Influence of Impregnation and Coprecipitation Method in Preparation of Cu/ZnO Catalyst for Methanol Synthesis

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Abstract. Cu/ZnO catalyst was succesfully prepared using a coprecipitation method. The mixing procedure of the $Cu(NO_3)_2$, $Zn(NO_3)_2$ and Na_2CO_3 solutions had an important influence on the characteristics of the catalyst. The best catalyst obtained was the one prepared with slow mixing of the salt solutions and a CuO/ZnO molar ratio of 50:50. This raw catalyst had a maximum surface area of about 61.6 m^2/g. Increasing the CuO/ZnO molar ratio caused an agglomeration of precipitated particles, reducing the surface area. A much better catalyst was obtained using an impregnation method, in which γ-Al_2O_3 was used as support. The impregnated catalyst had a surface area of about 151 m^2/g. Activity tests were carried out in a fixed-bed reactor containing 1 g of catalyst and a flow of syngas at a rate of 60 mL/min. The reaction temperature was 170°C and the pressure was 20 barg. The best coprecipitated catalyst gave a CO conversion of about 10%, while the impregnated catalyst gave a CO conversion of up to 69%.

Keywords: *catalyst activity; catalyst crystallinity; co-precipitation method; Cu/ZnO catalyst; direct DME synthesis; impregnation method; pore properties; XRD analysis.*

1 Introduction

Conversion of biomass to methanol via gasification is one of the future challenges for the utilization of biomass as a source of fuel and chemicals. Methanol is an intermediate chemical that can be converted into gasoline via the MTG process (methanol to gasoline) or via other chemicals such as dimethyl ether, olefins and formaldehyde.

The first technology of methanol synthesis was BASF, introduced in 1923, using ZnO-Cr_2O_3 catalyst at a severe condition with a pressure in the range of 240-350 bar and a reaction temperature of 350-400°C. A significant improvement of methanol synthesis was achieved in the 1960s with the use of a more active Cu/ZnO catalyst, resulting in an improvement of the operating

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conditions to 60-80 bar and 250-280°C, thus reducing the energy consumption and the operation costs [1].

Research and development of metanol synthesis is still a concern up untill now, particularly to improve the performance of the catalyst. Base catalyst of Cu/ZnO is usually made using coprecipitation followed by calcination and reduction. The characteristics and activity of the catalyst depend on the conditions of coprecipitation, such as metallic ion concentration, temperature and pH, as well as the length of aging time.

Preparation of catalyst via the coprecipitation method may be carried out using solutions of $Cu(NO_3)_2$, $Zn(NO_3)_3$, $Al(NO_3)_2$ and Na_2CO_3 [2]. A good catalyst may be obtained from precipitation with a pH of about 6.5 and a precipitation temperature of 70°C. The length of aging time also plays an important role in the activity of the catalyst.

Catalyst may also be prepared using Cu,Zn,Al-nitrates and ammonium hydroxide. The precipitation is then carried out at a pH of 7 and a temperature of 65°C [3]. In this method, the precipitate is a mixture of Cu,Zn-hydroxycarbonate and Cu,Zn-hydroxynitrate. This precipitate is then dried at 120°C for 20 hours, followed by calcination at 330°C. During precipitation using Cu,Zn-nitrates and ammonium hydroxide there is no change in pH. Meanwhile, during precipitation using Cu,Zn-nitrates and sodium-carbonate a decrease in pH is observed after 22 minutes, which then slowly increases back to its original value. This change in pH indicates the change in solid phase from amorphous to crystalline phase of rosasite $(Cu,Zn)_2CO_3(OH)_2$ and aurichalcite $(Cu,Zn)_5CO_3(OH)_6$.

The effect of the presence of Al on the catalyst activity has been studied by Bahrens, *et al.* [4]. The best concentration of Al was about 3-4% of the mass fraction of Al to (Cu+Zn+Al). At this Al concentration, the activity is 143% compared to that with a concentration of 13%, and 179% compared to that of binary catalyst of CuO/ZnO. This significant difference in catalyst activity is probably due to the different pore structure as an effect of the precipitation condition.

