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A novel process for preparation of a $Cu/ZnO/Al_2O_3$ ultrafine catalyst for methanol synthesis from $CO_2 + H_2$: comparison of various preparation methods

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Abstract

The effect of preparation methods on the structure and catalytic behavior of $Cu/ZnO/Al_2O_3$ catalysts for methanol synthesis from hydrogenation of carbon dioxide has been studied. The $Cu/ZnO/Al_2O_3$ ultrafine catalysts obtained by a novel gel-coprecipitation process exhibited higher catalytic activity for the synthesis of methanol from $CO_2 + H_2$. The results showed that isomorphous substitution took place between copper and zinc in the precipitates prepared by the novel process. Preparation methods have a significant influence on the structure of the catalyst and catalytic activity for methanol synthesis from hydrogenation of carbon dioxide.

Keywords: Oxalate gel-coprecipitation; $Cu/ZnO/Al_2O_3$ catalyst; CO_2 hydrogenation; Methanol synthesis

1. Introduction

The effective utilization of CO_2 is of great significance from the point of view of global environmental protection, and has attracted much attention. One means of utilization of CO_2 is synthesis of methanol from CO_2 hydrogenation. However, the $Cu/ZnO/Al_2O_3$ catalyst prepared by conventional coprecipitation methods, having a considerably high activity for methanol synthesis from

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syngas, exhibits a very poor activity for the hydrogenation of CO_2 [1]. Therefore, many efforts have recently been made to develop new catalysts for methanol synthesis from $CO_2 + H_2$ [2–6]. Supported Pd catalysts [7,8] showed a higher selectivity for methanol production, but its catalytic activity and space time yield (STY) of methanol were very low. Koeppel and Baiker [9] prepared Cu/ZrO_2 catalysts for the synthesis of methanol from carbon dioxide hydrogenation by conventional precipitation, ion exchange and impregnation methods, and investigated the influence of the preparation variables on the catalytic behavior of copper/zirconia catalysts. High activity and selectivity for the synthesis of methanol from $CO_2 + H_2$ have been obtained in their work. Inui et al. [1] reported that the $Cu/ZnO/Al_2O_3$ catalyst prepared by the intrinsic uniform gelatin method showed higher activity for methanol synthesis from CO_2 hydrogenation. It indicated that the catalytic activity was greatly influenced by the preparation methods.

In this paper, a novel method of the oxalate gel-coprecipitation method was proposed to prepare a $Cu/ZnO/Al_2O_3$ ultrafine catalyst. The structure, morphology and catalytic activity of the catalysts were studied.

2. Experimental

2.1. Preparation of catalyst

Three $Cu/ZnO/Al_2O_3$ catalysts, all with a molar ratio of copper, zinc and aluminum 45:45:10, were prepared by different methods. A typical procedure to prepare a precursor CZA01 is as follows: an aqueous solution (1 M) of 20% excess of oxalic acid is added rapidly to a mixed aqueous solution (each 0.1 M) of copper nitrate, zinc nitrate and aluminum nitrate at room temperature under vigorous stirring. The precipitates are formed and separated by centrifuge, then dried at 110°C overnight. The precipitates show no volume shrinkage during the drying process. This method is referred to as conventional oxalate coprecipitation. A novel procedure to prepare a precursor CZA02 is similar to the procedure of preparing the precursor CZA01 mentioned above. However, the solvent used in the novel procedure is ethanol (provided by Shanghai Chemical Reagent Institute, a.r. reagent, purity $\geqslant$ 99.5%). The volume of the precipitates prepared by the novel procedure is shrunk to 1/5 of its original volume after drying. Obviously, the precipitates show a gel character. This novel method is referred to as oxalate gel-coprecipitation. The precursor CZA03 is prepared by the conventional carbonate coprecipitation method. A mixed aqueous solution of copper nitrate, zinc nitrate and aluminum nitrate (each 0.1 M) and a solution of sodium carbonate (0.1 M) are added slowly and simultaneously into 100 ml of deionized water at 80°C with vigorous stirring. The pH is kept constant at 6.5–7.0. The precipitates are aged at 50°C for 30 min under gentle stirring, and then filtered and thoroughly washed with hot deionized water. The precipitates are dried at 110°C overnight.

Moreover, in order to investigate the change of structure and morphology with the change of the composition, a series of precursors of oxalate precipitate with various compositions were also prepared by the novel process.

All precipitates were calcined on a muffle oven at 150°C for 1 h, 200°C for 1 h, 250°C for 1 h, 300°C for 1 h and 360°C for 4 h.

