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Preparation of Cu/ZnO catalyst using a polyol method for alcohol-assisted low temperature methanol synthesis from syngas

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Abstract−A polyol method was used to prepare Cu/ZnO catalysts for alcohol-assisted low temperature methanol synthesis from syngas. Unlike conventional low temperature methanol synthesis, ethanol was employed both as a solvent and a reaction intermediate. Catalyst characterization revealed that Cu/ZnO catalysts were successfully and efficiently prepared using the polyol method. Various preparation conditions such as PVP concentration and identity of ZnO precursor strongly influenced the catalytic activity of Cu/ZnO catalysts. Copper dispersion and catalyst morphology played key roles in determining the catalytic performance of the Cu/ZnO catalyst in alcohol-assisted low temperature methanol synthesis. A high copper dispersion and platelike Cu/ZnO structure led to high catalytic activity. Among the catalysts tested, 5_Cu/ZnO_Zn(Ac)$_2$ had the best catalytic performance due to its high copper dispersion.

Keywords: Polyol Method, Copper Dispersion, Methanol Synthesis, Alcohol-assisted, Low Temperature

INTRODUCTION

Zinc oxide-supported copper (Cu/ZnO) catalysts are used for methanol production from synthesis gas [1,2]. Cu/ZnO has also been widely investigated as a catalyst for various other reactions such as ethanol dehydrogenation and the water-gas shift reaction [3-6]. Cu/ZnO catalysts are generally prepared through a conventional co-precipitation method. However, advanced methods, including sol-gel, polyol, and modified co-precipitation, have also been used to prepare Cu/ZnO catalysts to improving its catalytic properties [7-13]. Of the advanced preparation methods, the polyol method is a particularly effective and easy way to synthesize nano-size metallic powders with uniform size and shape [14-16].

In recent years, the polyol method has been studied by many researchers [17-20]. This research has revealed that crystallite size and shape can be controlled by varying reduction temperature, pH, and nucleation-protective agent concentration [17,18]. Moreover, metal nano-particles can be obtained in large quantities with the polyol method. For supported metal catalysts, highly monodispersed nano-sized metallic particles are formed [19,20]. To our knowledge, however, no one has attempted to prepare Cu/ZnO catalyst for methanol production using a polyol method.

In a typical polyol method, polyol chemicals (ethylene glycol, diethylene, glycerol, and tetraethylene glycol) act as both a reaction medium and reducing agent. In the polyol process, the metal precursor is reduced through a redox reaction between the metal precursors and the polyol chemicals. Therefore, reaction temperature is important for successful formation of the designed material, because the oxidation potential of polyol chemicals decreases with increasing reaction temperature [17,21-23]. Nucleation-protective chemicals such as polyvinylpyrrolidone (PVP) are occasionally employed to prevent sintering and agglomeration of metal particles [23,24]. These factors indicate that various preparation conditions strongly affect the activity of catalysts prepared through a polyol method.

The catalytic industrial process (ICI process) from syngas, which comprises hydrogen, carbon dioxide, and carbon monoxide, is a well-known commercial process for methanol production, which is a platform chemical for manufacturing various important chemicals such as dimethyl ether, formaldehyde, and acetic acid. However, this catalytic process has severe thermodynamic limitations, leading to a low one-pass conversion [1-3,25]. Thus, the cost of producing methanol is high due to low syngas conversion. Although two low temperature methanol synthesis (LTMS) processes have been proposed by Brookhaven National Laboratory (BNL) and the Christiansen group to overcome the problems of the commercial methanol production process [26-31], both LTMS processes have demonstrated serious catalyst deactivation. The catalyst deactivation was attributed to the trace amounts of carbon dioxide and water in the syngas, leading to additional separation of the feedstock. Accordingly, commercialization of the LTMS processes proposed by BNL and the Christiansen group has been limited [30,31].

