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Cu-Zr-Zn catalysts for methanol synthesis in a fluidized bed reactor

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ABSTRACT

Ten Cu-Zr-Zn catalysts prepared by reverse coprecipitation were evaluated for use for methanol synthesis at 230–270 °C and 4 MPa. The catalysts were characterized by N_2O-chemisorption, X-ray diffraction, scanning electron microscopy, and their attrition resistance and particle size distribution. The data showed that many of the catalysts had suitable activity, shape, size and mechanic strength. Catalyst stability during reaction at 260 °C for 120 h was also studied. The catalyst with the composition of Cu:Zr:Zn = 4.5:3:1.5 was optimal for methanol synthesis in a fluidized bed reactor.

1. Introduction

Methanol is a fundamental product in the chemical industry and its production capability has been increasing due to its wide use as a chemical feedstock, especially for clean energy resources. Since the 1970s, fixed bed reactors have been used with Cu/ZnO-based catalysts for methanol synthesis [1]. However, the reactions in methanol synthesis from syngas ($CO + 2H_2 = CH_3OH + 90.4$ kJ, $CO_2 + 3H_2 = CH_3OH + H_2O + 49.33$ kJ, $CO + H_2O = CO_2 + H_2 + 40.96$ kJ) are highly exothermic and effective heat removal is required. Unfortunately, it is not easy to do this with fixed bed reactor. A fluidized bed reactor is much more efficient in heat transfer.

Although most methanol synthesis works have been focused on enhancing the per pass conversion of carbon monoxide by the development of more active catalysts [2], some researchers have explored the use of fluidized bed reactor. Compared with fixed bed reactor, fluidized bed is not only much better at heat transfer, but it is also less expensive to manufacture. More importantly, the temperature uniformity in the whole reactor and the avoidance of diffusion limitation by the use of much smaller catalyst particles have greatly improve methanol synthesis production efficiency. Wagialla and Elnashaie [3] carried out a theoretical investigation on methanol synthesis in a fluidized bed reactor and discussed the difference between methanol synthesis in fixed bed and fluidized bed reactors, and showed that a 30% improvement can be obtained with a fluidized bed. Tabis [4] and Rahimpour et al. [5,6] have done a lot of work on the optimization of fluidized bed reactor design for methanol synthesis.

Although there were been investigations on the reactor and its design, studies on the catalyst used in a fluidized bed have been few. Unlike the catalysts in a fixed bed, the catalysts in a fluidized bed reactor are subject to attrition from collisions between catalyst particles and with the reactor wall [7]. In the fluidized bed methanol synthesis investigations mentioned above, researchers used fixed bed catalyst that was ground to small directly. The catalyst used for methanol synthesis in a fixed bed is usually a Cu-Zn-Al catalyst based on the catalyst invented by ICI (Imperial Chemistry Industry) researchers. This kind of catalyst is poor in attrition resistant performance and cannot be used for long-term methanol synthesis in a fluidized bed reactor.

In the present work, a series of Cu-Zr-Zn catalysts were prepared and evaluated. They were characterized by N_2O-chemisorption, X-ray diffraction (XRD), scanning electronic microscopy (SEM), and their attrition resistance and particle size distribution (PSD). Some of these catalysts performed well and their attrition resistance and catalytic stability reached the basic standard for a fluidized bed.

2. Experimental

2.1. Catalyst preparation

Ten catalysts were prepared by the sodium carbonate (Beijing Chemical Corporation) coprecipitation method. Three metal salt solutions (1.2 mol/L $Cu(NO_3)_2$, 0.6 mol/L $ZrOCl_2$ and 1.2 mol/L $Zn(NO_3)_2$) were premixed in the specific catalyst compositions and added dropwise to a sodium carbonate solution (1.2 mol/L, preheated to 70 °C) that was stirred vigorously. The addition of the mixed solution was stopped when the pH reached 7. Then the product slurry was maintained at 70 °C for 1 h, filtered and washed in deionized water several times. A gel-like catalyst precursor was

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Table 1
Molar composition and metallic copper specific area of the ten catalysts prepared.

