

## Selective Hydrogenation of Carbon Dioxide to Methanol on Cu-ZnO/SiO<sub>2</sub> Catalysts Prepared by Alkoxide Method

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Hydrogenation of CO<sub>2</sub> to methanol was carried out on Cu-ZnO/SiO<sub>2</sub> catalysts at 493 K and 3 MPa with a flow rate of 100 cm<sup>3</sup> min<sup>-1</sup> (H<sub>2</sub>/CO<sub>2</sub>=2). Higher selectivity (>90%) was observed on the catalysts prepared by the alkoxide method than on a conventional catalyst prepared by the impregnation method. The selectivity was higher on the catalysts pretreated with H<sub>2</sub> at a higher temperature, except at 873 K. The activity of the catalyst pretreated at 873 K was extremely low, probably because of alloy formation. The results of XRD, XPS, and EXAFS demonstrate that the active species for methanol formation is a large metallic Cu particle covered with a partially oxidized layer interacting with highly dispersed ZnO.

Carbon dioxide is selectively hydrogenated to methanol on supported Cu-Zn catalysts (Cu-ZnO/MO<sub>x</sub>).<sup>1-3)</sup> The active site is supposed to be metallic Cu in this system, and a synergistic effect of Cu and Zn is noted where the methanol yield and selectivity increase in the presence of Zn. It is of much importance to elucidate the interaction between Cu and Zn in the system for a better understanding of this effect. Dispersion of the metals is one of the key factors determining the interaction. It has been reported that dispersion of metals can be well controlled in the catalysts prepared by the alkoxide method.<sup>4-9)</sup> From this point of view, Cu-ZnO/SiO<sub>2</sub> catalysts were prepared by this method, and the particle sizes of metals were uniformly controlled by changing the pretreatment temperature. The pretreatment effects on the selectivity are discussed.

### Experimental

Silica supported Cu-Zn catalysts (Cu-ZnO/SiO<sub>2</sub>; 5 wt% Cu and 5 wt% Zn) were prepared from tetraethyl orthosilicate, copper(II) and zinc nitrates (or acetates), and ethylene glycol by

the alkoxide method, according to the procedure reported by Sodesawa et al.<sup>8,9)</sup> A conventional Cu-ZnO/SiO<sub>2</sub> catalyst was prepared by the incipient wetness method as a reference, by impregnating copper(II) and zinc nitrate solutions to Davison #57 silica gel (300 m<sup>2</sup> g<sup>-1</sup>). The catalysts were calcined at 673 K for 10 h, sieved into 16—32 mesh (0.5—1 mm in diameter), and reduced in a H<sub>2</sub> stream (100 cm<sup>3</sup> min<sup>-1</sup>) in a temperature range from 573 to 973 K for 4 h.

One gram of a catalyst was packed in a fixed bed flow reactor made of stainless steel, and hydrogenation of carbon dioxide was carried out by passing a pre-mixed gas (CO<sub>2</sub>:H<sub>2</sub>:Ar=3:6:1, 100 cm<sup>3</sup> min<sup>-1</sup>) at 493 K and 3 MPa. The effluent gas was analyzed by on-line gas chromatography. The products detected were methanol, CO, CH<sub>4</sub>, and H<sub>2</sub>O.

The particle sizes of metals in the catalysts were evaluated by XRD (X-ray diffraction) line broadening and CO chemisorption. The concentrations and the oxidation states of metals in the catalysts were determined by XRF (X-ray fluorescence analysis), XPS, and EXAFS (extended X-ray absorption fine structure).

### Results

The results of CO<sub>2</sub> conversion on the Cu-ZnO/SiO<sub>2</sub>

Table 1. Results of CO<sub>2</sub> Hydrogenation on Cu-ZnO/SiO<sub>2</sub> Catalysts<sup>a)</sup>