Alcohol-assisted low temperature methanol synthesis has attracted much attention as an alternative method to produce methanol. In particular, alcohol is used as both a solvent and a reaction intermediate, and accordingly, the catalyst deactivation can be avoided. This is because carbon dioxide and water are used as reaction intermediates in the reported reaction pathway for alcohol-assisted low temperature methanol synthesis. In addition, this catalytic reaction requires low temperature (150-170 °C) and pressure (30-50 bar).

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Therefore, developing an efficient catalyst for this reaction is key to commercializing the process for the production of methanol [32-34].

In this study, we prepared an efficient zinc oxide-supported copper (Cu/ZnO) catalyst for alcohol-assisted low temperature methanol synthesis using a polyol method. The prepared catalysts were characterized through XRD, ICP-AES, SEM, and TEM analyses, and the activity of prepared catalysts was examined with a batch-type reactor. The effects of various preparation conditions, such as H_2 treatment, PVP concentration, and metal precursor in the polyol process, on catalytic activity were investigated. The optimal conditions to prepare a Cu/ZnO catalyst through a polyol method were established.

EXPERIMENTAL

Cu/ZnO catalysts were prepared by using a polyol method with various preparation conditions, as briefly presented in Fig. 1. Copper acetate ($Cu(CH_3COO)_2$, Wako Pure Chemical) was used as the copper precursor along with various zinc oxide precursors, including ZnO_synthesized, ZnO_commercial (Wako Pure Chemical), and zinc acetate ($Zn(CH_3COO)_2$, Wako Pure Chemical). ZnO_synthesized was prepared through the calcination of zinc nitrate ($Zn(NO_3)_2\cdot 6H_2O$, Wako Pure Chemical) at 500 °C under an air stream. The molar ratio of Cu/Zn in all Cu/ZnO catalysts was fixed at 1. The detailed procedure for preparing Cu/ZnO catalysts was as follows. Known amounts of copper acetate and zinc oxide precursor were added to ethylene glycol, which was used as both a solvent and a reducing agent. Polyvinylpyrrolidone (PVP, M_w=10,000, Sigma-Aldrich) was sequentially added to the ethylene glycol solution to finely disperse metal precursors. The resulting solution was thoroughly mixed at room temperature for 5 h under vigorous stirring. Reduction by ethylene glycol was at 198 °C for 3 h under refluxing conditions, and the resulting mixture was cooled to room temperature. The mixture was filtered and washed with ethanol. After the sample was dried at 80 °C, it was treated at 350 °C for 2 h in a hydrogen stream to remove any remaining organic compounds on the catalyst surface. The prepared catalysts were denoted as X_Cu/ZnO_Y, where X and Y represent the weight ratio of PVP/Cu and zinc oxide precursor, respectively.

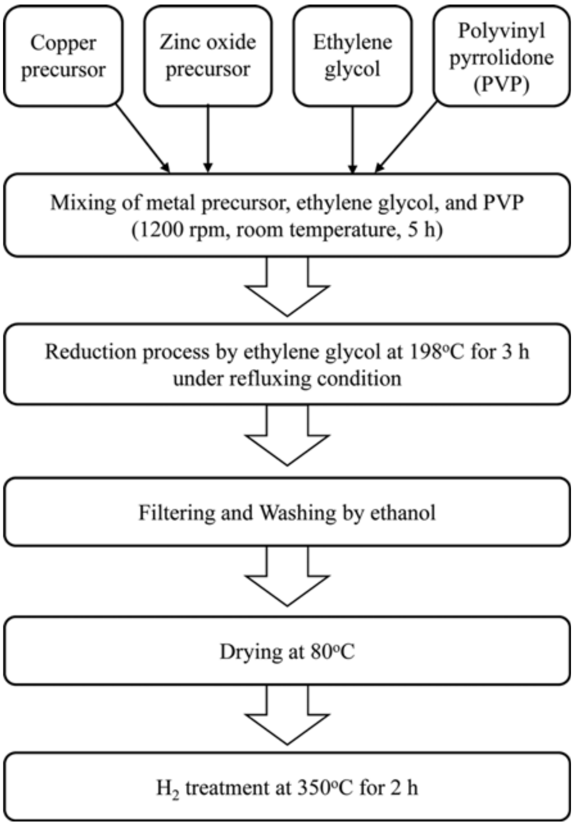

Fig. 1. Schematic diagram of the preparation of Cu/ZnO catalysts using a polyol method.