Catalyst	Composition			Metallic copper specific area (m^2/g)
	Cu	Zn	Zr	
A-1	1.5	4.5	3	16.7
A-2	3	3	3	18.2
A-3	4	2	3	38.4
A-4[a]	4.5	1.5	3	39.2
A-5	5	1	3	32.4
B-1	4.5	1.5	1.5	53.2
B-2	4.5	1.5	2	48.7
B-3	4.5	1.5	2.5	42.6
B-4[a]	4.5	1.5	3	39.5
B-5	4.5	1.5	4	28.6

[a] A-4 and B-4 were two same-composed catalysts prepared for under the same conditions.

obtained that was kneaded in a kneader with 1 wt% polyvinyl alcohol solution, which was used as an organic binder for catalyst mechanic strength improvement. Next, the precursor was spray dried in a spray dryer. In the spray dried process, the inlet temperature was 200 °C and the outlet temperature was 90 °C. The obtained near-spherical catalysts were calcined in a muffle oven at 400 °C for 2 h. These catalysts were named according to their compositions and divided into two groups. Group A, with the ratio of Cu/Zn varied, comprised five catalysts with (Cu + Zn):Zr = 6:3 named A-1 to A-5. Group B comprised the other five catalysts named B-1 to B-5 with the composition Cu:Zn = 4.5:1.5 and Zr content varied (see Table 1). A-4 and B-4 have the same composition, but were prepared separately using the same experimental conditions.

2.2. Catalytic activity evaluation

The catalytic properties of the catalysts were evaluated in a laboratory fixed bed reactor. Before reaction, the catalyst was pretreated in 4% (v/v) H_2/N_2 (GHSV = 2500 mL $gcat^{-1}$ h^{-1}) at atmospheric pressure by raising the temperature from ambient to 230 °C over 10 h. Then the inlet gas was switched to the reaction gas (GHSV = 5000 mL $gcat^{-1}$ h^{-1}) composed of 5.3 vol% carbon dioxide, 26.3 vol% carbon monoxide and 68.4 vol% hydrogen. The reaction was carried out at 4 MPa and temperatures from 230 to 270 °C. The first effluent sample was taken for analysis after the system had attained steady state. Carbon monoxide conversion (Xco) was defined as

$$\mathrm{Xco} = \frac{F_{\text{methanol,out}}}{F_{\text{co,in}}} \qquad (1)$$

where $F_{\text{methanol,out}}$ and $F_{\text{co,in}}$ are the molar flow of methanol and CO, respectively. Subscripts out and in denote the flow out of or into the reactor.

2.3. Catalyst characterization

N_2O-chemisorption is the accepted routine for metallic copper specific surface area measurement [8,9]. In the present work, the metallic copper surface area was determined by the method of Vandergrift et al. [8]. This method is also termed N_2O titration. It consists of three main reduction or oxidation procedures, with the amount of hydrogen consumption during the reduction process before and after N_2O-chemisorption, and the ratio of surface copper to bulk copper obtained. The metallic copper surface area was calculated by using the molar stoichiometry of $N_2O/Cu_{(s)} = 0.5$ and an average value of 1.46×10^{19} copper atoms/m^2 [10].

The catalysts were characterized on a Bruker D8 advance X-ray diffractometer. Nickel-filtered Cu Kα radiation ($\lambda = 1.54 \times 10^{-10}$ m) was used as the X-ray source, which was used at 40 kV and 20 mA. The X-ray pattern was recorded in the 2θ range between 10° and 90°. The morphology of the catalysts before reaction was characterized by a JSM 7401F scanning electron microscope operated at 3 kV and 20 mA.

The mechanical strength of the catalysts was measured using ASTM-D-5757-00, which is a standard method for the determination of attrition and abrasion of powdered catalysts by air jets. In this standard, the catalyst mechanical strength was evaluated by the Air Jet Index (AJI), which is the percentage of fine particles smaller than 10 μm carried out of the fluidized bed by a high velocity gas in a 5 h period. The apparatus used was self-constructed in accordance with the standard.