Our study focused on the effects of Cu/Zn mass ratio and method of preparation of catalyst Cu/ZnO, especially volume of solvent and procedure of mixing during coprecipitation. Eight types of catalysts were prepared using coprecipitation and one catalyst was prepared using impregnation. Coprecipitation was directed at obtaining catalysts with mass ratios of Cu/Zn of 50:50, 75:25 and 25:75 (see Table 1). One coprecipitated catalyst was prepared with addition of Al.

2 Experimental Set-up

Our study consisted of three steps: preparation of the catalysts as the main experimental work, followed by characterization of the catalysts, and finally activity testing of the catalysts.

2.1 Catalysts Preparation

Applying the coprecipitation method, solutions of 0.1M $Cu(NO_3)_2$ and 0.1 M $Zn(NO_3)_2$ were mixed in a batch reactor equipped with a magnetic stirrer. A solution of 1 M Na_2CO_3 was added as precipitator and more water was added. Coprecipitation was carried out at a constant temperature of 65°C and a constant pH of 7. All chemicals were purchased from Merck.

Table 1 Preparation of catalyst using coprecipitation.

Catalyst Code [1]	Cu:Zn:Al (%w/w) [2]	Solution mixed (mL) $Cu(NO_3)_2$ 0.1 M	$Zn(NO_3)_2$ 0.1 M	Na_2CO_3 1.0 M	Water added (mL)	Oxide Yield (g)
C50/50/00/300/E/A	50:50:00	189.0	184.0	36.0	300	2.75
C50/50/00/300/E/W	50:50:00	189.0	184.0	36.0	300	2.73
C75/25/00/300/E/A	75:25:00	283.0	92.0	37.0	300	2.82
C25/75/00/300/E/A	25:75:00	94.0	276.0	37.0	300	2.74
C60/30/10/300/E/A	60:30:10	226.0	110.0	40.0	300	5.60
C50/50/00/300/D/A	50:50:00	189.0	184.0	36.0	300	2.72
C50/50/00/450/D/A	50:50:00	189.0	184.0	36.0	450	2.73
C50/50/00/600/D/A	50:50:00	189.0	184.0	36.0	600	2.72
CM12/8/80 [3]	12:08:80	-	-	-	-	-

[1] E = slow mixing, D = direct mixing all solutions, A = with aging, W = without aging
[2] Mass ratio of $Cu(NO_3)_2$ to $Zn(NO_3)_2$ to $Al(NO_3)_3$
[3] Impregnation

Two procedures of mixing were applied for catalyst preparation. In the first procedure, $Cu(NO_3)_2$, $Zn(NO_3)_2$ and Na_2CO_3 solutions were mixed directly into water without controling pH. In the second procedure, $Cu(NO_3)_2$, $Zn(NO_3)_2$ and Na_2CO_3 solutions were added slowly into water with controling pH at a relatively constant value of about 7. The direct mixing may lead to a rapid nucleus growth, resulting in a lower surface area than using slow mixing.

The precipitate was then dried at a temperature of 110°C for 24 h, followed by calcination at a temperature of 350°C for 1 h with a heating rate of 5°C/min. The raw catalyst obtained after the calcination of the precipitate contained

CuO/ZnO, which must undergo carefully reduction to Cu/ZnO prior to its utilization in methanol synthesis.

In the impregnation method, solutions of Cu $(NO_3)_2$ and $Zn(NO_3)_2$ were impregnated on a solid support of γ-Al_2O_3. Drying, calcination and reduction were also applied to this raw catalyst.

2.2 Catalysts Characterization

The BET surface areas of the raw catalyst were determined by nitrogen-physioadsorption using a Quantochrome surface area and pore size analyzer, model Nova 3200e. Degassing of the sample prior to the BET analysis was carried out at a temperature of 300°C for 4 hours. Gas sorption was carried out at a temperature of -195.8°C.

The phase of the catalysts was analyzed on a Bruker D8 Advance X-ray diffractometer (XRD) with Cu-K radiation at 40 kV, 30 mA. The morphology was observed using a scanning electron microscope (SEM), type JSM-6360LA with energy dispersive X-ray system.

2.3 Activity Test of Catalysts

The activity of the catalysts was evaluated in a fixed-bed reactor with a diameter of 1.7 cm and a length of 39 cm. The bed height was about 3.8 cm. Before being utilized for methanol synthesis, about 1 gram of raw catalyst was activated using a gas mixture of 5% H_2 and 95% N_2, flowing at a rate of 120 mL/min. The activations were carried out at a temperature of 200°C for 2 hours. The activated catalyst was kept inside the reactor and prevented from having contact with air.