Crystalline phase of Cu/ZnO catalysts prepared through a polyol method was investigated using XRD measurements (X'pert-pro, PANalytical) with Cu-Kα radiation (λ=1.54056 Å) at 40 kV and 40 mA. The observed phase was identified by its characteristic diffraction peaks using JCPDS. ICP-AES analysis (Prodigy, Teledyne Leeman Labs) was also conducted to confirm the chemical composition of the Cu/ZnO catalysts. Surface morphology of the Cu/ZnO catalysts was examined by SEM analysis (JSM-6700F, JEOL). Copper dispersion and particle size in the catalysts were determined by TEM analysis (JEM-2100F, JEOL).

Alcohol-assisted low temperature methanol synthesis from syngas was carried out over Cu/ZnO catalysts in a stainless steel autoclave reactor (180 ml). The catalytic reaction was performed at 150 °C and 50 bar for 20 h. The gas reactant composition was fixed at CO : CO_2 : H_2=30 : 5 : 65, and 3 g of catalyst and 50 ml of ethanol were placed in the autoclave reactor at room temperature. Prior to the reaction, the reactor was sufficiently purged with carbon dioxide. After the reactor was pressurized to 36 bar with feed gas, it was heated to 150 °C. The reactor pressure finally reached 50 bar as the temperature increased, and the reaction was started under vigorous stirring. After the reaction, the reactor was cooled to room temperature, and the liquid products were analyzed with a gas chromatograph (YL-6500, Yonglin) equipped with a flame ionization detector (FID). To quantify the liquid products, 2-propanol was employed as an internal standard.

RESULTS AND DISCUSSION

Previous reports have indicated that the prepared sample should be treated with hydrogen gas in the polyol process [17] to remove any remaining organic compounds on the sample surface. To confirm the effect of hydrogen treatment, the catalytic activities of 3_Cu/ZnO_commercial before and after hydrogen treatment at 350 °C for 2 h were compared (Fig. 2). The amount of methanol produced over 3_Cu/ZnO_commercial catalyst with hydrogen treatment was approximately five times greater than that without hydrogen treatment. In addition, the amount of by-products, such as methyl acetate and ethyl acetate, was drastically higher in the presence of hydrogen treatment. Ethyl acetate was likely produced through ethanol dehydrogenation catalyzed by Cu/ZnO [35]. Therefore, hydrogen treatment can be considered a requirement to remove organic compounds from the catalyst surface and to expose all active sites.

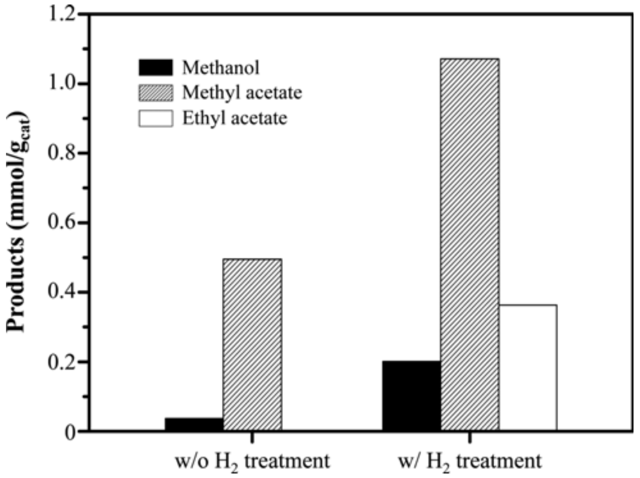

Fig. 2. Effect of hydrogen treatment on the catalytic activity in alcohol-assisted low temperature methanol synthesis from syngas.