The particle size distributions (PSDs) of the catalysts were measured by a Mastersizer (Malvern Corp.). Before measurement, catalyst powder was added to deionized water and ultrasonically dispersed for 2 min. Then the PSD was determined by the laser method.

3. Results and discussion

3.1. Catalyst activity and methanol selectivity

For methanol synthesis, our research group has reported a fibrous catalyst that is much more active than the commercial industrial catalysts generally used [2]. This catalyst is so active that the carbon monoxide per pass conversion can almost reach as high as the thermodynamic equilibrium [11]. However, this catalyst cannot be used in a fluidized bed reactor because of its poor mechanical strength. To develop a new catalyst for methanol synthesis in a fluidized bed, we carried out a variety of experiments and found that a Cu-Zn-Zr catalyst obtained from a gel-like precipitate possesses sufficient activity and mechanical strength.

Copper crystallites are regarded as the basic active sites on Cu-based catalysts, and many investigations have related their activity with copper dispersion or something similar [12,13]. Zinc oxide, on the other side, is regarded as a promoter that serves as atomic hydrogen supplier [14]. Zirconia was also found to enhance the activity of Cu-based methanol catalysts [15,16], but the detailed mechanism is still unknown. For the purpose of screening to get an active and attrition resistant catalyst, a series of catalysts of different compositions were prepared, evaluated and characterized. Group A catalysts were designed to determine the optimal Cu/Zn ratio, which is believed to be important for methanol synthesis activity. Group B catalysts were designed to determine the optimal (Cu + Zn)/Zr ratio, which is important for both catalytic activity and attrition resistance.

Fig. 1 shows the relation between the Cu/Zn ratio of the catalysts and their activities. As the Cu/Zn ratio increased, the activity of the Group A catalysts first increased and then decreased. It is well known that too low or too high a Cu/Zn ratio is unfavorable for high carbon monoxide conversion: a low Cu content gives less methanol synthesis active sites and a low ZnO content gives inadequate promoter for the catalytic site. The best ratio of Cu/Zn in our system was 4.5:1.5.

The catalytic activities of the Group B catalysts are shown in Fig. 2. When the Cu/Zn ratio was kept at 4.5:1.5, the activity decreased monotonically as the ZrO_2 content increased. This can be explained by that in the range of the ZrO_2 content investigated, the increase in ZrO_2 content decreased the amount of copper active site per mass catalyst. However, this result also does not contradict the promotional effect of zirconia because the amounts of ZrO_2 used here were so large that they exceeded the content range where ZrO_2 promotion can be seen. The ZrO_2 content was selected here to be in this range used to determine the optimal ZrO_2 amount for good mechanical strength.

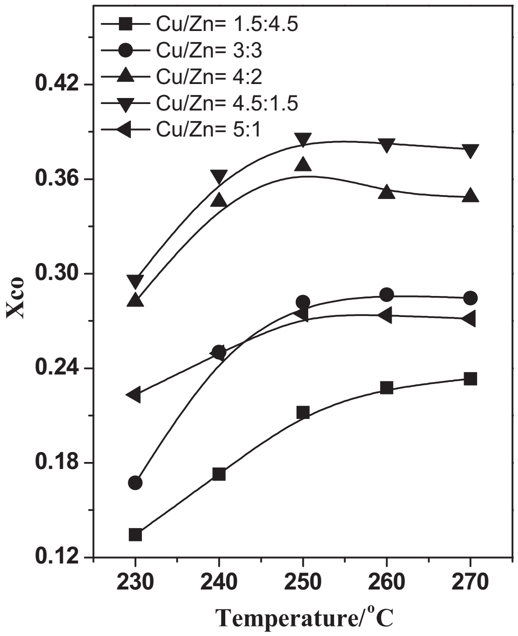

Fig. 1. Activities of Group A catalysts with different Cu/Zn ratios.

