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Methanol synthesis from CO_2 over Cu/ZnO catalysts prepared from various coprecipitated precursors

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Abstract

Various precursors of Cu/ZnO catalysts were prepared by coprecipitation methods. By varying the conditions of coprecipitation, precursors having different structures (aurichalcite, malachite, hydrozincite, or their mixture) were obtained at given Cu/Zn ratios, ranging from 30/70 to 70/30. In a wide range of the Cu/Zn ratios, the catalysts derived from the precursors containing aurichalcite exhibited high performance in the methanol synthesis from CO_2. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Methanol synthesis from CO_2 is one means of utilizing CO_2. Coprecipitated Cu/ZnO-based catalysts exhibit high performance for this reaction. For the binary system, coprecipitated precursors consisted of hydrozincite $Zn_5(CO_3)_2(OH)_6$, aurichalcite $(Cu_x,Zn_{1-x})_5(CO_3)_2(OH)_6$, malachite $Cu_2(CO_3)(OH)_2$, rosasite $(Cu_x,Zn_{1-x})_2(CO_3)(OH)_2$, or their mixtures [1,2]. The structures of the precursors varied with the Cu/Zn molar ratio, the preparation method employed and the conditions of the preparation. The activity of Cu/ZnO-based catalysts for the methanol synthesis is known to depend on the catalyst precursors [1–4]. However, the activities were often evaluated for the catalysts derived from the precursors having different Cu/Zn molar ratios. Even though the activities were compared at the same catalyst composition, the composition was limited in a narrow range of Cu/Zn molar ratios [3,4].

In the present study, the precursors of Cu/ZnO catalysts are prepared from copper and zinc nitrates and sodium bicarbonate by coprecipitation methods. It is shown that the structures of the precursors are greatly affected by the rate of addition of the nitrates and the concentration of the sodium bicarbonate solution. On the basis of these results, precursors having different structures are successfully obtained at given Cu/Zn ratios ranging from 30/70 to 70/30. Methanol synthesis from CO_2 is carried out over Cu/ZnO catalysts derived from these precursors. It is shown that the catalysts prepared from aurichalcite are more active than those prepared from the other precursors for the reaction.

2. Experimental

Precursors of Cu/ZnO catalysts with Cu/Zn molar ratios in a range from 30/70 to 70/30 were prepared by

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coprecipitation methods similar to that adopted by Porta et al. [5]. Fifty cm^3 of a 1 M solution of copper and zinc nitrates was added to 100 cm^3 of a 1.2 M solution of $NaHCO_3$ (pH 8.2) over a period of 90 min (method 1) or 20 min (method 2) at 338 K under continuous stirring. The precipitates formed were further aged for 90 min under stirring at the same temperature. The precipitates were then filtered out, washed with hot distilled water, and dried in air at 373 K overnight. In some of the runs, the concentration of $NaHCO_3$ used for the preparation was varied and the total amount of $NaHCO_3$ was kept at 0.12 mol by varying the volume of the solution.

Precursors, thus prepared, were calcined in air at 623 K for 4 h. The catalyst was first reduced in a reactor with a helium stream containing 3 vol% of H_2 at 483 K for 1 h. The reduction temperature was then raised stepwise from 483 to 523 K at 10 K/h and, finally, kept at 523 K for 1 h under a pure H_2 stream.

The prepared precursors were analyzed by the X-ray diffraction (XRD) method, differential thermal analysis (DTA) and thermal gravimetric analysis (TGA). XRD spectra were measured on an XRD diffractometer by using Ni filtered CuK_α radiation. DTA and TGA runs were carried out in air at a heating rate of 10 K/min. Amounts of the precursors were determined on the basis of the integrated intensities of the XRD peaks or DTA peaks of the mechanically mixed authentic samples in variable ratios.

The crystallite sizes of CuO and ZnO of the calcined catalysts and that of Cu were evaluated from the full width at half maximum of the CuO(111), ZnO(100) and Cu(111) XRD peaks by using the Scherrer equation. A correction for the instrumental broadening was carried out.

Methanol synthesis from CO_2 was carried out with a CO_2–H_2 mixture ($CO_2/H_2=1/9$) in a flow reactor at atmospheric pressure. Turnover frequency of the reaction was calculated by using the copper dispersion of the reduced catalysts determined by temperature-programmed oxidation with N_2O [6].

3. Results and discussion

Composition of the precursors with Cu/Zn ratios of 70/30 to 30/70 was greatly affected by the rate of the addition of the nitrates to the $NaHCO_3$ solution [7]. Fig. 1 summarizes the variation of the composition with Cu/Zn ratio for the precursors prepared by methods 1 and 2. The precursors prepared by method 1 consist of malachite at the Cu/Zn ratios between 70/30 and 50/50. At the Cu/Zn ratio of 30/70, the precursors prepared by this method consists of a mixture of malachite and hydrozincite. The structures of the precursors prepared by method 2 were different from those of the precursors prepared by method 1. At the Cu/Zn ratio of 30/70, the precursor produced by method 2 only comprises aurichalcite. At higher Cu/Zn ratios, the precursors prepared by this method are mixtures of aurichalcite and malachite.