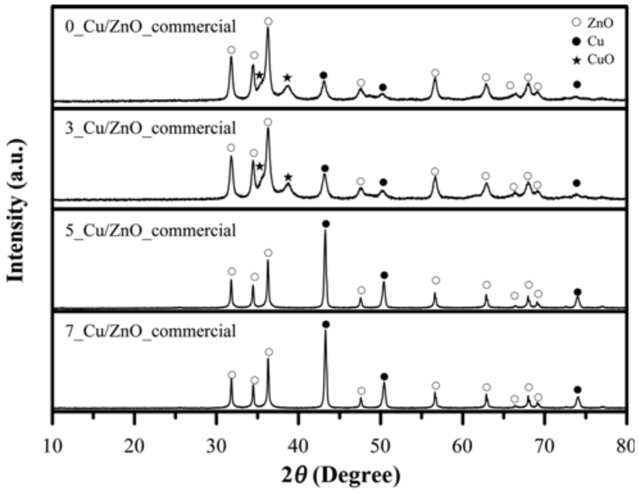

Fig. 3. XRD patterns of X_Cu/ZnO_commercial catalysts prepared at different PVP concentrations (X).

To prevent sintering and agglomeration of metal particles, nucleation-protective agents, such as polyvinylpyrrolidone (PVP), can be used in the polyol process. The PVP concentration and molecular weight used in the polyol process have been reported to strongly affect the physical properties of the resulting sample [23,24]. Therefore, the effect of PVP concentration on the catalytic activity of Cu/ZnO catalysts was investigated in alcohol-assisted low temperature methanol synthesis from syngas. We prepared a series of X_Cu/ZnO_commercial catalysts using a polyol method with various PVP concentrations (X=0-7). Here, X represents the weight ratio of PVP/Cu used in the polyol process, and commercial zinc oxide was used as the ZnO precursor. The weight ratios of Cu/Zn determined using ICP-AES analyses were approximately 1 for all X_Cu/ZnO_commercial catalysts (Table 1), and these values agreed well with the desired values.

Fig. 3 shows the XRD patterns of X_Cu/ZnO_commercial catalysts prepared at different PVP concentrations (X). The main diffraction peaks for the ZnO (101) and Cu (111) phases were observed in all X_Cu/ZnO_commercial catalysts at 2θ=36.3° and 43.2°, respectively. Interestingly, 0_Cu/ZnO_commercial and 3_Cu/ZnO_commercial catalysts prepared at low PVP concetrations showed the characteristic diffraction peaks at 2θ=35.5° and 38.7°. These peaks were due to the CuO diffraction pattern, which indicates the formation of CuO by the oxidation of metallic copper into copper oxide during the polyol process. Because metallic copper has been considerd as a main active site in low temperature methanol synthesis from syngas, X_Cu/ZnO_commercial catalysts prepared at low PVP concentrations (X=0 and 3) might have poor catalytic performance.

Table 1. Chemical composition and crystallite size of X_Cu/ZnO_commercial catalysts prepared with different PVP concentrations (X)

Catalyst	Cu/Zn[a]	Crystallite size (nm)[b]	
		ZnO (101)	Cu (111)
0_Cu/ZnO_commercial	0.9	38.7	33.6
3_Cu/ZnO_commercial	1.0	43.3	27.1
5_Cu/ZnO_commercial	0.9	36.3	23.4
7_Cu/ZnO_commercial	1.0	39.6	31.5

[a] Molar ratio of Cu/ZnO catalysts was determined using ICP-AES analysis

[b] Crystallite size was calculated using the Scherrer equation

SEM analyses were conducted with an aim of investigating the effect of PVP on the surface morphology of Cu/ZnO catalysts, and the obtained figures for X_Cu/ZnO_commercial catalysts are shown in Fig. 4. Only the 5_Cu/ZnO_commercial catalyst retained a platelike structure, while the other catalysts had a three-dimensional random structure. The PVP concentration strongly affected the Cu/ZnO catalyst morphology. Considering the high catalytic activity of the 5_Cu/ZnO_commercial catalyst, a platelike structure of Cu/ZnO catalysts seems to be favorable for alcohol-assisted low temperature methanol synthesis from syngas.