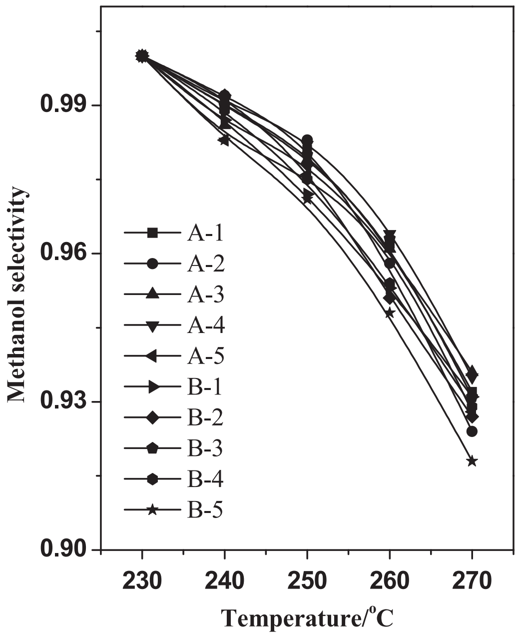

Fig. 3. Methanol selectivity of all Cu-Zr-Zn catalysts prepared in this work.

The methanol selectivities of the ten catalysts were almost the same. The data are shown in Fig. 3. The selectivity to methanol decreased gradually as the reaction temperature increased. When the reaction temperature was lower than 250 °C, the selectivity was nearly 100%. When the reaction temperature was 260 °C or 270 °C, some carbon monoxide was converted to methane, leading to a decrease in methanol selectivity.

3.2. N_2O-chemisorption

To better understand catalysts' active site center in the catalysts, catalysts' metallic copper specific area (Table 1) were measured and correlated with their methanol synthesis activity. The relation of the metallic copper surface area and methanol synthesis activity at 230 °C is presented in Fig. 4. All the points fell near the diagonal, which suggested a linear relationship between catalytic activity and copper surface area. This result was in good agreement with many other studies [17,18], which reproved that metallic copper was the active site center of methanol synthesis. Too much ZrO_2 have no more promotion effect. It was inferred that ZrO_2 might be coated on some copper oxide particles, leading to the decreasing of metallic copper specific area. Here, superfluous ZrO_2 were added purely to improve catalysts' attrition resistance at the price of activity sacrifice.

3.3. XRD

The XRD patterns of the ten catalysts are shown in Fig. 5. These catalysts had the same crystalline phases. All the diffraction peaks were due to the crystalline phases of CuO or ZnO. No clear peak due to the ZrO_2 phase was seen due to the relatively low calcination temperature (400 °C). According to the literature [19,20], the ZrO_2 phase appears after calcination above 500 °C. In all the XRD patterns, the rather featureless peaks implied an amorphous phase of the catalyst component or small crystallites. Our previous work found that a smaller crystallite size gave a higher activity

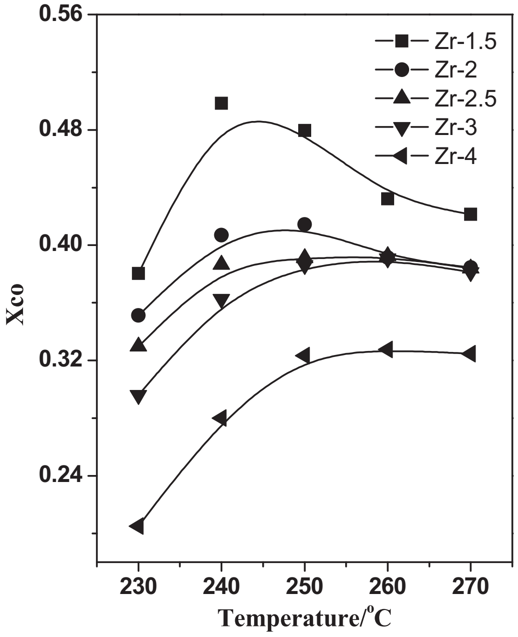

Fig. 2. Activities of Group B catalysts with different (Cu + Zn)/Zr ratios.

