requirements that facilitate the concurrent or later production of electronic products, and (3) conformity of style throughout a conference proceedings.

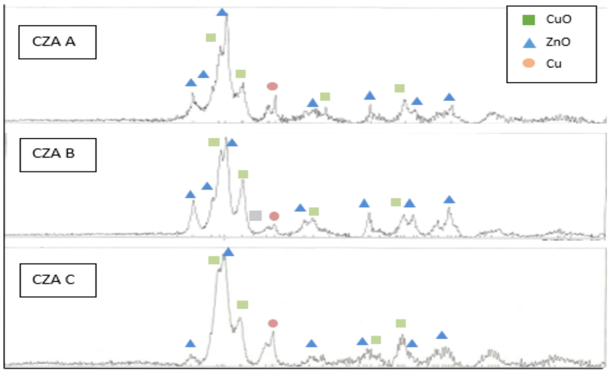

Figure 1 Difractionpattern of CZA A, B, danC catalyst

CuO crystals that observed from the diffractogram showed the presence of Cu oxide components that have not been optimally reduced to Cu active site. Besides from the reduction process, the presence of CuO crystals can also be caused by air oxidation factors, exposure of samples after the reduction process in the air can affect the oxidation of the Cu component to CuO.

3.2.2 FE-SEM Analysis

FE-SEM analysis showed the morphology of the catalyst surface. Based on the FE-SEM analysis of the CZA C catalyst shown in Figure 2, it is seen that there is a collection of ZnO clusters in the yellow circle, between Cu particles. In the picture, it can be seen also several of Cu sintering as shown by the red arrow. This sintering is probably caused by the low content of ZnO and Al2O3 on CZA C catalyst components, so that the border of Cu particles by ZnO spacers is not optimal. The presence of this sintering Cu has an impact on catalyst activity, sintering Cu can lead to deactivation of the catalyst because the active side of Cu is covered by other Cu components, thus limiting the contact of the active side of Cu with the reactant CO and H2[9].

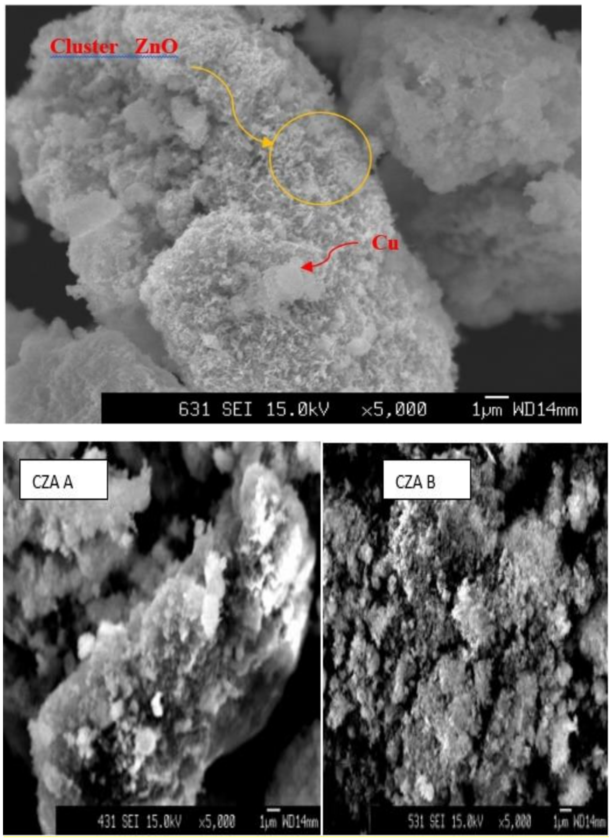

Figure 2 Surface Morphology of CZA A, B and C Catalyst

3.2.3 EDX and BET Analysis

EDX analysis aims to analyze the elements or chemical characteristics of the sample[10]. BET analysis is used to determine the surface area, pore volume and pore diameter of the catalyst based on physical adsorption of nitrogen or helium on the surface of the catalyst.

Table 1. EDX and BET results in the composition of catalyst components

Catalyst	Cu (%)	Zn (%)	Al (%)	SA$_{BET}$ (m^2/g)	Vp (cm^3/g)
CZA A	57.27	41.03	1.57	76.88	0.3165
CZA B	62.22	35.98	1.8	60.53	0.2242
CZA C	66.86	32.44	0.70	53.64	0.1868

From the results of EDX analysis a ratio of the composition of Cu: Zn: Al end of catalyst from CZA A is 57: 42: 1.6% wt, CZA B is 62: 36: 1.8% wt, and CZA C is 67: 32: 0.7% wt. The composition of the ratio between Cu and Zn must be conditioned on certain comparisons so that performance of active site Cu becomes optimal[11].CZA C catalyst has the lowest content of ZnO and Al2O3 even though the Cu content is the highest compared to other catalysts. This factor can affect sintering of CZA C as shown in FE-SEM results in Figure 2. The low ZnO and Al2O3 content can reduce the surface area of the catalyst so that the side dispersion Cu is not evenly distributed.