The catalytic activity of X_Cu/ZnO_commercial catalysts prepared at different PVP concentrations (X) is presented in Fig. 5. As expected, little methanol was produced over X_Cu/ZnO_commercial catalysts prepared at low PVP concentrations (X=0 and 3). As the PVP concentration increased, the amount of methanol produced over X_Cu/ZnO_commercial catalysts increased to a maximum, and then decreased as the PVP concentration increased further. Consequently, the amount of methanol produced over X_Cu/ZnO_commercial catalysts exhibited a volcano-shaped curve with respect to PVP concentration (X). The maximum amount of methanol was obtained over the 5_Cu/ZnO_commercial catalyst (ca. 1.7 mmol/g$_{cat}$). Therefore, it is thought that PVP played an important role in finely dispersing copper particles in the Cu/ZnO catalyst, while the excessive PVP concentration was unfavorable for preparing an efficient Cu/ZnO catalyst through a polyol method.

The crystallite sizes of Cu and ZnO in X_Cu/ZnO_commercial catalysts were examined with the Scherrer equation ($D=K\lambda/\beta\cos\theta$, where K is the Scherrer constant, λ is the X-ray wavelength, and D is the mean crystallite size) to elucidate the effect of PVP con-

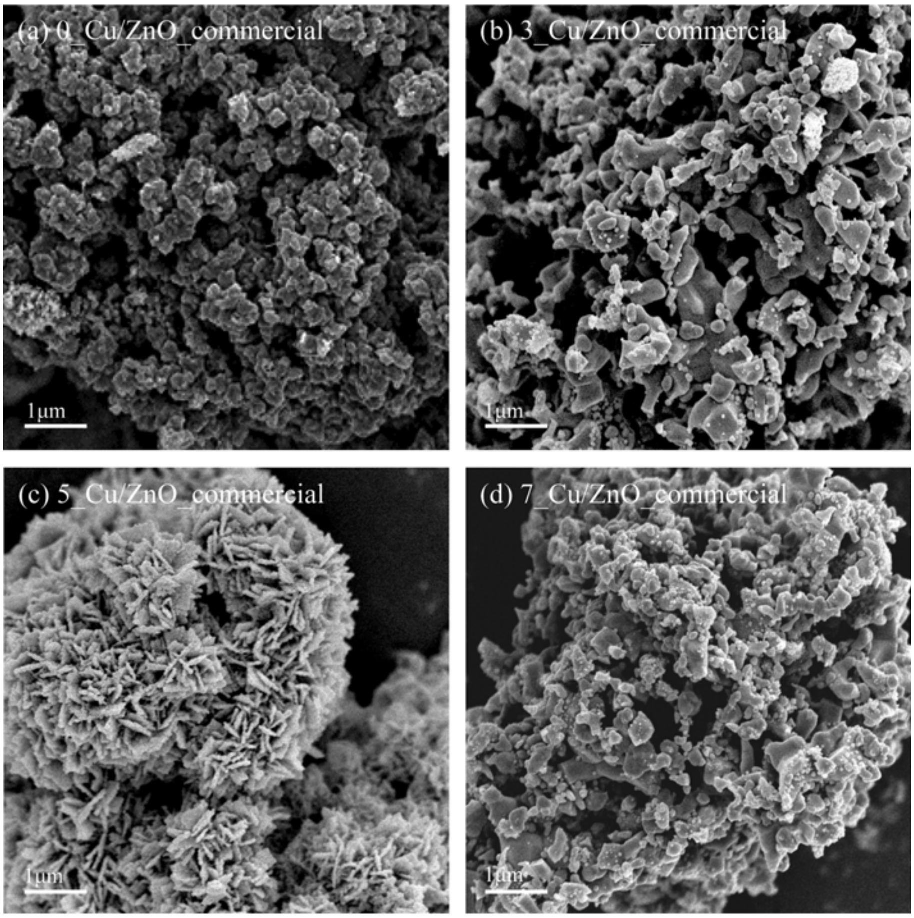

Fig. 4. SEM images of X_Cu/ZnO_commercial catalysts prepared at different PVP concentrations (X).

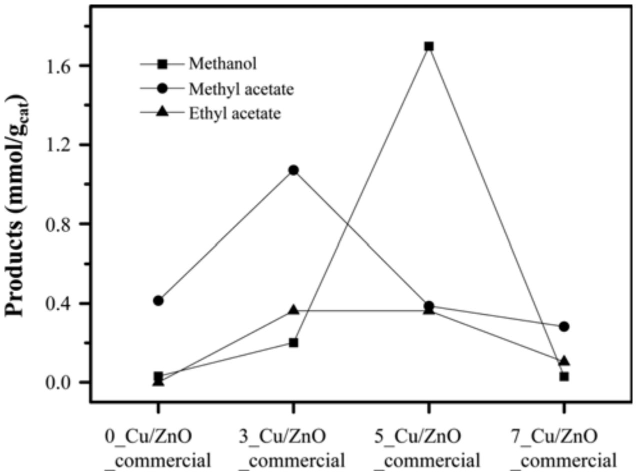

Fig. 5. Catalytic activity of X_Cu/ZnO_commercial catalysts after a 20 h-catalytic reaction, plotted as a function of PVP concentration (X).