Run	Preparation method	H <sub>2</sub> Pretreat. temp./K	Yield/mmol g <sup>-1</sup> h <sup>-1</sup>			Selectivity/%		
			CH <sub>3</sub> OH	CO	CH <sub>4</sub>	CH <sub>3</sub> OH	CO	CH <sub>4</sub>
1	Impregnation <sup>b)</sup>	623	1.30	0.72	0.002	64.3	35.6	0.1
2	Impregnation <sup>b)</sup>	973	0.91	0.39	0.001	70.0	30.0	0.1
3	Alkoxide (nitrate) <sup>b)</sup>	573	0.45	0.47	0.001	48.9	51.0	0.1
4	Alkoxide (nitrate) <sup>b)</sup>	673	0.87	0.34	0.001	71.9	28.0	0.0
5	Alkoxide (nitrate) <sup>b)</sup>	773	0.31	0.053	0.001	85.9	13.9	0.3
6	Alkoxide (nitrate) <sup>b)</sup>	873	0.001	0.007	0.001	—	—	—
7	Alkoxide (nitrate) <sup>b)</sup>	973	0.30	0.031	0.001	90.6	9.1	0.3
8	Alkoxide (acetate) <sup>c)</sup>	573	0.35	0.52	0.001	40.2	59.7	0.1
9	Alkoxide (acetate) <sup>c)</sup>	673	0.56	0.30	0.001	64.8	35.1	0.1
10	Alkoxide (acetate) <sup>c)</sup>	773	0.091	0.024	0.001	78.3	21.0	0.8
11	Alkoxide (acetate) <sup>c)</sup>	873	0.021	0.018	0.001	53	45	2
12	Alkoxide (acetate) <sup>c)</sup>	973	0.196	0.027	0.001	87.4	12.2	0.5
13	Alkoxide Cu/SiO <sub>2</sub> <sup>c)</sup>	973	0.003	0.031	0.001	10	87	3

a) Reaction conditions:  $T=493$  K,  $P=3$  MPa, CO<sub>2</sub>:H<sub>2</sub>:Ar=3:6:1, flow rate=100 cm<sup>3</sup> min<sup>-1</sup>. b) Prepared from nitrates.

c) Prepared from acetates.

catalysts are summarized in Table 1. The selectivities to methanol and CO were about 64–70% and 36–30% on carbon basis on a conventional catalyst prepared by the impregnation method (Runs 1–2). A trace amount of CH<sub>4</sub> was detected as a by-product. On the catalysts prepared by the alkoxide method (Runs 3–12), the selectivity to methanol rose to 91% with a rise in reduction temperature, accompanied by a decrease in the catalytic activity (total yield). The activity on the catalysts prepared from acetates (Runs 8–12) was generally lower than that from nitrates (Runs 3–7). The activity was extremely low on the catalysts reduced at 873 K (Runs 6 and 11). The catalyst without Zn did not show high activity (Run 13), and gave CO as a main product.

Elemental analytical data obtained by XRF are listed in Table 2. The amount of Cu was almost unchanged by pretreatment with H<sub>2</sub>, and the amount of Zn decreased with a rise in the pretreatment temperature. After reduction at 973 K, the amounts of Zn in the catalysts prepared from nitrates and acetates were 0.8 and 0.2 wt%, respectively.

X-Ray diffraction patterns of calcined catalysts prepared by the alkoxide method did not show any peaks, indicating that the oxides were amorphous, or the

particle sizes were smaller than 3 nm. After reduction, XRD patterns showed exclusively the peaks for metallic Cu. The absence of Zn (and/or ZnO) peaks implies that Zn species are highly dispersed in the catalysts. The sizes of Cu crystallites were estimated on the basis of the peak width according to the Scherrer's equation,<sup>10</sup> and are given in Table 3. The crystallite sizes of metallic Cu in the catalysts prepared from nitrates and acetates increased with a rise in the pretreatment temperature, in a range of 20–50 nm and 7–12 nm, respectively. The particle size estimated by CO chemisorption, however, did not always agree with that estimated by XRD line broadening. Although the values coincided with each other in the conventional catalysts prepared by the impregnation method, the value from XRD line broadening was much smaller than that from CO chemisorption in the catalysts prepared by the alkoxide method.

Figures 1-1 and 1-2 show XRD peaks at about  $2\theta=43^\circ$ , corresponding to metallic Cu. Concomitantly with the changes in the peak widths, the peak positions shifted to lower angles by  $0.3^\circ$ , with a rise in the pretreatment temperature up to 873 K. The width of 873 K-pretreated catalysts prepared from acetates was  $1.3^\circ$ , and was much larger than that expected in this series. By considering the fact that the position of the corresponding peak of brass (a Cu-Zn alloy) was observed at  $2\theta=42.1^\circ$ , these results indicate that a Cu-Zn alloy was partially formed by reduction at higher temperatures. The peak position shifted back to a larger angle when the catalysts were pretreated at 973 K: This is because of a lowering of the Zn concentration due probably to its loss by sublimation, as verified by XRF.