The catalyst activity tests were carried out using a synthesis gas composed of 63.33% H_2, 31.67% CO and 5% N_2 at a pressure of 20 barg. The reactor was first heated slowly to the reaction temperature of 170°C. The synthesis gas was introduced with a flow rate of 60 mL/min into the reactor when the reactor temperature reached 170°C. Gas samples were taken from the inlet and outlet of the reactor and its composition was measured using a gas chromatographer.

3 Result and Discussion

The amount of oxides after calcination (CuO and ZnO) was about 2.7 g (see Table 1). As the stoichiometric amount of CuO and ZnO would be about 2.75 g, these results indicate that all Cu^{++} and Zn^{++} ions were already precipitated completely. Moreover, the ratio of CuO/ZnO was found at about 48.5:51.5, close to the ratio of mol-weight of Cu and Zn, i.e. 63.5:65.4. Thus, $CuCO_3$ and

$ZnCO_3$ may have precipitated at the same rate and went on to complete precipitation.

3.1 Catalyst Characterization

In the aging process, the structure of the precipitate changed from amorphous to crystalline [4-6]. This phenomenon was also observed in our experiments with the change in color of the precipitate from blue to green. The amorphous and crystalline precentages of are presented in Table 2.

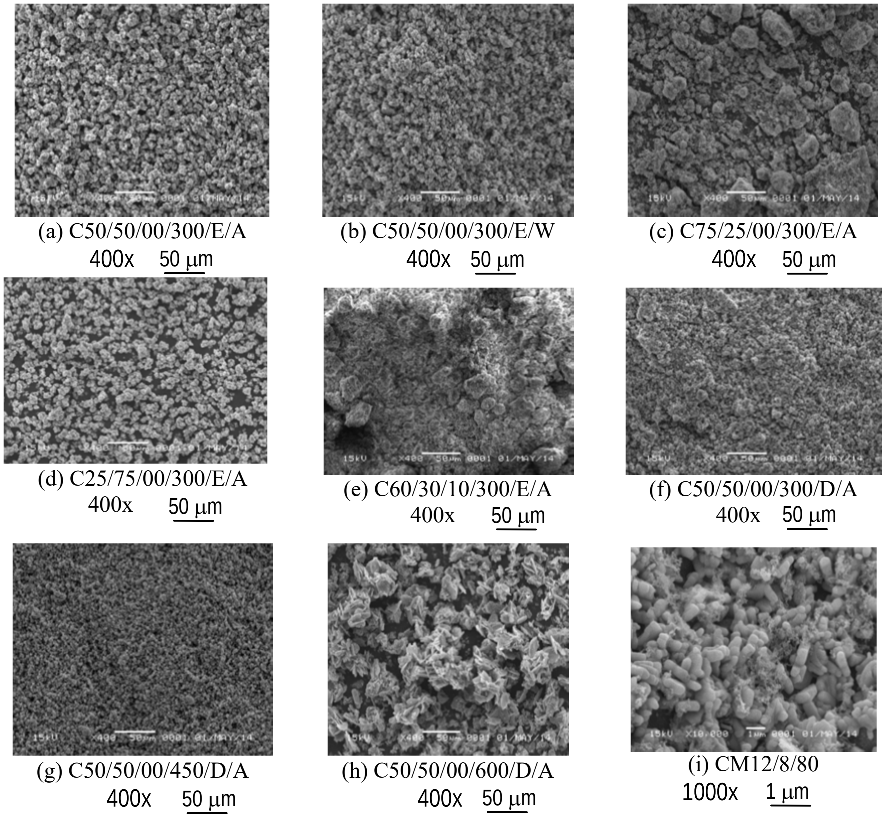
Table 2 Catalyst characterization.