centration on metal particle dispersion. The Cu and ZnO crystallite sizes were calculated from the strongest peaks of Cu (111) (2θ= 43.2°) and ZnO (101) (2θ=36.3°), respectively, and the results are summarized in Table 1. The 5_Cu/ZnO_commercial catalyst had the smallest Cu crystallite size (ca. 23.4 nm), while the 0_Cu/ZnO_commercial had the largest Cu crystallite size (ca. 33.6 nm). The 7_Cu/ZnO_commercial catalyst also had a relatively large Cu crystallite size. Therefore, PVP concentration probably has a strong influence on the Cu crystallite size of Cu/ZnO catalysts prepared by using a polyol method. Among the X_Cu/ZnO_commercial catalysts, the 5_Cu/ZnO_commercial catalyst, which had the smallest Cu crystallite size, produced the most methanol.

To confirm the copper dispersion and particle size in X_Cu/ZnO_commercial catalysts, TEM analysis was performed. As expected, the 5_Cu/ZnO_commercial catalyst had a small relatively uniform copper particle size (Fig. 6). The copper particle sizes of Cu/ZnO_commercial catlaysts as measured by TEM analysis were similar to the sizes measured by XRD. Once again, we confirmed that the PVP concentration strongly affects the copper dispersion and particle sizes of Cu/ZnO catalysts, and thus, its catalytic activity.

PVP has been widely used as a polymer stabilizer and an effective nucleation-protective agent in the polyol method [22,23]. PVP can prevent sintering of metal particles and yields homogeneous nano-sized metal catalysts [14,24]. Accordingly, PVP concentration strongly affects the metal dispersion and morphology of catalysts prepared with a polyol method. Our experimental results clearly revealed that the metal dispersion and mophology of Cu/ZnO catalysts were easily controlled by the PVP concentration in the polyol