Figure 2-1 shows the Fourier transforms of Cu K-edge EXAFS of used catalyst samples and standard samples, with phase-shift correction. The spectrum of metallic Cu (a) shows a peak at 2.7 Å, corresponding the Cu-Cu

Table 2. XRF Analysis of Cu-ZnO/SiO<sub>2</sub> Catalysts Prepared by the Alkoxide Method

H <sub>2</sub> Pretreated temp./K	Nitrate <sup>a)</sup>		Acetate <sup>b)</sup>	
	Cu/wt%	Zn/wt%	Cu/wt%	Zn/wt%
— <sup>c)</sup>	5.1	6.2	5.3	5.5
673	6.1	4.9	5.1	5.3
773	5.7	4.7	5.1	5.3
873	5.8	4.0	6.1	3.9
973	5.6	0.8	5.8	0.2

a) Prepared from nitrates. b) Prepared from acetates.  
c) Calcined.

Table 3. Particle Size of Cu-ZnO/SiO<sub>2</sub> Catalysts

Sample No.	Preparation method	H <sub>2</sub> Pretreat.	FWHM <sup>a)</sup>	Crystallite size	CO adsorbed	Particle size	TOF <sup>d)</sup>
		temp./K	deg.	nm	mol g <sup>-1</sup>	nm	h <sup>-1</sup>
1	Impregnation <sup>b)</sup>	623	0.43	24	44	20	46
2	Impregnation <sup>b)</sup>	973			12	70	108
3	Alkoxide (nitrate) <sup>b)</sup>	573	0.50	20			
4	Alkoxide (nitrate) <sup>b)</sup>	673	0.43	24	5	200	240
5	Alkoxide (nitrate) <sup>b)</sup>	773	0.43	24			
6	Alkoxide (nitrate) <sup>b)</sup>	873	0.29	40			
7	Alkoxide (nitrate) <sup>b)</sup>	973	0.25	50	<0.1	—	—
8	Alkoxide (acetate) <sup>c)</sup>	573	1.36	7	19	50	46
9	Alkoxide (acetate) <sup>c)</sup>	673	1.18	8	13	70	66
10	Alkoxide (acetate) <sup>c)</sup>	773	0.98	9	9	120	13
11	Alkoxide (acetate) <sup>c)</sup>	873	(1.30)	(7)	5	150	8
12	Alkoxide (acetate) <sup>c)</sup>	973	0.76	12	0.6	1600	370
13	Alkoxide Cu/SiO <sub>2</sub> <sup>c)</sup>	973	0.42	25			

a) Full width at half maximum of an XRD peak at  $2\theta=43^\circ$ . b) Prepared from nitrates. c) Prepared from acetates.  
d) Turnover frequency.

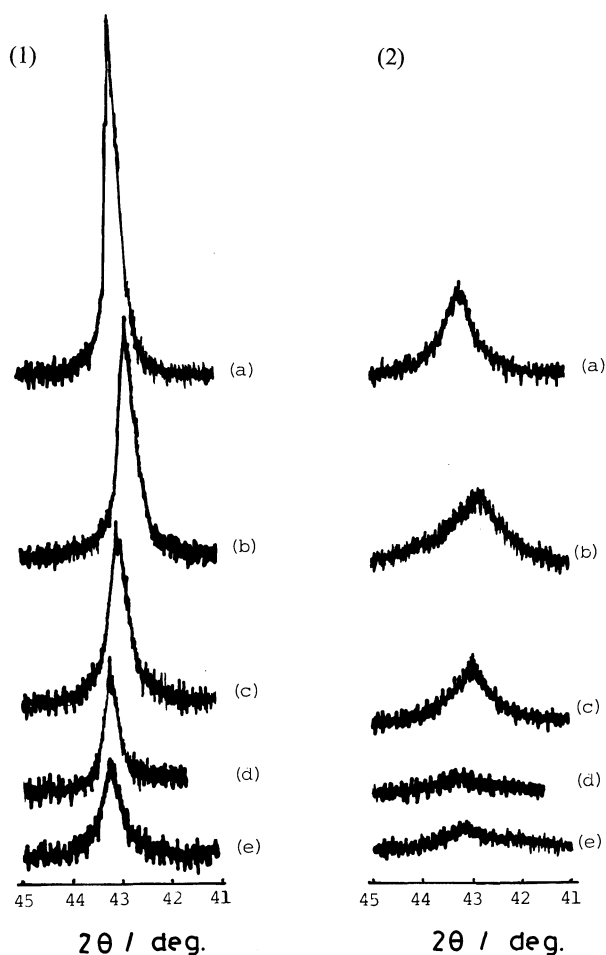


Fig. 1-1. XRD Profiles of Cu-ZnO/SiO<sub>2</sub> catalysts prepared by the alkoxide method from nitrates and reduced with H<sub>2</sub> at (a) 973 K, (b) 873 K, (c) 773 K, (d) 673 K, and (e) 573 K.