2.2. Catalyst characterization

The catalyst samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), nitrogen physisorption measurements, nitrous oxide titration and thermal analysis (TG/DTG).

XRD patterns were recorded using a Rigaku Dmax-rA X-ray diffractometer with CuKα radiation. TEM was measured with a Hitachi H600 scan-transmission electron microscope. Full nitrogen adsorption/desorption isotherms at −196°C were obtained after outgassing of the sample under vacuum at 150°C for 4 h, using a Micromeritics ASAP2000 physical adsorption apparatus. Specific surface area (S_{BET}) is calculated using a value of 0.162 nm^2 for the cross-sectional area of the nitrogen molecule [10]. Pore size distributions were determined following the BJH method [11] using the equation of Halsely [12]. Nitrous oxide experiments were carried out using a pulse technique similar to that reported by Evens et al. [14]. Copper metal surface areas (S_{Cu}) were calculated assuming 1.46×10^9 copper atoms per m^2 [13,14] and an adsorption stoichiometry of $Cu_{(s)}/O_{ads} = 2$. The accuracy of the copper surface area measurement is within 5%.

Thermogravimetric (TG/DTG) studies were carried out using a Dupont-951 thermoanalyzer. Measurements were performed in air or nitrogen with a heating rate of 5°C min^{-1}.

2.3. Catalytic activity testing

The catalytic activity for hydrogenation of CO_2 was measured with a continuous tubular flow fixed-bed microreactor as shown in Fig. 1. The catalyst (40–60 mesh size, 0.5 ml) was packed into a stainless steel reactor (i.d. = 6.0 mm) and reduced in flowing premixed H_2/Ar (5/95) flow of 40 ml min^{-1} (NTP). The temperature was raised to 240°C at a heating rate of 2°C min^{-1} and held for 10 h. While being cooled to 110°C the reduction gas was switched to a reactant gas ($CO_2/H_2 = 1/3$). The reaction was carried out at a pressure between 0.5 and 4.0 MPa and the temperature in the range of 180°C to 300°C and at a space velocity (SV) of 3600 h^{-1} to 10000 h^{-1}. The flow rate of reactant gas was controlled by a mass flow controller. The reaction temperature was controlled by a temperature controller and measured with a chromel–alumel

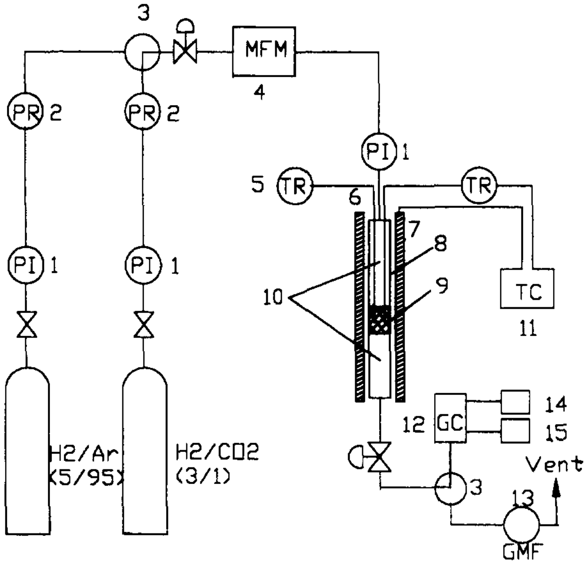

Fig. 1. Schematic diagram of the reaction apparatus: (1) pressure gauge, (2) pressure regulator, (3) gas exchange value, (4) mass flow meter, (5) temperature recorder, (6) thermocouple, (7) electric oven (8) reactor, (9) catalyst, (10) silica, (11) temperature controller, (12) gas chromatograph, (13) bulb gas flow meter, (14) recorder, (15) integrator.

thermocouple. The pressure was controlled and monitored by a pressure regulator. The products were analyzed by an on-line gas chromatograph with a thermal conductivity detector. Two parallel connected columns were employed. Porapak-Q column (2 m) is used to separate CH_3OH, dimethyl ether, higher alcohol and other hydrocarbon products. TDX-01 column (2 m) (provided by Tian-Jing No. 2 Chemical Regent Company) was used to separate CO, CO_2 and CH_4. The alternation of the two columns was performed by two valves connected to the system. The stainless steel line between reactor and GC was heated by a heating tape at 150°C to avoid condensation of some products. The conversion of CO_2 is defined as: (mol carbon dioxide converted to all products)/(mol carbon dioxide in the feed gas). The methanol selectivity is defined as: (mol methanol)/(mol carbon dioxide converted to all products). The error of the conversion and selectivity measurements is $\leqslant 4\%$ of the obtained value.