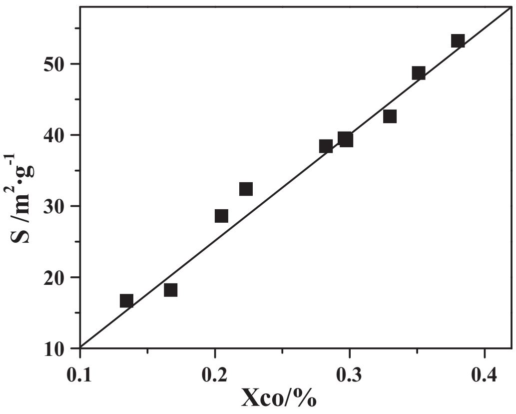

Fig. 4. Metallic copper surface area versus CO conversion.

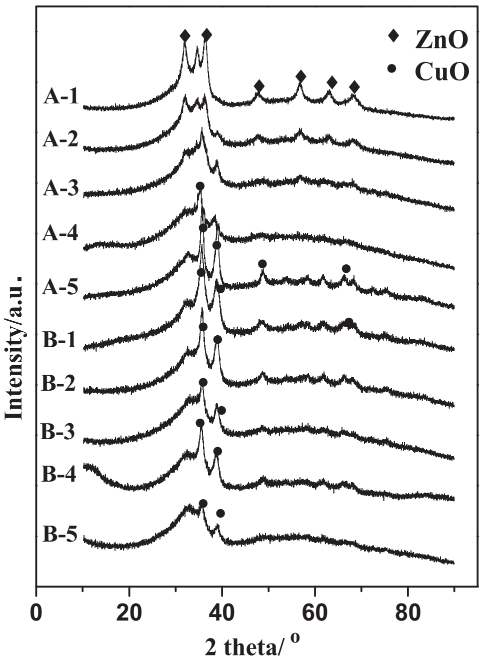

Fig. 5. XRD patterns of the ten Cu-Zr-Zn catalysts.

for methanol synthesis [21]. A comparison of the diffraction peak intensities showed that these roughly reflected the compositions of the catalysts listed in Table 1.

3.4. *Attrition resistance*

The AJI data of the Group A and B catalysts are shown in Fig. 6. The AJI of the Group B catalysts showed a drastic decrease from B-1 to B-5, indicting that the AJI decreased as the ZrO_2 content increased. This meant that ZrO_2 played an important role in catalyst mechanical strength enhancement. For the Group A catalysts, the AJI gradually increased from A-1 to A-5. In the Group A catalysts, the ZrO_2 content remain unchanged, which then implied that more Cu and less Zn is unfavorable for catalyst mechanical strength, but the influence is limited. Generally, a fluidized catalyst should have an AJI below 0.05 to be acceptable. From considering activity and attrition resistance, A-4 catalyst is the optimal catalyst for fluidized bed methanol synthesis. In the following experiments, A-4 was used as the catalyst.

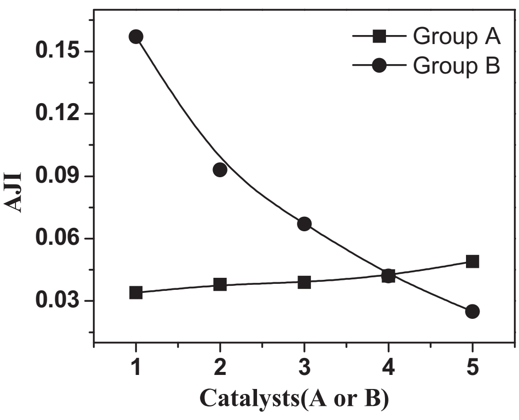

Fig. 6. AJI values of Group A and B catalysts.

