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Structure and activity of Cu/ZrO_2 and K-Cu/ZrO_2 catalysts

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Abstract

In this work, the Cu/ZrO_2 catalysts, in which the support zirconia is made by supercritical drying, exhibit high activity and selectivity for the synthesis of methanol from CO/H_2. Potassium is an effective promoter for the catalysts. EXAFS results reveal that the copper atoms in the reduced and used catalysts are predominantly in the zero valent state and in the course of reaction the copper particles redispersed to a higher dispersion state.

Keywords: Cu/ZrO_2; Methanol synthesis; EXAFS; Aerogel; Zirconia

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1. Introduction

Although $Cu/ZnO/Al_2O_3$ catalysts have dominated the world market for the commercial production of methanol, attempts have still been made to develop new catalyst systems with better performance. In recent years, a number of alternative catalysts have been reported. For example, palladium catalysts [1], thorium–copper intermetallic catalysts [2] and copper–rare-earth catalysts [3,4] have been shown to be active and selective for methanol synthesis from CO/H_2. However, the palladium catalysts exhibit lower activity compared to commercial catalysts, while the thorium–copper and copper–rare-earth alloy catalysts are readily deactivated by CO_2. Zirconia supported copper catalysts seem to be of particular interest because, such as the $Cu/ZnO/Al_2O_3$ system, they are active and selective for the synthesis of methanol from CO/H_2, CO_2/H_2 and $CO/CO_2/H_2$ [5,6]. In this work, the activity of ultrafine zirconia supported copper catalysts was studied.

The active species of Cu-based catalysts for methanol synthesis, which is related to the chemical state of copper, are still subject to considerable controversy [7]. In the subsequent work, Cu/ZrO_2 catalysts and their precursors were studied by the EXAFS method to reveal the chemical state of the copper.

2. Experimental

2.1. Preparation of CuO/ZrO_2 catalysts

Hydrous zirconia was made by precipitation at room temperature at a terminal pH of 10.0 [8] with ammonium hydroxide as a precipitating agent. The precipitate was aged in the mother liquor for 13 h, and washed with distilled water until it was free from chloride ions. The filtered

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hydrous zirconia was washed with absolute alcohol to remove the water in the pores. After the last washing step, the hydrous zirconia was dried in a supercritical atmosphere of ethanol at 533 K and 7.5 MPa. The BET surface area (S_{BET}), specific pore volume (V_p), pore diameter maximum in pore size distribution (D_p^{max}) and average particle diameter (d) of the zirconia were 219.8 m^2/g, 0.411 cm^3/g, 8.5 nm and 7.72 nm, respectively.

The CuO/ZrO_2 catalysts were prepared by impregnation. The aerogel of zirconia formed as described above was used as a support and was impregnated by aqueous solutions of $Cu(NO_3)_2$. The samples were then dried at 383 K and calcined at 623 K.

2.2. *Preparation of reduced samples*

The CuO/ZrO_2 catalysts were reduced by temperature programmed reduction (rising temperature at a rate of 0.7 K/min) and kept under flowing H_2 at a maximum temperature of 523 K for 3 h. After reduction, the samples were put into liquid paraffin under an atmosphere of hydrogen and sealed for characterization.

2.3. *Catalyst testing*

5 cm^3 of CuO/ZrO_2 catalyst was charged into a 1.2 cm i.d. stainless steel reactor and activated in situ by H_2 (temperature programmed reduction as stated above). The reacting gas was $CO/2H_2$ (containing about 1.6% CO_2). The products were analyzed off-line with a gas chromatograph. The samples of spent catalysts were those operated for 30 h.

2.4. *EXAFS characterization*

EXAFS measurements were made at 4 a WIB beamline of the Beijing Synchrotron Radiation Facility. The energy of the storage ring was run at 2.2 GeV and the current was 20–25 mA. The synchrotron X-ray beam was monochromated with double crystalline Si(111). Two ion chambers filled with Ar were used for the detector system. The high order harmonics were eliminated by detuning the double crystal monochromater. CuO and Cu were chosen as model compounds for deriving the structure parameters of the samples.