3. Results and discussions

3.1. Structure and morphology of oxalate precursors

The XRD patterns of the oxalate precursors prepared by conventional oxalate coprecipitation and the novel gel-coprecipitation are shown in Fig. 2. The major diffraction peaks for the sample prepared by conventional method were observed

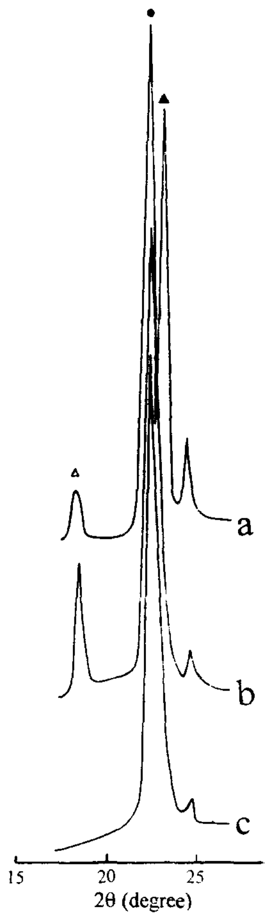

Fig. 2. XRD patterns of the precipitates prepared by various methods. (a) conventional oxalate coprecipitation (Cu:Zn:Al = 45:45:10), (b) oxalate gel-coprecipitation (Cu:Zn:Al = 45:45:10) and (c) oxalate gel-coprecipitation (Cu:Zn:Al = 60:30:10). △: α-$ZnC_2O_4 \cdot 2H_2O$, ●: $CuC_2O_4 \cdot xH_2O$, ▲: β-ZnC_2O_4.

at 2θ angles of 18.6°, 22.9° and 23.7°. But only two major diffraction lines for the precursor prepared by the novel method were observed at 2θ angles of 18.6° and 22.9°. The peaks at 2θ of 18.6°, 22.9° and 23.7° were identified as the diffraction lines of α-$ZnC_2O_4 \cdot 2H_2O$, $CuC_2O_4 \cdot xH_2O$ and β-ZnC_2O_4, respectively. It indicates that no β-ZnC_2O_4 is formed in the novel process. Among the three species, $CuC_2O_4 \cdot xH_2O$ (Moolooite, orthorhombic, with space lattice Pnnm) is the crystal disordered along the b_0 direction. If the water content is in the range of $0 \leqslant x \leqslant 1$, $CuC_2O_4 \cdot xH_2O$ is of the zeolitic type. The spacing and intensity of its XRD may vary slightly with x. A very weak diffraction line at 18.6° compared to 22.9° was observed for the sample with Cu/Zn ratio of 1, and only a diffraction line of the $CuC_2O_4 \cdot xH_2O$ phase is observed for the sample with a Cu/Zn ratio of 2. It indicates that a considerable amount of zinc

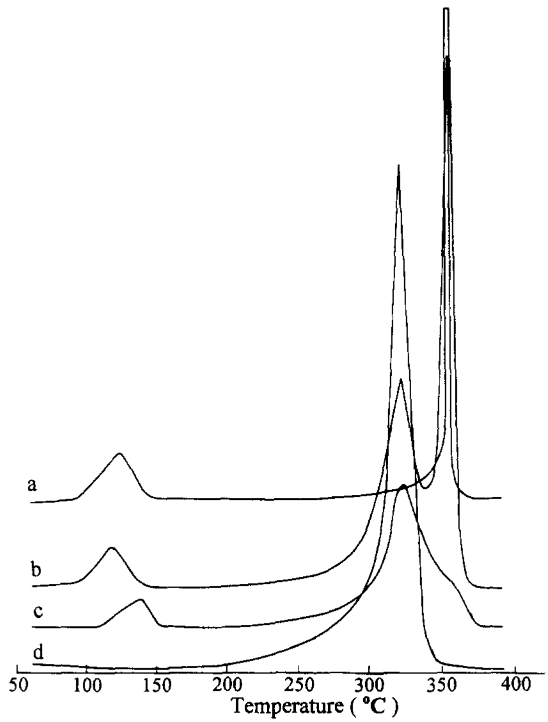

Fig. 3. DTG patterns of the oxalate precipitates with various composition prepared by gel-coprecipitation method. (a) (Cu:Zn:Al = 10:80:10), (b) (Cu:Zn:Al = 30:60:10), (c) (Cu:Zn:Al = 45:45:10), (d) (Cu:Zn:Al = 60:30:10).

