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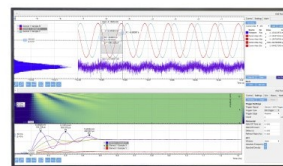
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Methanol Production from Biomass Syngas using Cu/ZnO/Al₂O₃ Catalyst

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Abstract. Synthesis gas, also known as syngas, produced from biomass materials has been identified as a potential source of renewable energy. Syngas mainly consists of CO and H₂, which can be as raw materials for methanol synthesis using a catalyst in a fixed bed reactor. In recent times, methanol production has been significantly augmented in energy and chemical industries as it is an essential molecule for chemical synthesis and other utilities such as clean transportation fuel. The assessment of methanol production for low cost, low temperature, and low pressure was conducted by a catalyst that has been developed. The role of the catalyst is the key to achieve optimal conditions through lower activation energy. The focus of this work has the performance test of Cu/ZnO/Al₂O₃ Catalyst to methanol production from syngas. First, the catalyst was prepared by the co-precipitation and impregnation method. The as-synthesized catalyst was then characterized using XRD, XRF, SEM-EDX, and BET. The result of XRD showed the catalyst has the same component (Al, Cu, Zn) with different crystallite diameter of CuO. The result of the SEM showed catalyst was collected on one site, but still in a relatively good distribution. From the BET surface area analyzer, the catalyst synthesized through the impregnation method (113.62 m²/g) has a bigger surface area than the co-precipitation method (43.26 m²/g) and commercial catalyst (64.75 m²/g). The catalytic activity of Cu/ZnO/Al₂O₃ catalysts in methanol production from syngas was preliminarily tested and compared with that commercial one. The result showed that hence the catalytic activity of Cu/ZnO/Al₂O₃ catalysts through co-precipitation and impregnation method was still inferior (0.96 % and 1.25 % yield methanol) compared to commercial one (1.26 % yield methanol), they were potential to be used as a catalyst in the methanol production from syngas.

INTRODUCTION

Methanol is a very valuable chemical with a variety of uses, either as a fuel or as a building block for the synthesis of other chemicals. Methanol is produced at 30–40 million tons per year around the world from CO/CO₂/H₂ [1]. Syngas mainly consists of CO and H₂. The syngas of biomass gasification is an intermediate product that can be converted further to various types of alternative fuels especially methanol. Due to its extensive and great demand, it is expected to develop a methanol synthesis catalyst and process with higher efficiency.

Methanol production on the industrial scale started in 1923. ZnO-Cr₂O₃ catalyst developed by BASF needed harsh reaction conditions (300 to 400 °C, 15–20 MPa). Methanol is primarily produced from carbon monoxide, carbon dioxide, and hydrogen via the commercial catalytic process, which was first developed by ICI Co. Ltd in 1966 [2]. The introduction of copper-containing catalyst (copper-zinc-based oxide), which was developed by ICI

Co. Ltd, moderated the reaction conditions, but still including high temperature and high pressure (250–300 °C, 10 MPa) for the commercial ICI high-temperature methanol synthesis.

The ideal method is to produce methanol at low energy by using a high-performance catalyst, which must be highly active, selective for methanol production, and stable for long periods during continuous operation. To reduce energy costs, a more active and effective catalyst is required. In order to increase the catalyst activity and selectivity of catalyst, the catalyst preparation methods have been developed for methanol production from biomass syngas. The particle size, surface area, metallic surface area and composition of the crucial factors for achieving higher catalytic activity [3]. Various catalysts have been used in methanol synthesis, with studies often focusing on Cu/ZnO/ γ -Al₂O₃.

Generally, the co-precipitation method is often used to prepare the Cu/ZnO catalyst with different bases. However, the Cu/ZnO oxides prepared by the co-precipitation method is unstable and easily cause the sintering of Cu at high temperature, resulting in the low dispersion degree of Cu in the catalyst. Recently, the impregnation method has been developed to prepare the Cu/ZnO catalyst [4-7].