3. Results and discussion

3.1. *Activity of catalysts*

Table 1 shows the activity of the Cu/ZrO_2 catalysts for methanol synthesis from $CO/2H_2$. For a CuO content in CuO/ZrO_2 between 20%

Table 1

Activity of catalysts at 503 K, 4.0 MPa and 5000 h^{-1}

Catalyst sample	1	2	3	4
CuO in CuO/ZrO_2 (wt%)	12	20	27	32
$S_{BET}(m^2/g)$	144	130	134	117
Conversion of CO (%) [a]	12.0	17.0	18.0	16.9

[a] Steady state conversion which was reached after about 15 h and hardly changed in 40 to 70 h.

Table 2

Activity of Cu/ZrO_2 and $K-Cu/ZrO_2$ at 4.0 MPa and 5000 h^{-1} and at different temperatures

Catalysts [a]	CuO/ZrO_2			0.8% K_2CO_3-CuO/ZrO_2			1.7% K_2CO_3-CuO/ZrO_2			0.47% K_2CO_3-CuO/ZrO_2		
T (K)	503	523	548	503	523	548	503	523	548	503	523	548
Conversion of CO (%)	18.0	27.0	31.9	24.0	37.1	39.1	13.6	24.4	33.4	21.6	34.5	36.5
Selectivity to CH_3OH	> 98	98	88.7	> 98	98.1	86.7	> 98	98	90.7	> 98	94.5	81.2
Selectivity to CH_4		2	4.4		1.9	4.1		2	4.8		2.6	8.3
Selectivity to CO_2			6.9			9.2			4.5		2.9	10.5

[a] $CuO:ZrO_2$ = 27:73 (wt) for all of the catalysts. The numeric values are the weight content of K_2CO_3 in K_2CO_3-CuO/ZrO_2.

Table 3
Yield of methanol on various catalysts from $CO/CO_2/H_2$ at 523 K

Catalyst	0.8% K_2CO_3-CuO/ZrO_2	CuO/ZrO_2	$CuO/ZnO/Al_2O_3$ [a]	CuO/ZrO_2 [b]
CuO in the catalyst (wt%)	27	27	60	1.27 [c]
P (MPa)	4.0	4.0	5.0	1.0
Space velocity	5000 h^{-1}	5000 h^{-1}	40000 h^{-1}	6400 $cm^3/h/g$
Yield of CH_3OH ($g/cm^3_{cat}/h$)	0.85	0.62	0.5	1.106 [d]

[a] From [9].
[b] From [5].
[c] wt% Cu in CuO/ZrO_2.
[d] $g/g_{Cu}/h$.

and 32%, the conversions of CO were nearly the same. Besides a trace of dimethyl ether and water, no other by-products were detected.

It can be seen from Table 2 that the temperature of reaction influenced the activity of the catalysts significantly. At 548 K and 523 K (temperature in the catalyst bed) the maximum conversion of CO to methanol was observed for the Cu/ZrO_2 and K-promoted Cu/ZrO_2 catalyst, respectively. With the increase in temperature, the selectivity to methanol decreased while the selectivity to CH_4 and CO_2 increased. It is apparent from Table 2 that potassium was an effective promoter for the CuO/ZrO_2 catalysts. When 0.8 wt% of K_2CO_3 was added to the CuO/ZrO_2 catalysts, the conversion of CO at 523 K increased from 27% to 37% with little change of selectivity. Table 3 lists the activity