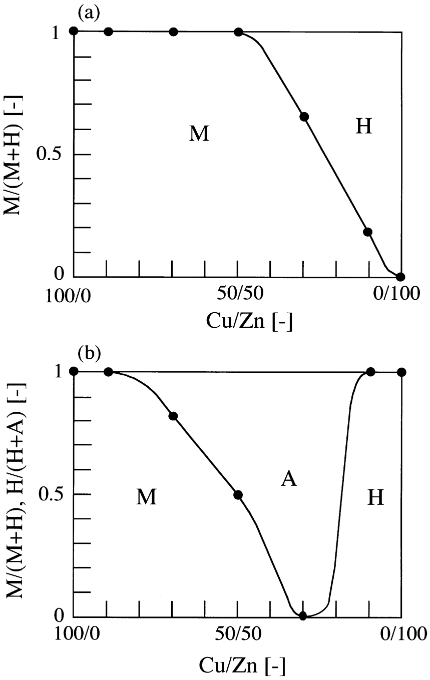

Fig. 1. Variation of the composition of precursor with Cu/Zn ratio. (a) method 1; and (b) method 2. M, malachite; H, hydrozincite; and A, aurichalcite.

DTA measurements of the precursors showed that the peak of the decomposition of hydrozincite or malachite was broader and shifted to higher temperatures than that of pure copper malachite or pure zinc hydrozincite. This suggested that, in the Cu–Zn binary systems, zinc(II) and copper(II) ions were incorporated, respectively, in malachite (zincian-malachite) and in hydrozincite (copper–hydrozincite).

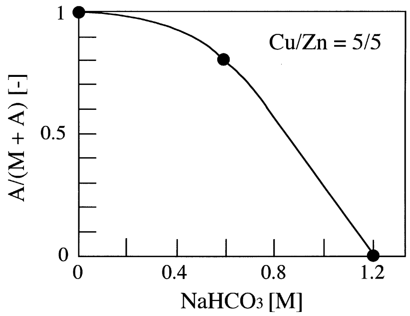

Fig. 2. Effect of the $NaHCO_3$ concentration on the composition of precursor. Precursors were prepared by method 1.

The concentration of $NaHCO_3$ solution used for the preparation also exerts strong influence on the structures of the precursors. Fig. 2 illustrates the variation of the structure of the precursors with the concentration of the $NaHCO_3$ solution. In case of lower concentrations of $NaHCO_3$, the precursor contains more aurichalcite. In 0.1 M solution of $NaHCO_3$, aurichalcite is selectively produced even at the Cu/Zn ratio of 50/50.

Based on these results, we obtained precursors having different structures at Cu/Zn ratios ranging from 30/70 to 70/30 by varying the preparation conditions, such as the rate of the addition of the nitrates and the concentration of the $NaHCO_3$ solution. In Table 1, the composition of the precursors prepared, the crystallite sizes of CuO and ZnO for calcined catalysts and that of Cu for reduced catalysts are listed. The crystallite sizes of CuO and ZnO tend to decrease with increasing contents of aurichalcite in the precursor. This is further evidenced for the crystallite size of Cu. The catalysts prepared from the precursor containing aurichalcite have smaller copper crystallites, regardless of the Cu/Zn ratio.

Table 1
Effects of the structure of the precursor on the crystallite size

Catalyst	Cu/Zn	Precursor [a] (mol% of A)	Crystallite size (nm) CuO	ZnO	Cu
1	30/70	M+H (0)	8.1	12.3	12.8
2	30/70	A (100)	4.9	9.1	5.3
3	50/50	M (0)	10.5	11.1	11.6
4	50/50	A+M (50)	9.1	8.3	8.2
5	50/50	A (100)	7.6	7.7	5.3
6	60/40	M (0)	8.0	8.8	12.8
7	60/40	A+M (40)	9.5	9.2	10.8
8	60/40	A+M (70)	10.3	7.5	11.8
9	70/30	M (0)	8.2	9.1	12.7
10	70/30	A+M (20)	8.3	6.8	11.9

[a] M, zincian-malachite; H, copper-hydrozincite; A, aurichalcite (number in the parentheses represents mol% of A in the precursor).

Aurichalcite has a complex sheet structure in which tetrahedral and octahedral layers alternate in the (100) direction. Hinmelfarb et al. [8] previously suggested that zinc(II) and copper(II) ions in aurichalcite are preferentially located at tetrahedral and octahedral sites, respectively, and, thus, the sheet structure of aurichalcite results in a fine interdispersion of CuO and ZnO in the calcined catalysts. This fine interdispersion should cause the highly dispersed Cu crystallites in the reduced catalysts obtained from the precursors containing aurichalcite.

The catalysts derived from the precursors, thus prepared, were then subjected to the methanol synthesis from CO_2. Table 2 compares the effects of the structure of the precursors on methanol synthesis. It is to be noted that the catalysts prepared from the precursors, rich in aurichalcite, always show high activity and selectivity for the methanol synthesis at various Cu/Zn ratios. At given Cu/Zn ratios, these catalysts also exhibit high turnover frequencies for the methanol synthesis. Comparison of the results in Tables 1 and 2 suggests that the turnover frequency varies with the copper dispersion at given Cu/Zn ratios. However, it is evident that the turnover frequency of the methanol formation is not simply dependent on the crystallite size of Cu, as seen from Tables 1 and 2. The turnover frequency also varies with the Cu/Zn ratio.