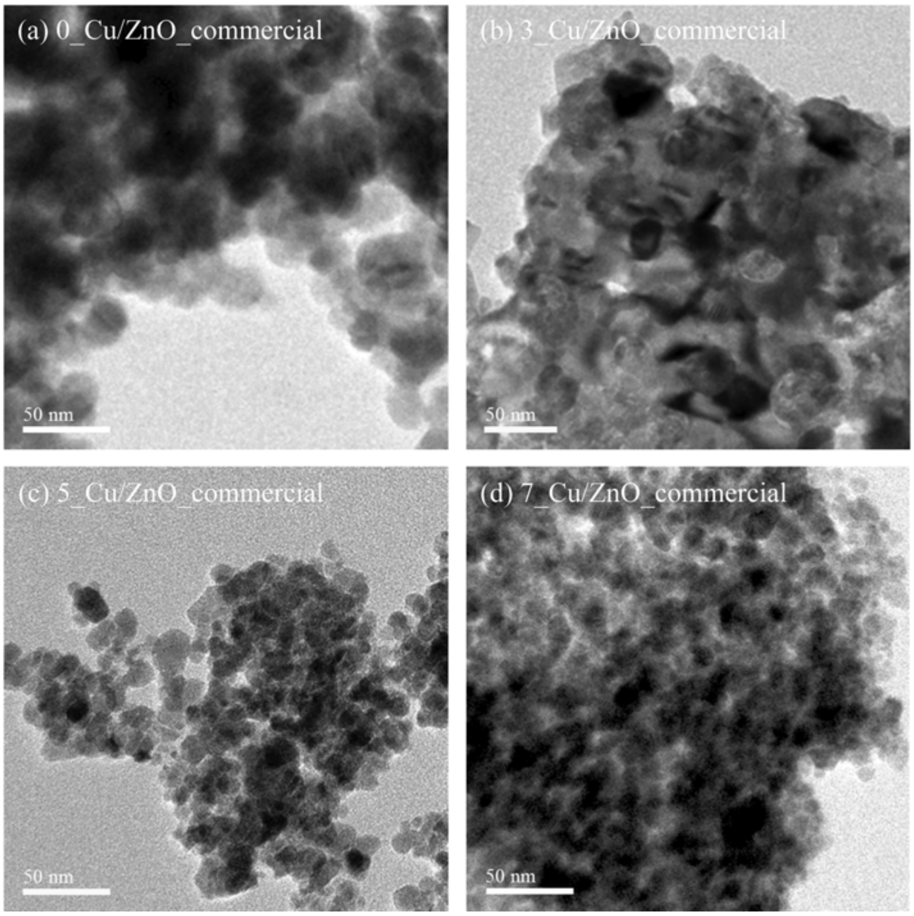

Fig. 6. TEM images of X_Cu/ZnO_commercial catalysts prepared at different PVP concentrations (X).

process. Therefore, PVP concentration is a crucial factor to determine the catalytic activity of metalic catalysts prepared using a polyol method.

The effect of the ZnO presursor on the catalytic activity of Cu/ZnO catalysts was also investigated. Cu/ZnO catalysts were prepared by using three different ZnO precursors. For comparison, the weight ratio of PVP/Cu was fixed at 5. The ZnO precursors were zinc oxdie snynthesized by the calcination of zinc nitrate in an air stream (ZnO_synthesized), commercial zinc oxide (ZnO_commercial), and zinc acetate (ZnO_Zn(Ac)$_2$). The catalytic activities of Cu/ZnO catalysts differed greatly depending on the ZnO