is incorporated into the $CuC_2O_4 \cdot xH_2O$ structure. This can be confirmed further by the thermogravimetic (TG/DTG) analysis for the precipitates of oxalate with various compositions. In the differential thermal gravimetric (DTG) spectra (Fig. 3), three peaks for the loss of weight are observed at 110°C, 322°C and 358°C. The peak at about 110°C is due to the desorption of physically absorbed water. The peaks at 322°C and 358°C are ascribed to the decomposition of oxalate precipitates, which are denoted as the α and β peak, respectively. With the increase of copper content, the α peak increases while the β peak decreases. Obviously, α and β peaks could be assigned to the decomposition of CuC_2O_4 and ZnC_2O_4 phases, respectively. Only the β peak is observed when $Cu/Zn < 1/8$; and only the α peak is observed at $Cu/Zn > 2$. It indicates that the precipitates are present in the monophase under these two conditions. This means that only the ZnC_2O_4 phase is formed at lower copper content and only the CuC_2O_4 phase is formed at higher copper content. It indicates that the isomorphous substitution between Cu and Zn takes place in the precipitates prepared by the novel process. The diffraction peaks of the oxalate precursors prepared by novel method are broader than those by conventional method. This indicates that much smaller particles are formed in the novel oxalate gel-

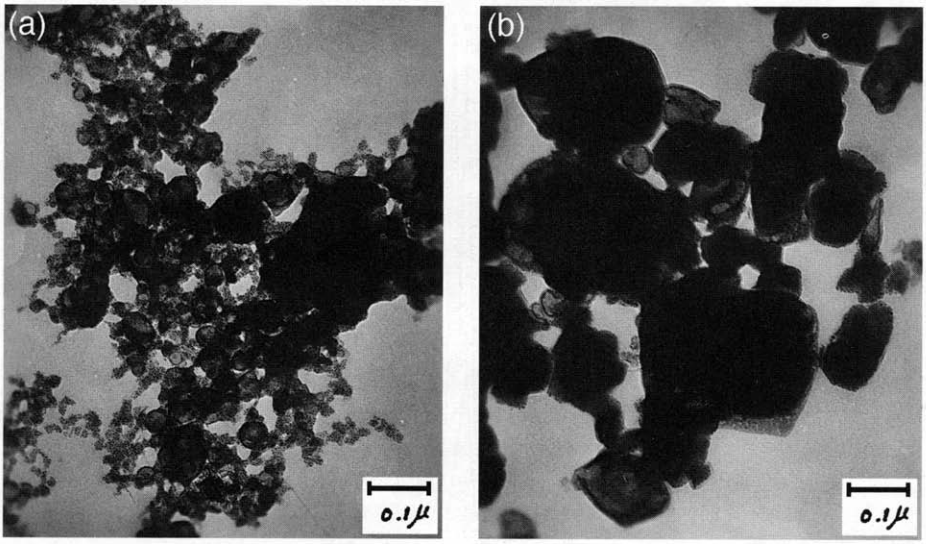

Fig. 4. TEM of the oxalate precipitates. (a) Prepared by the oxalate gel-coprecipitation method, (b) prepared by the conventional oxalate coprecipitation method.

coprecipitation process. The TEM photograph in Fig. 4 reveals clearly that very small quasi-spherical particles are formed in the novel process and much larger particles are detected in the precipitates prepared with the conventional method. Obviously, the novel method produces ultrafine particles of oxalate precursors, and ultrafine particles of the $CuO/ZnO/Al_2O_3$ catalyst should be formed by decomposition of the oxalates at suitable conditions.

3.2. Characterization of calcined catalysts

The XRD pattern of the oxides is shown in Fig. 5. When the precursors are calcined according to the calcination procedure described above, only broad diffraction lines of CuO and ZnO are observed in the pattern (a). It indicates that the ultrafine particle catalyst is formed in the novel method.

It is also found from Table 1 that the copper metal surface area of the catalyst prepared by the novel method (CZA02) are significantly higher than those prepared by other methods (CZA01 and CZA03). It indicates that the copper dispersion of the catalyst prepared by the novel method is much higher than that of catalyst prepared by other methods. Namely, the oxalate gel coprecipitation method derives a much smaller copper crystallite size.