Fig. 1-2. XRD Profiles of Cu-ZnO/SiO<sub>2</sub> catalysts prepared by the alkoxide method from acetates and reduced with H<sub>2</sub> at (a) 973 K, (b) 873 K, (c) 773 K, (d) 673 K, and (e) 573 K.

bond length. A peak at 2.0 Å in the spectrum of CuO (b) is assigned to the Cu–O distance, and peaks at 3.0 and 3.4 Å are assigned to the Cu–O–Cu distances. The used catalyst prepared by the impregnation method (c) shows two peaks at 2.0 and 2.6 Å and a shoulder at about 3 Å, indicating that the Cu phase of the catalyst is a mixture of metallic Cu and an oxide. From the EXAFS profiles (d)–(g) of used catalysts prepared from nitrates by the alkoxide method and reduced at temperatures 573–973 K, the oxidation states of Cu in the catalysts are presumed as follows: The copper in the used catalyst reduced at 573 K exists mostly as Cu<sup>2+</sup>, whereas it is metallic in the catalysts reduced at 673–973 K. Since the EXAFS measurement was conducted in open air, small Cu particles in the catalysts were partly reoxidized during the measurement.

Figure 2-2 shows the Fourier transforms of Zn K-edge EXAFS of used catalyst samples and standard samples, with phase-shift correction. The EXAFS profile of ZnO (a) exhibits peaks at 2.0 and 3.3 Å, corresponding to the Zn–O and Zn–O–Zn distances, respectively. Only the former peak is mainly observed in the profile of used catalyst prepared by the impregnation method (b), suggesting that the Zn species in the catalyst is isolated and in the form of highly dispersed ZnO. A similar argument holds for the profiles of used alkoxide catalysts pretreated at 573 and 673 K (c and d). On the contrary, the used alkoxide catalyst pretreated at 873 K (e) shows two peaks at 2.0 and 2.6 Å. The position of the former peak was the same as that in other catalysts, and corresponds to the Zn–O distance. The latter is supposed to reflect the Zn–M distance, where M is a metal, indicating that a part of Zn is metallic. This results supports the possibility of alloy formation by the reduction at 873 K, if we could identify M as Cu (the atomic radii of Cu and Zn are very close to each other.)

Table 4 summarizes the XPS results for the catalysts reduced in situ in a temperature range of 673–973 K, together with that for a standard sample. The binding energies were corrected by referring to the C 1s peak of

Table 4. XPS Analysis of Cu–ZnO/SiO<sub>2</sub> Catalysts

Starting material	H <sub>2</sub> Pretreat. temp./K	E <sup>a</sup> /eV		FWHM <sup>b</sup> /eV		I <sup>c</sup>	
		Cu	Zn	Cu	Zn	Cu	Zn
Nitrate	(Calcined)	934.0	1024.0	3.1	2.4	4.5±1.7	8.4±1.5
Nitrate	673	933.3	1023.7	2.6	2.7	4.3±2.6	6.9±2.0
Nitrate	773	933.2	1023.2	2.4	3.1	3.6±1.8	7.2±1.4
Nitrate	873	933.5	1024.0	2.5	2.7	7.7±3.0	9.3±3.7
Nitrate	973	933.4	—	2.2	—	5.5±1.9	1.5±1.3
Acetate	673	933.5	1023.8	2.2	2.7	4.7±2.6	12.0±2.2
Acetate	773	933.4	1023.9	2.3	2.9	4.7±2.4	16.8±2.9
Acetate	873	933.4	1023.5	2.3	2.8	3.4±2.2	8.0±2.6
Acetate	973	933.3	—	2.1	—	3.6±3.0	2.5±2.3
Cu (metal) <sup>d</sup>	—	932.2	—	1.5	—	—	—

a) Values referenced to adsorbed carbon with C 1s=285.0 eV. b) Full width at half maximum. c) Relative intensity; Si=100. d) Standard sample.