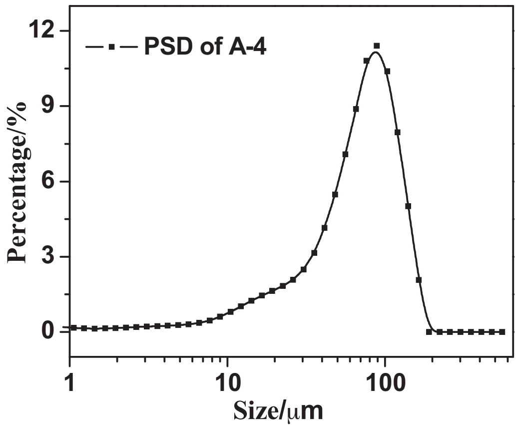

Fig. 7. Particle size distribution of A-4 catalyst.

3.5. *PSD*

The catalysts obtained after spray drying had similar PSDs (all the catalysts were spray dried under the same conditions. Therefore, there should be no evident difference in their PSDs). As an example, the PSD of A-4 is shown in Fig. 7. Most of the catalyst particles were in the range 10–200 μm and the volumetric average size was 62.4 μm. The bulk densities of the ten spray dried catalysts were about 0.65 g cm^{-3}. These particles should be classified as Geldart-A particles. So, the catalysts should be easily fluidized [22].

3.6. *SEM*

Four SEM images of A-4 catalyst are shown in Fig. 8. It is shown in Fig. 8(1 and 2) that most of catalyst particles were near-spherical. Pham et al. [23] reported that spherical particles were more attrition resistant than non-spherical particles. The particle shape indicated the prepared catalysts would have high attrition resistance. In accordance with the PSD measured by the Mastersizer, most of the particles were ten to a hundred micrometer. Fig. 8(3 and 4) shows microscopic views of the catalyst powder sphere. The A-4 catalyst was found to comprise wedge-like particles. It can be inferred that this kind of microstructure can provide more effective active sites for methanol synthesis, and maybe hindered copper crystallites from sintering during a long-term methanol synthesis reaction.

3.7. *Catalyst stability*

High activity, high selectivity and long life time are the three essential requirements for an excellent catalyst. Unlike FCC catalyst, a Cu-based catalyst used for methanol synthesis cannot be regenerated online. Thus, a long life time is of special significance for fluidized bed methanol synthesis. In the preparation of the fluidized bed catalysts, many binders were also used for the improvement of attrition resistance. Unfortunately, it was found in our experiments that all the binders such as Al_2O_3, SiO_2 and kaolin caused the catalytic activity to drop significantly as the reaction was run for a longer time. The present series of catalysts does not use any such binders.

It is shown in Fig. 9 that the prepared Cu-Zr-Zn catalyst showed high stability for methanol synthesis. To investigate the catalyst stability, 260 °C was used as the reaction temperature for the acceleration of deactivation (230 °C is usually used for methanol synthesis) [24]. For a reaction time as long as 120 h, no obvious deactivation was observed. This proved the high catalyst stability of the Cu-Zr-Zn catalyst (A-4).