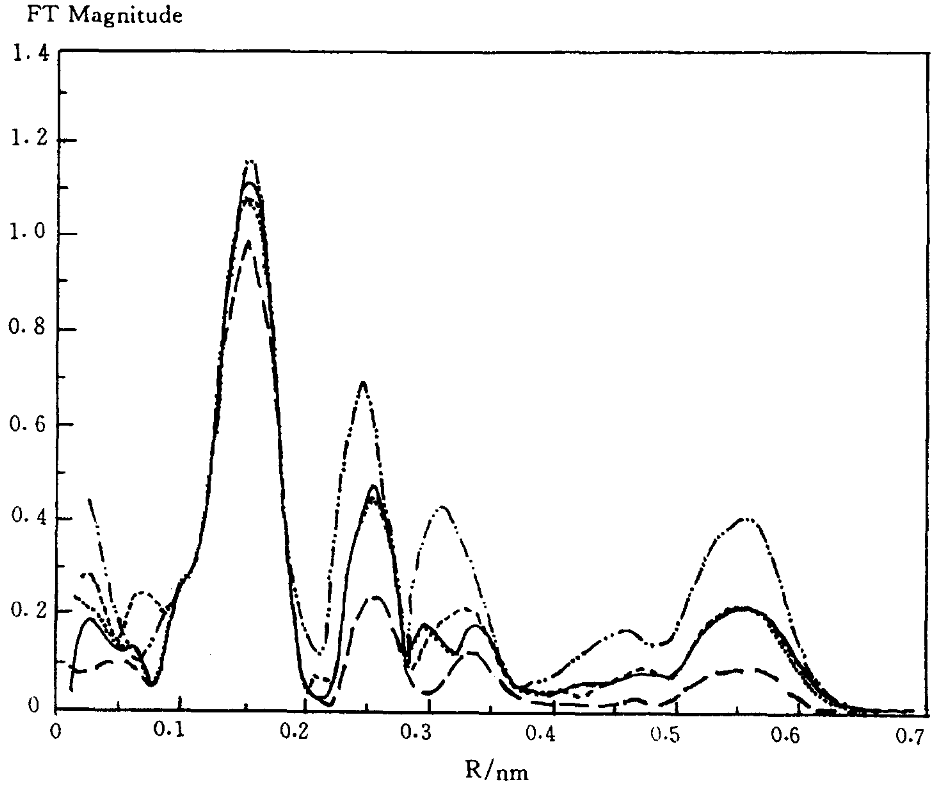

Fig. 1. Fourier transform of Cu K-edge EXAFS spectra for CuO/ZrO_2: (-··-) CuO; (–) sample 4; (···) sample 3; (—) K-CuO/ZrO_2; (– –) sample 1.

Table 4
Structural parameters of the first shell derived from EXAFS data for catalyst precursors

Catalyst sample	1	3	4	K-CuO/ZrO$_2$	Pure CuO
R(Cu-O)	1.95	1.95	1.95	1.95	1.96
N(Cu-O)	3.6	3.9	4.0	4.0	4.0
σ^2	0.007	0.006	0.006	0.006	

of different catalysts. It can be seen that the ultrafine ZrO$_2$ supported copper catalysts exhibited high activity for MeOH synthesis from CO/CO$_2$/H$_2$.

3.2. EXAFS characterization

Table 4 gives the coordination numbers and the bond distance for the first shell of the Cu–O pair. The values were nearly the same as that of pure CuO. The FT spectra (Fourier transform of the EXAFS) of the Cu K-edge for CuO/ZrO$_2$ samples were much like that of pure CuO (Fig. 1), while the bond distance of their second shell was a little larger than that of pure CuO. These results revealed that the coordination surrounding the copper in Cu/ZrO$_2$ is slightly different