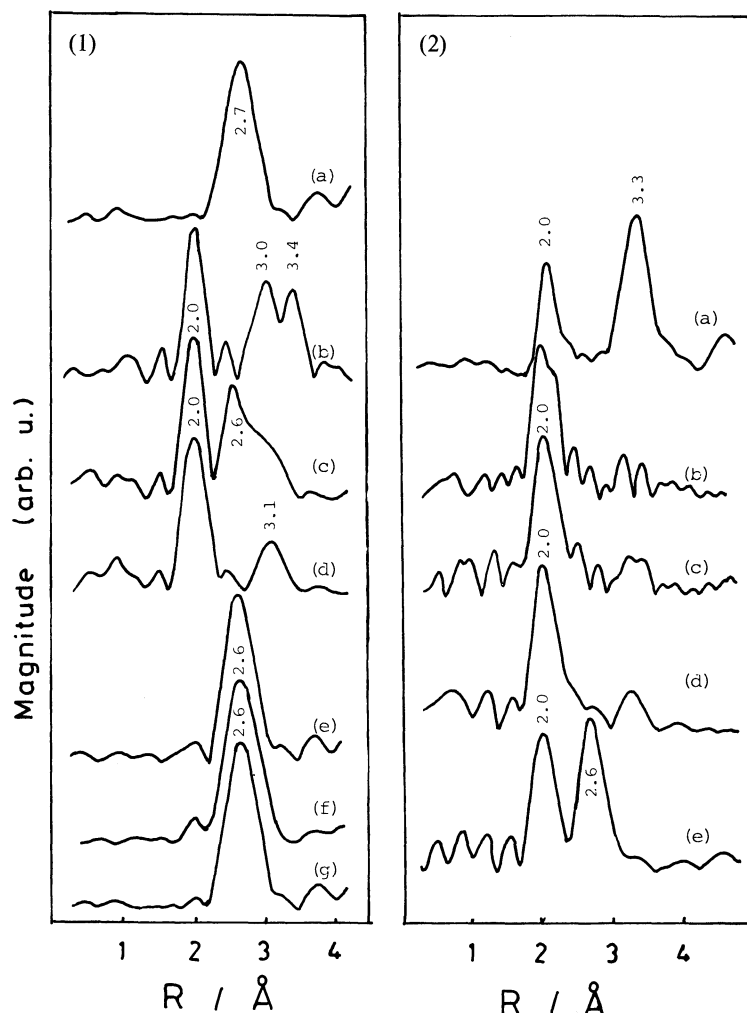


Fig. 2-1. Fourier transforms of Cu K-Edge EXAFS, with phase-shift correction, of (a) Cu, (b) CuO, (c) used Cu-ZnO/SiO<sub>2</sub> catalyst prepared by impregnation and reduced at 623 K, (d) used Cu-ZnO/SiO<sub>2</sub> catalyst prepared by the alkoxide method and reduced at 573 K, (e) used Cu-ZnO/SiO<sub>2</sub> catalyst prepared by the alkoxide method and reduced at 673 K, (f) used Cu-ZnO/SiO<sub>2</sub> catalyst prepared by the alkoxide method and reduced at 873 K, and (g) used Cu-ZnO/SiO<sub>2</sub> catalyst prepared by the alkoxide method and reduced at 973 K.

Fig. 2-2. Fourier transforms of Zn K-Edge EXAFS, with phase-shift correction, of (a) ZnO, (b) used Cu-ZnO/SiO<sub>2</sub> catalyst prepared by impregnation and reduced at 623 K, (c) used Cu-ZnO/SiO<sub>2</sub> catalyst prepared by the alkoxide method and reduced at 573 K, (d) used Cu-ZnO/SiO<sub>2</sub> catalyst prepared by the alkoxide method and reduced at 673 K, and (e) used Cu-ZnO/SiO<sub>2</sub> catalyst prepared by the alkoxide method and reduced at 873 K.

contamination carbon in the samples as an internal standard. The binding energy of the Cu 2p<sub>3/2</sub> peak in reduced catalysts is in a range of 933.2–933.5 eV, which is higher than that of metallic Cu by 1.0–1.3 eV, and lower than that of calcined catalyst by 0.5–0.8 eV. The peak width (FWHM) is also larger than that of metallic Cu. These results indicate that the valency of surface Cu on the reduced catalysts is positive, but less than +2. By considering the fact that the escape depth of photoelectrons is a few nm, the binding energies reflect

the average valency of Cu at near surface. The binding energy of the Zn 2p<sub>3/2</sub> peak of reduced catalysts is in a range of 1023.5–1024.0 eV, and is almost the same as that for calcined catalyst, which is supposedly in a form of ZnO. Because the chemical shift of the peak is small between Zn<sup>2+</sup> and Zn<sup>0</sup>, it is difficult to determine the oxidation state of Zn on the catalysts from the binding energy.