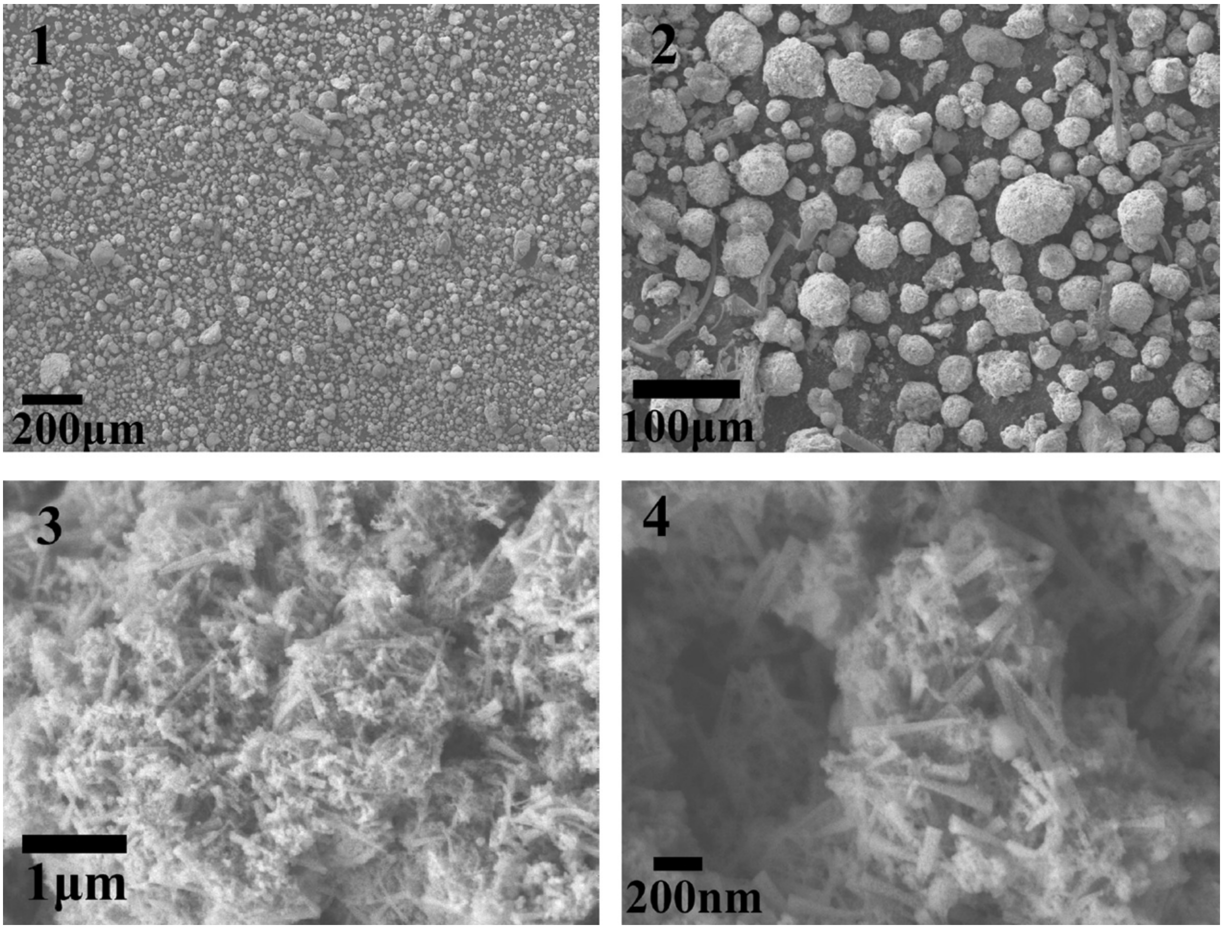

Fig. 8. SEM images of A-4 catalyst with different magnifications.

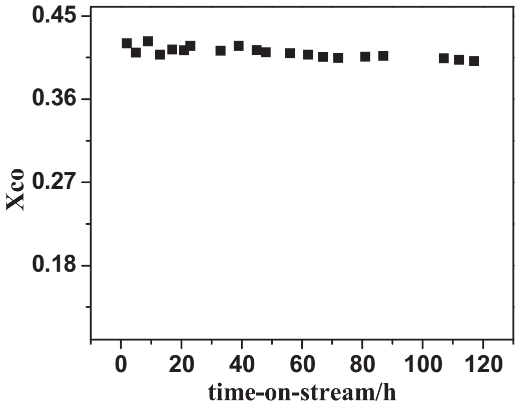

Fig. 9. Long-term activity of A-4 catalyst at the reaction temperature of 260 °C (up to 120 h).

4. Conclusions

The methanol synthesis activity of Cu-Zr-Zn catalysts first increased and then decreased as the Cu/Zn ratio increased, but monotonically decreased as the (Cu + Zn)/Zr ratio decreased. The attrition resistance increased as the ZrO_2 content increased. Taking activity and attrition resistance into consideration, the optimal composition was Cu:Zr:Zn = 4.5:3:1.5. PSD and SEM characterization indicated that the catalyst particles were suitable for use in a fluidized bed reactor. More importantly, the catalysts prepared in this work showed good catalytic stability during methanol synthesis in a fluidized bed reactor.

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