The BET surface area and the pore size distribution of the calcined catalyst are measured by N_2 adsorption at $-196°C$. The results are shown in Table 1 and Fig. 6. It is noticed that the catalyst prepared by the oxalate gel-coprecipitation has a higher BET surface area, larger pore volume and mean pore size than those prepared by other methods. It indicates that the particles of CuO and ZnO

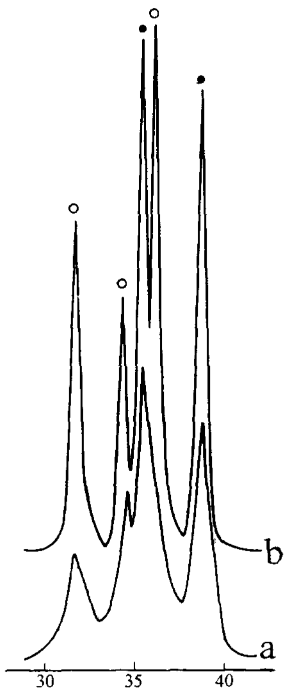

Fig. 5. XRD patterns of calcined $CuO/ZnO/Al_2O_3$ catalysts. (a) CZA02 (prepared by the oxalate gel-coprecipitation method), and (b) CZA01 (prepared by the conventional oxalate coprecipitation method). ○: ZnO, ●: CuO.

in the catalysts prepared by this new preparation method are much smaller. It is consistent with the results from the XRD and copper metal surface area. It is observed from Fig. 6 that the pore size distribution depends on the preparation method. The catalysts prepared by the conventional carbonate coprecipitation method have a broader pore size distribution, and its mean pore diameter of 10.1 nm is smaller than those of the catalysts prepared by the oxalate gel-coprecipitation method.

Table 1
Properties of the catalysts

Catalyst	Composition Cu/Zn/Al (at.-%)	BET surface area [a] ($m^2 g^{-1}$)	Pore volume ($ml g^{-1}$)	Pore diameter (nm)	Cu metal surface area [a] ($m^2 g^{-1}$)	Cu metal crystallite size [b] (nm)
CZA01	45/45/10	46.8	0.20	16.3	11.5	29.3
CZA02	45/45/10	63.8	0.23	13.8	28.8	10.7
CZA03	45/45/10	48.7	0.13	10.1	17.2	17.3

[a] The accuracy of the copper surface area is within 5%.
[b] The accuracy of the crystallite sizes determined is approximately 20%.

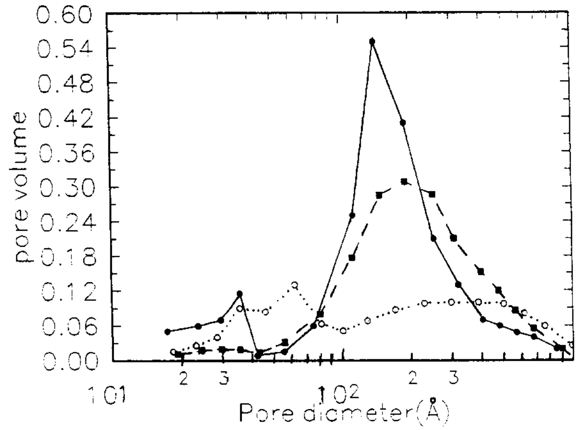

Fig. 6. Pore distribution of $CuO/ZnO/Al_2O_3$ catalysts prepared by various methods. ■: CZA01 (prepared by the conventional oxalate coprecipitation method), ●: CZA02(prepared by the oxalate gel-coprecipitation method, ○: CZA03(prepared by the conventional carbonate coprecipitation method).

3.3. Characterization of reduced catalysts

The XRD patterns of the reduced catalysts in Fig. 7 show obviously that copper oxide in the catalysts is completely reduced to metallic Cu, and no Cu_2O or CuO phases are detected. The mean crystallite size of metallic copper (D_{Cu}) is estimated from the half width of (111) reflection of Cu, using the Sherrer

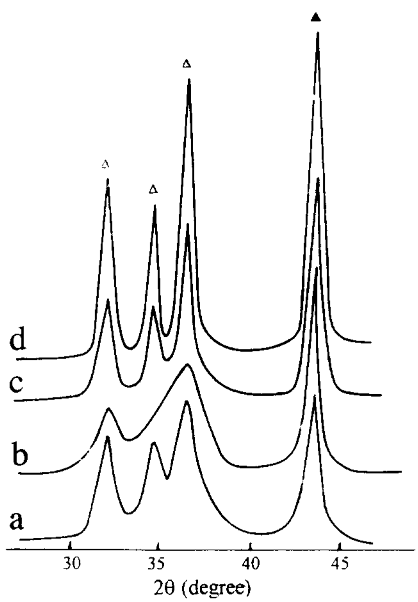

Fig. 7. XRD patterns of reduced $Cu/ZnO/Al_2O_3$ catalysts. (a) CZA02, (b) CZA02 (decomposition in vacuum), (c) CZA01. (d) CZA03. △: ZnO, ▲: Cu.