Although the change in the surface Cu concentration by pretreatment was within an experimental error, the Zn

concentration decreased after reduction at 973 K. This result implies that the amount of surface Cu did not correlate with the catalytic activity, and that the amount remaining Zn is sufficient to give the high selectivity toward methanol. A relatively higher concentration of surface Zn than Cu was noted on the catalysts pretreated below 873 K, in comparison with the bulk values obtained by XRF.

### Discussion

A large discrepancy between the Cu particle sizes estimated by XRD line broadening and by CO chemisorption was observed in the catalysts prepared by the alkoxide method, although they coincided with each other in the case of conventional catalysts prepared by the impregnation method. The discrepancy is most probably ascribed to (1) the location of metals and (2) a particle size effect of metals in SiO<sub>2</sub>: Metals in an impregnated catalyst are mostly located on the outer surface of catalyst particles, whereas metals in catalysts prepared by the alkoxide method exist mainly inside silica matrices. Moreover, small particle metals in silica matrix are reported to hardly adsorb CO, because of a strong interaction with SiO<sub>2</sub>.<sup>11)</sup> Consequently, CO could not be adsorbed on the most part of metals in the catalysts prepared by the alkoxide method, resulting in overestimation of the particle sizes by CO chemisorption. The smaller numbers of available metallic species outside the catalyst particles coincide with the apparent low activity of the catalysts prepared by the alkoxide method, as pointed out above. Thus, the turnover frequency (TOF) on the catalyst prepared by the alkoxide method is not necessarily lower than the conventional catalyst prepared by the impregnation method.

The selectivity to methanol was higher with catalysts pretreated at a higher temperature in general, when the starting materials and the catalyst preparation procedure were identical. The Cu particle size in the catalysts increased with a rise in the pretreatment temperature. This implies that a larger particle size of metallic Cu is preferable to methanol formation. The selectivity was, however, not always governed by the particle size only. A high selectivity up to 87% was obtained on the catalyst prepared from acetates by the alkoxide method, even though the Cu crystallite sizes were smaller than those in the catalysts prepared from nitrates. The reason is not clear, but we could point out a possibility that a better interaction between Cu and Zn could be accomplished on the catalysts from acetates by high dispersion of metals in the catalyst precursors, and that a better synergistic effect might overcome the particle size effect. Preparation of highly dispersed catalysts by adding or using carboxylates, instead of inorganic salts, is also reported elsewhere.<sup>12,13)</sup>

The catalytic activity and selectivity to methanol were

low on the catalyst without Zn: This indicates a crucial role of Zn in the catalysis. The selectivity was observed to increase, however, with a decrease in the Zn concentration to below 1 wt% by pretreating at high temperatures. The XPS results indicate that the Zn concentration was higher at the surface than in the bulk. High dispersion of Zn species was suggested from the results of XRD and EXAFS. These results demonstrate that the amount of Zn was sufficient for methanol selectivity, even though the bulk amount was less than 1%, and that a particle size effect was more important.

The activity of the catalysts pretreated at 873 K was extremely low. Alloy formation was suggested by the results of XRD and EXAFS. Therefore, the formation of alloy deteriorates the catalytic activity, even though Zn is needed for high selectivity.

The EXAFS results suggested that the oxidation state of bulk Cu in the used catalysts was mostly metallic when they had been pretreated above 673 K, while it was oxide when pretreated at 573 K. The latter was probably reoxidized during the measurement, because the initial phase identified by XRD was metallic, immediately after the reaction. Small particles of Cu may be oxidized more rapidly than larger ones in open air. On the other hand, XPS results suggested that the oxidation state of Cu on the surface of the catalysts reduced in situ was not metallic, but Cu<sup>δ+</sup>, regardless of the reduction temperature.

In conclusion, a higher selectivity to methanol was obtained in hydrogenation of CO<sub>2</sub> on Cu-ZnO/SiO<sub>2</sub> catalysts prepared by the alkoxide method than conventional catalysts prepared by the impregnation method, by controlling the particle size of Cu. From the results of characterizing reduced and used catalysts, the active species on the catalysts with a high selectivity was identified as a large metallic Cu particle covered with a partially oxidized phase interacting with highly dispersed Zn species (probably ZnO). Detailed investigation on the nature of this interaction and the reaction mechanism is currently in progress.

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