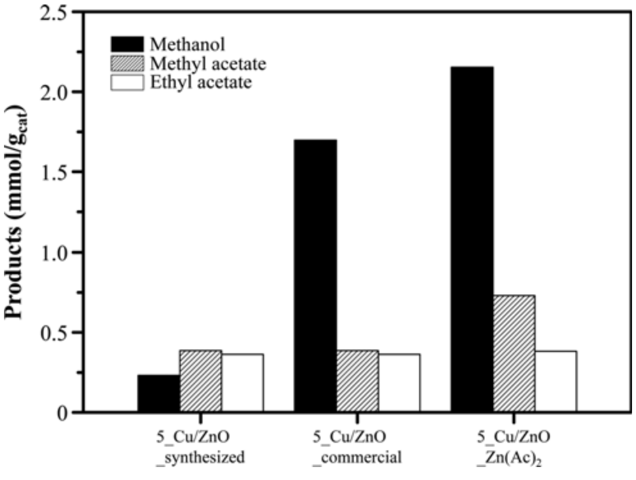

Fig. 7. Catalytic activity of 5_Cu/ZnO_Y prepared from different ZnO precursors (Y) after a 20 h-catalytic reaction.

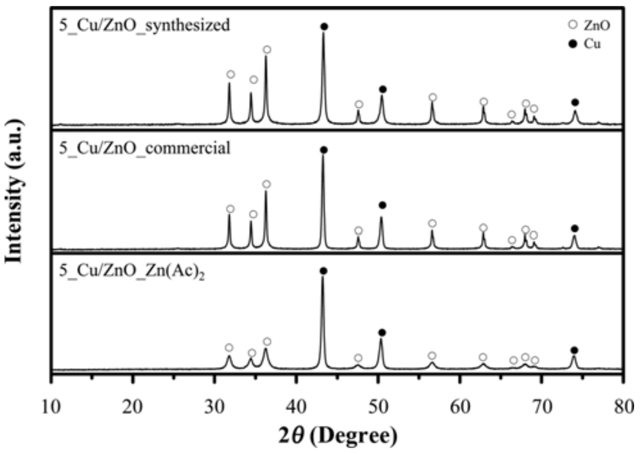

Fig. 8. XRD patterns of 5_Cu/ZnO_Y prepared from different ZnO precursors (Y).

precursor (Fig. 7). The 5_Cu/ZnO_Zn(Ac)$_2$ prepared from zinc acetate showed the best catlaytic performance.

XRD measurements revealed that all 5_Cu/ZnO_Y catalysts could be prepared using a polyol method regardless of ZnO precursor (Fig. 8). The Cu crystallite sizes determined with the Scherrer equation were affected by the ZnO precursor, although the calculation results are not shown. The 5_Cu/ZnO_Zn(Ac)$_2$ catalyst had the smallest Cu crystallite size, indicating that the ZnO precursor also affected the copper dispersion in Cu/ZnO catalysts, and thus, their catalytic activity. Therefore, the enhanced catlaytic activity of the 5_Cu/ZnO_Zn(Ac)$_2$ catalyst likely originated from its high copper dispersion.

CONCLUSION

Cu/ZnO catalysts prepared by using a polyol method were applied to alcohol-assisted low temperature methanol synthesis from syngas in a batch-type reactor. Successful formation of Cu/ZnO catalysts was confirmed using XRD and ICP-AES analyses. Various Cu/ZnO catalysts prepared using a polyol method produced a considerable amount of methanol. These results indicate that the polyol method is promising for preparing an efficient catalyst for alcohol-assisted low temperature methanol synthesis. The effects of various preparation conditions in the polyol process on catalytic activity were investigated. The PVP concentration and ZnO precursor strongly affected the Cu crystallite size and morphology of the Cu/ZnO catalyst, and accordingly, their catalytic activity. High copper dispersion and a platelike structure of the Cu/ZnO catalyst were favorable for producing methanol. The amount of methanol produced over X_Cu/ZnO_commercial catalysts showed a volcano-shaped curve with respect to PVP concentration (X). Zinc acetate was a suitable ZnO precursor for preparing Cu/ZnO catalysts by a polyol method. Consequently, the largest amount of methanol (ca. 2.2 mmol/g$_{cat}$) was obtained over the 5_Cu/ZnO_Zn(Ac)$_2$ catalyst with a high copper dispersion.

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