Previously, we studied the mechanism of the methanol synthesis from CO_2 over Cu/ZnO catalysts by the use of IR spectroscopy and temperature-programmed desorption method [9,10]. It was found that methoxide species formed on ZnO was responsible for the formation of methanol, the zinc methoxide species were produced via the hydrogenation of copper formate, and the rate of the hydrogenation was practically the same as that of the methanol synthesis. Hence, these results suggested that both, Zn and Cu on the surface of Cu/ZnO are involved in methanol synthesis. In conformity with this, several authors proposed that the Cu–O–Zn or Cu–Zn sites were active sites for methanol synthesis from CO_2 [11–14]. It was also suggested that the turnover frequency of the methanol

Table 2
Effects of the structure of the precursor on the activity of methanol synthesis [a]

Catalyst	Precursor [b] (mol% of A)	Rate (μmol/min/g-cat)		Turnover frequency × 10^5 (s^{-1})		S [c] (%)
		CH_3OH	CO	CH_3OH	CO	
1	M+H (0)	0.41	1.15	2.60	6.47	28.7
2	A (100)	2.02	2.32	4.73	5.44	46.5
3	M (0)	1.34	1.42	4.12	4.36	48.6
4	A+M (50)	3.17	2.44	6.94	5.34	56.4
5	A (100)	3.83	2.82	5.35	3.94	57.6
6	M (0)	1.49	2.32	4.07	6.34	39.1
7	A+M (40)	2.27	1.82	5.41	4.33	55.5
8	A+M (70)	4.17	3.09	10.7	7.96	57.4
9	M (0)	1.82	2.12	4.36	5.08	46.1
10	A+M (20)	2.69	1.70	6.0	4.12	61.3

[a] The reaction was carried out at 438 K with a CO_2/H_2 ratio of 1/9. W/F=0.005 g min/cm^3.
[b] M, zincian-malachite; H, copper-hydrozincite; A, aurichalcite.
[c] Selectivity to methanol.

synthesis varies by the surface structure of copper crystallites [14]. Nakamura et al. [14] carried out methanol synthesis from CO_2 over various Zn-deposited Cu single crystals. They showed that Zn deposited on Cu(111) promoted the reaction, while Zn deposited on Cu(110) and Cu(100) retarded the reaction. It is to be noted that an intensity ratio I(111)/I(200) of Cu(111) and Cu(200) peaks in the XRD patterns of the present Cu/ZnO catalysts increased with the increased content of aurichalcite in the precursors, suggesting that the morphology of the copper crystallites varied by the precursors. Hence, there was a possibility that the surface structures of copper crystallites varied with the structure of the precursor, resulting in the variation of the turnover frequency. Thus, high performance of the catalysts, derived from the precursors containing aurichalcite, can probably be ascribed to the preferential emergence of particular surface Cu sites, such as Cu(111) surface modified with ZnO and the high dispersion of Cu.

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References

[1] J.C.J. Bart, R.P.A. Sneeden, Catal. Today 2 (1987) 1.
[2] G. Ghiotti, F. Boccuzzi, Catal. Rev. Sci. Eng. 29 (1987) 151.
[3] D. Waller, D. Stirling, F.S. Stone, M.S. Spencer, Faraday Discuss. Chem. Soc. 87 (1989) 107.
[4] J.L. Li, T. Inui, Appl. Catal. A 137 (1996) 105.
[5] P. Porta, S. De Rossi, G. Ferraris, M. Lo Jacono, G. Minelli, G. Moretti, J. Catal. 109 (1988) 367.
[6] S. Fujita, S. Matsumoto, N. Takezawa, Catal. Lett. 25 (1994) 29.
[7] G.C. Shen, S. Fujita, N. Takezawa, J. Catal. 138 (1992) 754.
[8] P.B. Himelfarb, G.W. Simmons, K. Klier, R.G. Herman, J. Catal. 93 (1985) 442.
[9] S. Fujita, M. Usui, E. Ohara, N. Takezawa, Catal. Lett. 13 (1992) 349.
[10] S. Fujita, M. Usui, H. Ito, N. Takezawa, J. Catal. 157 (1995) 403.
[11] G.J. Millar, C.H. Rochester, S. Bailey, K.C. Waugh, J. Chem. Soc. Faraday Trans. 88 (1992) 2085.
[12] O.S. Joo, K.D. Jung, S.H. Han, S.J. Uhm, D.K. Lee, S.K. Ihm, Appl. Catal. A 135 (1996) 273.
[13] J. Nakamura, T. Uchijima, Y. Kanai, T. Fujitani, Catal. Today 28 (1996) 223.
[14] J. Nakamura, L. Nakamura, T. Uchijima, T. Watanabe, T. Fujitani, Studies Surf. Sci. Catal. 101 (1996) 1389.