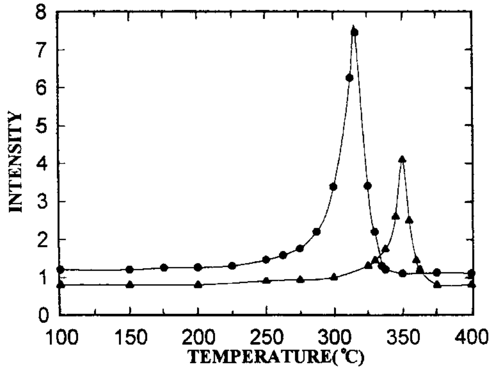

Fig. 8. DTG profiles of oxalate precursors in flowing air (●) and in nitrogen gas (▲).

equation: $D_{Cu} = 0.9\lambda/(\beta \cos \theta)$ after correction of the peak width for the contribution by instrumental broadening. The calculated results are listed in Table 1. It shows clearly that the catalyst prepared by the oxalate gel-coprecipitation has a much smaller copper crystallite size and larger copper surface area than the catalysts prepared by other methods. We found that the copper crystallite size of the catalyst obtained by decomposition in air and then reduced in H_2/Ar is much smaller than that by decomposition in vacuum directly. The reason can be ascribed to a different decomposition mechanism. The DTG curves shown in Fig. 8 reveal that the decomposition temperature of the oxalate precursor in air is about 40°C lower than that in nitrogen gas. The decomposition in vacuum condition produces metallic copper (see Fig. 7b).

3.4. Methanol synthesis by hydrogenation of CO_2

The catalytic activity and selectivity of methanol on various catalysts are listed in Table 2. Only two products (CH_3OH and CO) besides water are detected by gas chromatography. The yield of methanol from the catalyst prepared by the oxalate gel-coprecipitation (CZA02) is much higher than that

Table 2
Performance of methanol synthesis from $CO_2 + H_2$ on various catalysts

Catalyst	Compositions Cu/Zn/Al (at.-%)	SV [a] (h^{-1})	CO_2 conv. [a] (%)	CO select. [a] (%)	MeOH select. [a] (%)	Yield of MeOH [a] (mmol ml h^{-1})
CZA01	45/45/10	3600	19.3	77.7	22.3	1.73
		10000	16.8	76.6	23.4	4.35
CZA02	45/45/10	3600	19.3	63.7	36.3	2.81
		10000	17.6	62.1	37.9	7.37
CZA03	45/45/10	3600	15.8	77.2	22.8	1.45
		10000	15.1	78.1	21.9	3.68

[a] Reaction conditions: $T = 240°C$, $P = 2.0$ MPa, $CO_2/H_2 = 1/3$.

from the conventional carbonate coprecipitation (CZA03), while the yield of methanol from the catalysts prepared by the oxalate conventional coprecipitation (CZA01) is a little higher than that from the conventional carbonate coprecipitation (CZA03). It can be seen that there is no apparent correlation between the copper surface area measured by nitrous oxide titration and the catalytic activity. It indicates that the copper surface area alone cannot explain the catalytic behavior of the catalyst and the interaction of the copper particles with zinc oxide has an important influence on the catalytic activity. The catalysts have the same composition, but the yields of methanol vary significantly with the difference of preparation method. This can be attributed to the different structure and surface properties of the catalysts which is mentioned above.

4. Conclusions

An ultrafine $Cu/ZnO/Al_2O_3$ catalyst is produced by a novel oxalate gel-coprecipitation method. Preparation methods have a significant influence on the structure of the catalyst and catalytic activity for methanol synthesis from hydrogenation of carbon dioxide. Much of the zinc species is incorporated into the structure of $CuC_2H_4 \cdot xH_2O$ precursors which lead to form a ultrafine $CuO/ZnO/Al_2O_3$ catalyst when they are calcined in air at 360°C. The catalyst prepared by the oxalate gel-coprecipitation exhibits a higher activity for methanol synthesis from hydrogenation of CO_2 than those prepared by conventional methods.

Acknowledgements

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