Based on the results of the BET analysis in Table 1, it is known that the highest area (SABET) is shown by CZA A catalyst followed by CZA B catalyst, and the lowest CZA C catalyst. The surface area of the active side has an impact on the activity of the catalyst where the higher surface area of the catalys then distribution of active site in catalyst more evenly therefore contact with the feed will be increase[2].

3.3 Catalyst Activity Testing

The catalytic activity test was carried out using a continuous tubular fixed-bed reactor. The catalysts were used in this activity testing is catalyst hybrid CZA which already activated (Cu-ZnO/Al2O3-HZSM-5) A, B and C. According to another study, the most optimal yield for the synthesis of DME with Cu-ZnO/Al2O3-HZSM-5 hybrid catalyst is at temperature of 260 °C[2] at pressure 20 bar. Ratio of H2/CO = 2:1 has a fairly good equilibrium value.

3.3.1 Effect of Catalyst Activity on CO Conversion

CO conversion shows the amount of CO from a feed that has been converted into a product[12].According to another study, CO conversion is influenced by the activity of components Cu-ZnO/Al2O3 catalyst in the CZA hybrid catalyst[3]. To increase CO conversion, it is necessary to optimize the composition of Cu-ZnO/Al2O3 catalyst in a hybrid catalyst.In this study the optimization of the catalyst composition was carried out with variations in the amount of Cu from Cu-ZnO/Al2O3 catalyst components with each ratio is CZA A (57:42:1.6 %wt), CZA B (62:36:1.8 %wt), andCZA C (67:32:0.7 %wt).

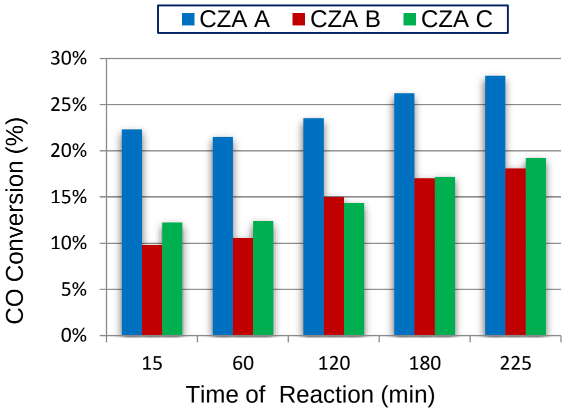

Figure 3 Graph the effect of catalyst activity on CO conversion

The highest CO conversion is produced by the hybrid catalyst CZA A at 225 minutes of reaction with a conversion value of 28.15%. the highest conversion of CZA C hybrid catalyst at 225 minutes with a conversion value of 19.23%, while the hybrid catalyst CZA B the highest conversion is 18.11% at 225 minutes.

The CZA A hybrid catalyst has the highest conversion which indicates that the catalyst has the most optimal Cu active side. CO conversion is influenced by the activity of active components Cu which play a role in the reactant adsorption (CO and H2) to be able to bond to each other to form methanol[13]. The optimal of Cu active side is due to the better dispersion of the active side at catalyst support. This can be shown from the results of the catalyst characterization test for CZA A, as an example is the high surface area (SABET) on CZA A catalysts as shown in Table 1.

Based on Figure 3, there is a trend for CO conversion to increase throughout the reaction time, this indicates that the catalyst activity is still increasing up to the 225 minutes of reaction. The increasing of CO conversion can be caused by in situ reduction factor of Cu active side. Where during the reaction process there is a flow of reactant gas H2 and CO, H2 besides play a role as a reactant is also a reducing gas. During the reaction H2 in reactants will play a role in reducing the remaining CuO so that the amount of active Cu will increase. With the increase of Cu active side, the interaction between reactants (CO and H2) will be more optimal therefore the conversion value becomes higher[9].

3.3.2 Effect of catalyst activity on yield DME

DME yield indicates the amount of DME produced in reaction to the entire product and reactant (which has not been converted) [12].

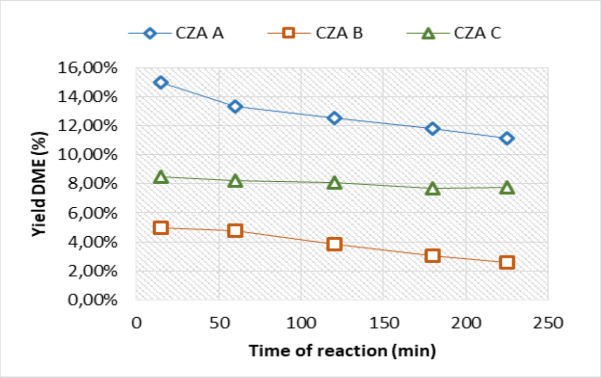

Figure 4 Graph the effect of catalyst activity on yield DME

In Figure 4, it is known that the highest yield is obtained on the CZA A hybrid catalyst with a reaction time of 15 minutes which yield value is15.03%. The highest CZA C yield hybrid catalyst was obtained in the 15 minutesof reaction with a value of 8.47%. While the highest hybrid CZA B yield catalyst was obtained in the 15 minutes of reaction with a value of 4.99%. Hybrid CZA A catalyst has the highest yield throughout the reaction time compared to other catalysts. Thehybrid catalyst CZA A has the highest yield of DME,this is influenced by the high conversion of CO and selectivity of DME compared to other products. The higher CO conversion and selectivity, will give the higher product yield, which will affect the high of DME yield.