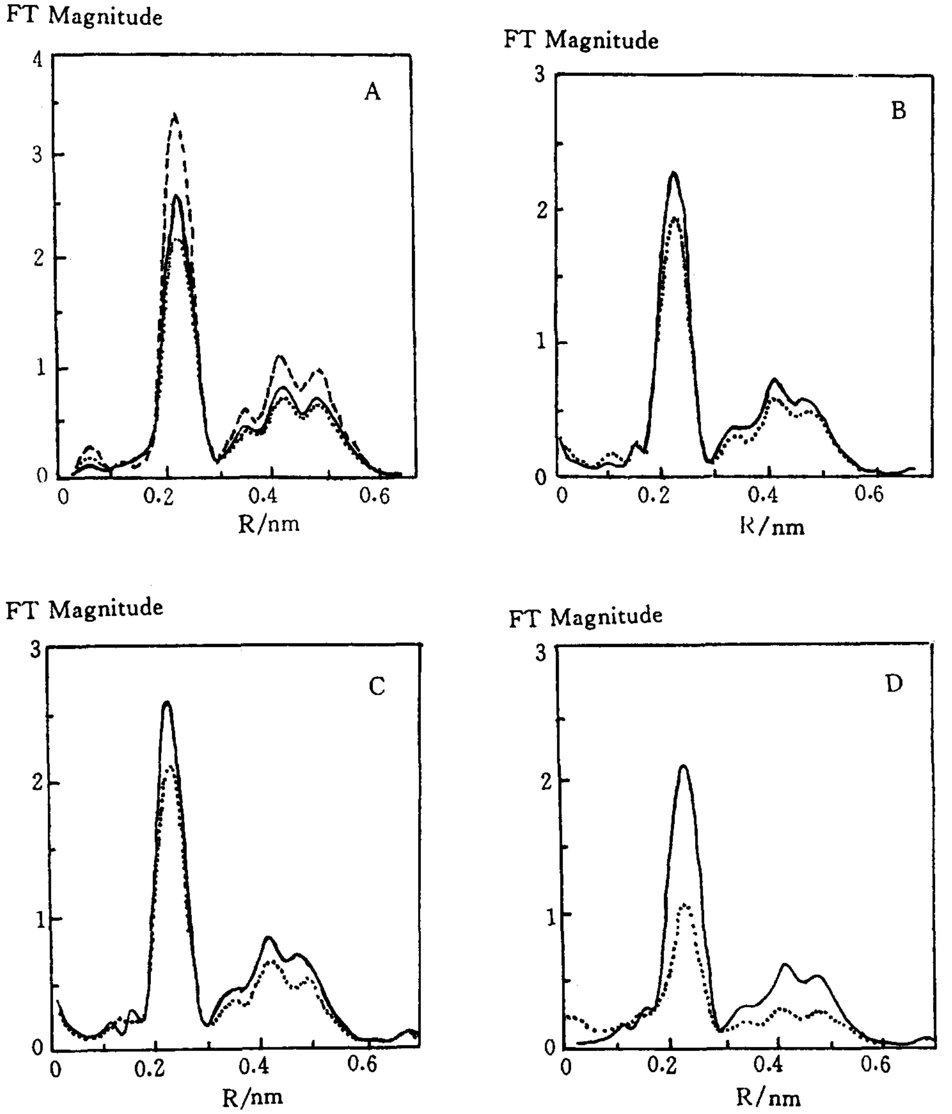

Fig. 2. Fourier transform of Cu K-edge EXAFS spectra for reduced (–), used (· · ·) catalysts and pure copper (—). A, K-Cu/ZrO$_2$ and pure copper; B, sample 3; C, sample 4; D sample 1.

Table 5
Structural parameters of the first shell derived from EXAFS data for reduced and used catalysts

Catalyst sample	Reduced catalyst				Used catalyst				Pure Cu
	1	3	4	K-Cu/ZrO$_2$	1	3	4	K-Cu/ZrO$_2$	
R(Cu-Cu)	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.55	2.56
N(Cu-Cu)	8.8	9.0	10.1	9.6	4.7	7.2	7.9	8.9	12
σ^2	0.009	0.010	0.0095	0.009	0.009	0.009	0.009	0.010	

from pure CuO and ZrO$_2$ support has an effect on the structure of the CuO. The reduced amplitude of the coordination peaks for sample no. 1 in which the CuO content was lower than that of the others (Fig. 1) was indicative of the presence of smaller CuO particles (crystal grain) [10,11]. The FT spectra of the Cu K-edge for K-promoted CuO/ZrO$_2$ and CuO/ZrO$_2$ in which the content of CuO is the same exhibited little difference, even the amplitude of the peaks had little change. This result indicated that the potassium promoter hardly affected the coordination structure of the CuO.

The coordination numbers and the bond distance of the nearest neighbor Cu–Cu pair for the reduced and used catalysts are listed in Table 5. The FT spectra of the Cu K-edge is shown in Fig. 2. That the bond distance of the Cu–Cu pair for the reduced and used samples were equal to that of pure copper and the FT spectra of the Cu K-edge for these samples like that of pure copper revealed that the copper atoms in the reduced and used samples were predominantly in the zero valent state. The amplitude of the coordination peaks for the reduced samples decreased with a decrease in copper content, showing that the particle size of copper decreased with a decrease in copper loading. For the used samples, the particle size of copper also decreased with a decrease in copper loading.

It is interesting to compare the EXAFS results of a sample in its used state and reduced state. The amplitude of the coordination peaks and the coordination numbers for the sample used were smaller than that for the reduced one. This result meant that in the course of reaction the particle size of the copper decreased; in other words, copper was redispersed to a higher dispersed state in the course of reaction. It is shown in Table 5 and Fig. 2 that this redispersion is less pronounced for K promoted Cu/ZrO$_2$ than for Cu/ZrO$_2$. A detailed study of the effect of the K-promoter is needed.

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