Sample	Surface area (m^2/g)	Pore volume (cc/g)	Pore diameter (Å)	Crystalinity level	
				Crystall	Amorphous
C50/50/00/300/E/A	58.24	0.436	299.1	67.5%	32.5%
C50/50/00/300/E/W	61.59	0.443	287.5	65.7%	34.3%
C75/25/00/300/E/A	36.11	0.241	266.6	69.0%	31.0%
C25/75/00/300/E/A	57.60	0.461	307.0	73.6%	26.4%
C60/30/10/300/E/A	77.02	0.578	300.3	45.0%	55.0%
C50/50/00/300/D/A	54.68	0.404	295.5	73.9%	26.1%
C50/50/00/450/D/A	57.60	0.338	234.6	68.4%	31.6%
C50/50/00/600/D/A	53.97	0.246	182.1	69.0%	31.0%
CM12/8/80	151.40	0.337	88.9	53.6%	46.4%

A slight difference in crystallinity due to the application of aging may be seen in catalyst C50/50/00/300/D/A (prepared with aging) against C50/50/00/300/D/W (without aging). Note that in the aging process, increasing the pH was observed in our experiments, which may be an indication of higher crystallinity formation. Observation of the pore size showed that the catalyst particles prepared without aging were finer than those with aging (analysis using SEM presented in Figure 1).

The effect of the salt molar ratio $Cu(NO_3)_2$ to $Zn(NO_3)_2$ during preparation on the amount of precipitates was negligible (Table 1–compare rows 1, 3, 4 and 6). The higher yield of C60/30/10/300/E/A was an exception, which may be due to the presence of Al_2O_3 (after calcination). The presence of Al_2O_3 on the CuO/ZnO precipitate was also confirmed by the degree of crystallinity (Table 2, row 5) and the SEM analysis (Figure 1(e)).

Based on the SEM analysis, the particle size of the raw catalyst appeared to be affected by the molar ratio of $Cu(NO_3)_2$ to $Zn(NO_3)_2$: the higher the molar ratio, the larger the particles and the more heterogeneous in size (compare Figures 1(a) and 1(e) to Figures 1(c) and 1(d)). Even for the Cu/Zn molar ratio of 75:25 (C75/25/00/300/D/A) agglomeration of CuO on the ZuO surface was observed (Figure 1(c)). On the other hand, for the Cu/Zn molar ratio of 25:75 (C25/75/00/300 /D/A), the CuO was distributed homogeneously on the ZnO surface (Figure 1(d)). Reproducing the preparation of equimolar ratio of Cu/Zn yielded satisfactory raw catalyst with respect to yield (Table 1, rows 1 and 5), pore properties (Table 2) and particle structures (Figures 1(a) and 1(f)).



(a) C50/50/00/300/E/A 400x 50 μm

(b) C50/50/00/300/E/W 400x 50 μm

(c) C75/25/00/300/E/A 400x 50 μm

(d) C25/75/00/300/E/A 400x 50 μm

(e) C60/30/10/300/E/A 400x 50 μm

(f) C50/50/00/300/D/A 400x 50 μm

(g) C50/50/00/450/D/A 400x 50 μm

(h) C50/50/00/600/D/A 400x 50 μm

(i) CM12/8/80 1000x 1 μm

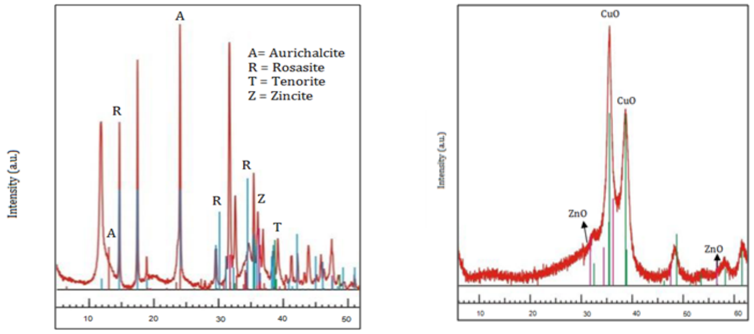
Figure 1 SEM analysis.

The procedure of mixing the salt solutions did not affect the yield of raw catalyst (Table 2, see row 6, row 7 and row 8). However the procedure influenced the characteristics of the raw catalyst to some extent, for instance: the cristallinity (C50/50/00/300/E/A vs C50/50/00/450/D/A), and also the pore mean diameter (C50/50/00/300/D/A, C50/50/00/450/D/A vs. C50/50/00/600/D/

A). SEM analysis confirmed these differences (Figures 1(f), 1(g) and 1(h)). These effects of the salt molar ratio and the mixing method on the characteristics of the raw catalyst are in line with those reported in the literature [3,6].