Agency for the Assessment and application of Technology (BBPT)-Indonesia in cooperation with Gunma University-Japan has been conducting assessment and application of environmentally friendly solid biomass wastes utilization technology under the SATREPS (Science and Technology Research Partnership for Sustainable Development) program to develop a catalyst for methanol synthesis from biomass syngas. The focus of this work has developed a low-cost catalyst for methanol synthesis. The catalyst of methanol synthesis was prepared by the impregnation method of Cu and Zn with Gamma alumina as a supported catalyst and also compared with the co-precipitation method.

MATERIALS AND METHODS

Materials

The material used is Copper (II) nitrate trihydrate Cu(NO₃)₂·3H₂O, Zinc nitrate Zn(NO₃)₂·6H₂O, and Al(NO₃)₃, γ -Al₂O₃, Na₂CO₃. The instruments in this research are fixed bed reactor for methanol synthesis, glassware, sampling bag, Shidmazu 8A Gas Chromatograph.

Catalyst Preparation

Cu/ZnO/ γ -Al₂O₃ catalysts were prepared by the co-precipitation and impregnation method. Co-precipitation method, a solution of metal nitrates [Cu(NO₃)₂, Zn(NO₃)₂, Al(NO₃)₃] and a solution of Na₂CO₃ as a precipitant were added simultaneously into a stirred and heated demineralized water. During the precipitation process, pH, temperature, and aging time were controlled. The precipitates aged for 30 minutes at 50°C then filtered and washed subsequently. After dried overnight at temperature 80°C, the hydroxy carbonate precursor was calcined at 350°C for 5 hours at a rate of 5°C/min.

The impregnation method, the preparation of the impregnan solution with the stable Cu-Zn active phase was characterized by no precipitate formation. Stability test could be done for 1 to 2 hours after the solution reached stability, impregnan solution with Cu-Zn phased could be used to soak Al₂O₃ support. γ -Al₂O₃ support was impregnated by catalysts active phase with the immersion method and allowed to stand for 1 hour. Samples were dried at 120 °C for 8 hours and calcined at a temperature of 360 °C for 2 hours.

TABLE 1. Composition of Catalyst

Catalyst Code	Composition (% wt)			Method
	Cu	Zn	γ -Al ₂ O ₃	
Cu/ZnO/ γ -Al ₂ O ₃	42.5	47.5	10	Co-precipitation
Cu/ZnO/ γ -Al ₂ O ₃	15	5	80	Impregnation

Methanol Synthesis

The catalytic was inserted in a continuous tubular fixed-bed reactor (Fig. 1.). The stability was tested at operating condition was adjusted at pressure 14 bar and temperature 220°C. A total of 1-2 gr catalyst was filled in the tubular reactor. Prior to the reaction step, the catalyst was reduced with H₂ flow at the operating temperature. The operating conditions were adjusted to a pressure of 14 bar and a temperature of 220-260 ° C. Gases was analyzed using GC Shimadzu 8A Generated methanol in order to prevent liquefaction of the catalyst, the piping after the catalyst layer Maintained at 150 °C. GC separation columns are Sieve 13X, SINCARBON ST was used for TCD.

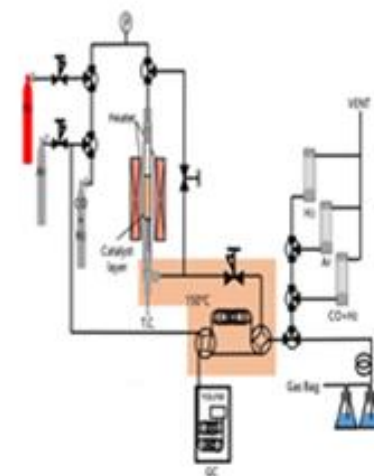


FIGURE 1. Experimental set up for methanol synthesis

Catalyst Characterization

The material composition of the catalyst is XRF analysis (EDX-7000 Shimadzu). Crystal structure is XRD analysis (Rint2100 Rigaku V = 32kV, I = 20mA). FE-SEM was used for surface observation. Also, BET specific surface area and total pore volume by BET specific surface area measurement was revealed.