4. CONCLUSION

Based on the results of the research, the catalyst activity testing and characterization for hybrid catalysts CZA A, B, and C,can be concluded that the catalyst with the most optimal ratio was CZA A hybrid catalyst with a ratio of Cu:Zn:Al of 57: 42: 1.6% wt. The ratio has good catalyst characteristics where after the catalyst activity testing CZA A showed the highest activity with the highest DME yield value is15.03% and CO conversion is 28.15%.

REFERENCES

[1] BPPT. 2016. Outlook Energi Indonesia : Pengembangan Energi untuk Mendukung Industri Hijau. ISBN 978-602-74702-0-0. Pusat Teknologi Sumberdaya Energi dan Industri Kimia (PTSEIK). BPPT

[2] Supramono, D., Priadi, H. 2014. Produksi Dimethyl-Ether Secara Langsung dari Gas Sintesis Menggunakan Katalis Cu-ZnO-Al2O3-ZSM-5. Departemen Teknik Kimia Fakultas Teknik. UI

[3] Hermansyah, H., Slamet., Fauziah, R., Siti., Restu,K., Wita. 2010. Sintesis Dimetil Eter Menggunakan Katalis Cu-Zn/γ-Al2O3 dalam Reaktor Fixed Bed.Seminar Rekayasa Kimia dan Proses ISSN : 1411-4216. Departemen Teknik Kimia Fakultas Teknik. UI

[4] Mao, D.S., Yang W M, Xia J C, Zhang B, Song Q Y, and Chen Q L. 2005.Highly effective hybrid catalyst for the direct synthesis of dimethyl ether from syngas with magnesium oxide-modified HZSM-5 as a dehydration component. Journal of Catalysis. 230: 140–149

[5] Iswanto, T., Rifa’i, M., Rahmawati, Y., Susianto. 2015. Desain Pabrik Synthetic Gas (Syngas) dari Gasifikasi Batu Bara Kualitas Rendah sebagai Pasokan Gas PT. Pupuk Sriwidjaja. Jurnal Teknik ITS. 4(2), ISSN: 2337-3539

[6] Yulistiani, F. 2009. Kajian Tekno Ekonomi Pabrik Konversi Biomassa Menjadi Bahan Bakar Fischer-Tropsch Melalui Proses Gasifikasi. Program studi Teknik Kimia. ITB

[7] Abudahrieh, J., Rooney, D., Goguet, A., Saih, Y. 2012.Activity and deactivation studies for direct dimethyl ether synthesis using CuO-ZnO-Al2O3 with (NH4)ZSM-5, HZSM-5 or γ-Al2O3. Chemical Engineering Journal. 203: 201-211

[8] J.-H. Fei, X.-J. Tang, Z-Y. Huo, H. Lou, X-M. Zheng. 2006. Effect of copper content on Cu-Mn-Zn/Zeolite-Y catalysts for synthesis of dimethyl ether from syngas. Catalysis communications7(11): 827-831

[9] Fichtl, B Mathias., Schlereth, David., David Schlereth, Nikolas Jacobsen, Igor Kasatkin,Julia Schumann, Malte Behrens, Robert Schlogl, Olaf Hinrichsen.2015. Kinetics of Deactivation on Cu/Zn/Al2O3 methanol synthesis catalysts.Journal Applied Catalysis A : General. 502:262-270

[10] Nugroho, Yusuf., Bayuseno. 2012. Analisis Kegagalan Las dan Rekomendasi Standard Operating Procedure (SOP) Pada Pengelasan Pipa Kondensor Pt. Siemens Indonesia. Thesis. Departemen Teknik Mesin. UNDIP

[11] Cai, M. Palčić, A. V. Subramanian, S. Moldovan, O.Ersen, V. Valtchev, V.V Ordomsky. 2015. Direct Dimethyl Ether from Syngas on Copper-Zeolite Hybrid Catalysts with a Wide Range of

Zeolite Particle Size. Journal of catalysis. 338: 227-238.

[12] Erena, J., Garoňa, R., Arandes, J.M., Aguayo, A.T., Bilbao, J. 2005. Effect of Operating conditions on the Synthesis of Dimethyl Ether over a CuO-ZnO-Al2O3/NaHZSM-5 bifunctionalCatalyst. Catalysis Today. 107–108: 467–473

[13] J.H. Flores, D.P.B. Peixoto, L.G. Appel, R.R. de Avillez, M.I.P. da Silva. 2011. The influence of different methanolsynthesis catalysts on direct synthesis of DME fromsyngas.Catalyst Today 172: 218–225.