As presented in Table 2, the BET surface area of C50/50/00/450/E/A (450 mL of added water) was larger than that of C50/50/00/600/E/A (600 mL of added water) and C50/50/00/350/E/A (350 mL of added water). Thus, the preparation of catalyst using 450 mL of added water (see also Table 1) was the best. The effects of preparation procedure, particularly the volume of solvent (added water) on particle size and homogenity has also been reported by Ertl [7]. Practically, saturation will be reached easier in coprecipitation with a higher salt concentration, so the rate of precipitation becomes faster. As a result, the particle size of the precipitate will be smaller and its surface area will be larger [7].

In our experiment, catalyst support of γ-Al_2O_3 with a surface area of 207 m^2/g was used in the impregnation method. As expected, the raw catalyst obtained from this method had a larger surface area (151.4 m^2/g) compared to that obtained from the coprecipitation method (see Table 2). Unfortunately, the surface area of this raw catalyst was only 75% of the surface area of support, probably due to agglomeration of CuO/ZnO and blockage on the pores (see SEM analysis of this raw catalyst in Figure 1(i)).



(a) After coprecipitation. (b) After calcination.

Figure 2 XRD pattern of C60/30/10/300/E/A.

As an addition to the above discussion, XRD pattern indicated that there was a change in crystal structure during the calcination of precipitate (Figure 2). The presence of tenorite, zincite, rosasite, and aurichalcite were detected in the precipitate C60/30/10/300/E/A before calcination (Figure 2(a)). Those compounds changed to crystalline CuO and ZnO (see Figure 2(b)).

3.2 Catalyst Activity

Because catalysts C50/50/00/300/E/A and C60/30/10/300/E/A were considered the best among the eight catalysts prepared using the coprecipitation method, the activity of these two catalysts was tested for methanol synthesis. The catalysts C50/50/00/300/E/A and C60/30/10/300/E/A yielded CO conversions of about 10% and 5% respectively (see Figure 3). These conversions were significantly lower compared to the conversion of up to 70% resulted from catalyst CM12/8/80 prepared using impregnation. In industry, the conversion of CO is in the range of 30-70%, but it may be beyond the equilibrium in a certain condition [8].

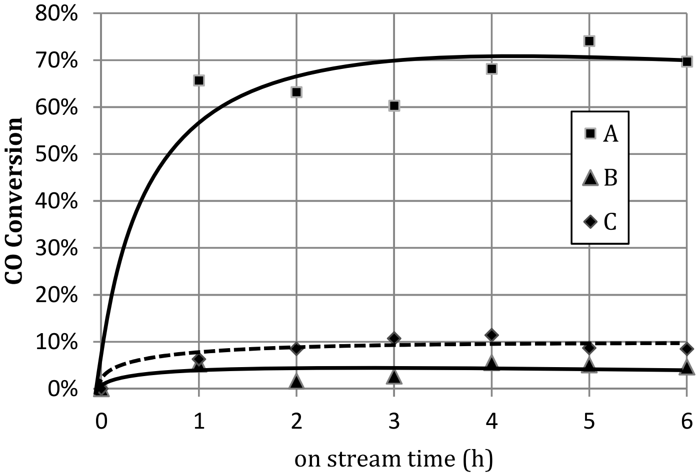


Figure 3 Progress of CO conversion in methanol synthesis. Catalyst: 1 g, temperature: 170°C, pressure: 20 barg, syngas (63.3% H_2, 31.7% CO and 5% N_2): 60 mL/min. Curve A: CM12/8/80, curve B: C50/50/00/300/E/A, curve C: C60/30/10/300/E/A.

4 Conclusions

In this study, it was found that the procedure of mixing of $Cu(NO_3)_2$, $Zn(NO_3)_2$ and Na_2CO_3 solutions, and the molar ratio of CuO/ZnO during the precipitation step in the coprecipitation method had an important influence on the characteristics of CuO/ZnO raw catalyst for methanol synthesis. A maximum surface area of 61.59 m^2/g was obtained in the catalyst with a CuO/ZnO molar ratio of 50:50. A better catalyst with a surface area of 151.4 m^2/g was obtained using impregnation of CuO/ZnO on γ-Al_2O_3 support. In a semi-continuous labscale reactor, the best co-precipitated catalyst and the best impregnated catalyst gave a CO conversion of about 10% and up to 69% respectively.

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