RESULT AND DISCUSSION

Catalyst Preparation

As well known, Cu-ZnO-Al₂O₃ catalysts have been widely applied in MeOH synthesis from syngas [8-9]. In Cu-ZnO-based catalysts, ZnO is regarded to provide active sites for hydrogen spillover, or as structure-directing support controlling the dispersion of metallic copper particles [10–11]. The synergetic interactions of Cu and ZnO can improve the hydrogenation of syngas containing H₂, CO and a small amount of CO₂. Other researchers have discovered that Cu-based catalysts supported on ZnO-Al₂O₃ mixed oxides exhibit high catalytic activity for MeOH synthesis from syngas.

Cu/ZnO/ γ -Al₂O₃ catalysts were prepared by the co-precipitation and impregnation method. Cu-nitrate and Zn-nitrate were raw materials that would be attached on / γ -Al₂O₃ the support for Cu and ZnO. Zn acts as a promotor to prevent the sintering of Cu. Cu would be oxidized on the catalyst and written as Cu[Zn]. Afterward, the CuO molecular would be in the form of the CuO/ZnO phase. Its reduction will be affected by ZnO. After catalyst preparation, the catalyst was characterization by XRF, XRD, SEM and BET surface area analyzer. XRF analysis of commercial catalyst and Cu/ZnO/ γ -Al₂O₃ catalyst shows in Fig. 2.

Figure 2 shows that the compositions of catalysts are different from theoretical ones. From XRF result, co-precipitation Cu/ZnO/ γ -Al₂O₃ catalyst has composition of Cu : Zn : Al : O are 50.372:17.43:2.818:29.37(%wt), and

commercial catalyst has composition of Cu: Zn: Al are 56.03: 10.711: 2.929: 30.321 (%wt) and impregnation Cu/ZnO/ γ -Al₂O₃ catalyst has composition of Cu: Zn: Al: O are 32.773 :1.8: 13.809: 51.618 (%wt).

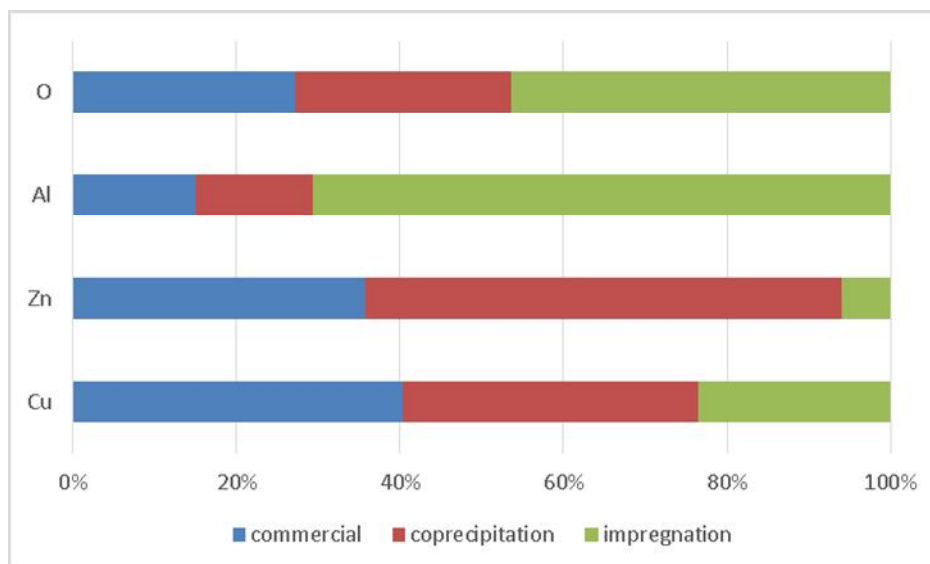


FIGURE 2. XRF Characterization of Catalyst

CuO crystals calculated from XRD results using the Scherrer equation. The diameter of the commercial catalyst shows in Table 2.

TABLE 2. Results of XRD Analysis

Catalyst Code	Crystallite diameter (nm)		
	CuO	ZnO	Al ₂ O ₃
Commercial	17.91	18.45	20.57
Co-precipitation	43.89	33.86	33.64
Impregnation.	35.92	0	31.87

Table 2 shows that the highest CuO crystallite diameter is co-precipitation. Although the coprecipitation Cu/ZnO/ γ -Al₂O₃ catalyst has a higher CuO content, the CuO crystallite size was small.

SEM characterization of catalyst shows in Fig. 3. SEM images can give detailed information on the structure of materials and the shape of individual particles. Commercial catalysts and co-precipitation and impregnation of Cu/ZnO/ γ -Al₂O₃ catalyst consisted of irregular particles in much larger and diverse agglomerates. Figure 3 shows both of catalyst was collected on one site, but still in the relatively good distribution.

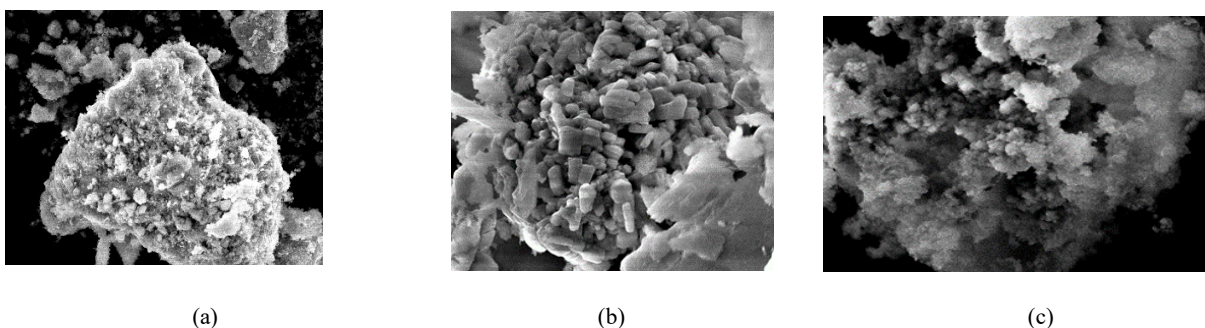


FIGURE 3. SEM Characterization; (a) Commercial catalyst, (b) co-precipitation (c) impregnation of Cu/ZnO/ γ -Al₂O₃

TABLE 3. Result of Surface Area Analyzer (BET)

Catalyst Code	Specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Mean pore radius (nm)	Method
Commercial	64.75	0.1672	1.66	
Cu/ZnO/ γ -Al ₂ O ₃	43.26	0.1674	12.2	Co-precipitation
Cu/ZnO/ γ -Al ₂ O ₃	113.62	0.1588	2.78	Impregnation method

The surface area of the catalyst prepared by co-precipitation and impregnation is 43.26 m²/g and 113.62 m²/g, and the commercial catalyst has surface area is 64.75 m²/g. The surface area of the catalyst prepared by impregnation higher than commercial catalyst and co-precipitation catalyst. This behavior can be explained by the pore-blockage of the support after the reaction.

Methanol Synthesis

It is important to note here that methanol synthesis from syn-gas is an exothermic reaction, a single stoichiometric reaction of methanol synthesis is shown in equation 1) which is an exothermic reaction.



Based on the reaction, to obtain 1 mole CH₃OH requires 1 mole of CO and 2 moles of H₂. The catalytic activity was tested 3 of catalysts, commercial catalysts and Cu/Zn/ γ -Al₂O₃, Cu-based catalyst was developed by GUNMA-BPPT (co-precipitation and impregnation). A total of 1-2 gr catalyst was filled in the fixed bed reactor. Prior to the reaction step, the catalyst was reduced with hydrogen flow at operating temperature. The operating conditions were adjusted to a pressure of 14 bar and a temperature of 220-260 °C The result of this performance test can be seen in Table 4.

TABLE 4. Yield Methanol of various condition towards the methanol products

Temperature (°C)	Yield Methanol (%wt)		
	Commercial	Co-precipitation	Impregnation method
230	1.26	0.2	0.24
240	0.34	0.44	0.32
250	0.6	0.96	0.6
260	0.27	0.79	1.25

Based on Table 4, the best methanol conversion from syngas is a commercial catalyst at an operation condition of 230 °C. The impregnation of Cu/ZnO/ γ -Al₂O₃ catalyst has higher methanol conversion than the co-precipitation catalyst because the impregnation catalyst has a higher surface area than the co-precipitation catalyst.

CONCLUSION

The best methanol conversion from syngas is a commercial catalyst at the operation condition of 230 °C. The impregnation of Cu/ZnO/ γ -Al₂O₃ catalyst has higher methanol conversion than co-precipitation catalyst

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