Effect of starting salt on catalytic behaviour of Cu–ZrO_2 catalysts in methanol synthesis from carbon dioxide

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Starting salts used in the co-precipitation of Cu–ZrO_2 precursors had marked influence on both activity and selectivity of resulting catalysts for methanol synthesis: chlorides increased the selectivity, suggesting the structure sensitivity of methanol formation reaction, while sulfates much enhanced the activity by affecting the dispersion of Zr species. A simultaneous use of copper chloride and zirconium sulfate greatly improved the activity and selectivity of the catalyst for methanol formation.

Keywords: CO_2 hydrogenation; copper–zirconia catalyst; methanol synthesis; preparation variables; starting salt

1. Introduction

Recently copper–zirconia catalysts have been found to be active and selective for methanol synthesis from carbon dioxide [1–8]. A significant influence of preparation variables as well as the preparation method has been reported for Cu–ZrO_2 catalysts of the same nominal composition [4,7,8]. In these investigations, the catalysts have been prepared mainly from copper and zirconyl nitrates. However, marked effects of starting materials on the properties of resulting catalysts have been reported in the preparation of supported metal catalysts. For instance, supported cobalt catalysts prepared from cobalt chloride always exhibit high selectivities in the hydrogenation of α, β-unsaturated aldehydes to unsaturated alcohols irrespective of the support employed [9,10]. The use of metal sulfates is effective to provide highly dispersed and consequently highly selective Fe–Cu/SiO_2 catalysts for partial hydrogenation of alkynes [11,12]. Therefore, the choice of the starting salt in the preparation of a Cu–ZrO_2

catalyst can also play an important role in hydrogenation of carbon dioxide. In this study, we have examined a series of Cu–ZrO_2 catalysts prepared by a co-precipitation method using a variety of starting salts of copper and zirconium.

2. Experimental

The Cu–ZrO_2 catalysts, containing 50 wt% of copper, were prepared by a co-precipitation method using salts of copper and zirconium and a slight (usually 10%) excess of Na_2CO_3 as the precipitating agent. A typical procedure to prepare a precursor from nitrates (CZ-N) was as follows: An aqueous solution (25 cm^3) of Na_2CO_3 was rapidly added to a mixed solution of copper nitrate (40 mmol) and zirconyl nitrate (21 mmol) in 150 cm^3 of deionized water at 293 K while vigorously stirring. The precipitate was aged at 348 K for 15 min with gentle stirring, and then filtered and thoroughly washed with hot water. Precipitations at varying temperatures (313–348 K) or with varying amounts of precipitant (10–50% excess) were also conducted for comparison. The final pH values were 8.2–8.4 for all preparations. The precipitate was dried at 383 K for 20 h and crushed to a powder. Precursors from chloride (CZ-C), sulfate (CZ-S), and acetate (CZ-A) were similarly prepared by using copper chloride/zirconyl chloride, copper sulfate/zirconium sulfate, and copper acetate/zirconyl acetate, respectively. The mixture of copper chloride and zirconium sulfate, and that of copper sulfate and zirconyl chloride, were also used to prepare precursors CZ-CS and CZ-SC, respectively.

The hydrogenation of CO_2 was carried out at a pressure of 0.9 MPa using a continuous tubular flow fixed-bed microreactor. The catalyst sample (0.5 g) was mounted in a stainless steel reactor (i.d. = 6 mm) and pre-reduced at 523 K for 1 h in a hydrogen flow of 100 cm^3 min^{-1} (STP). After cooling to 413 K the hydrogen flow was replaced with a reactant gas ($H_2/CO_2 = 3$) flow of 40 cm^3 min^{-1} (STP) and then the pressure was increased gradually to 0.9 MPa. The reaction temperature was increased stepwise (30 min per step of 20 K) to 573 K. The product gas was analyzed at each reaction temperature by using on-line gas chromatographs. Conversions, typically in the range 0–30%, are defined as: (mol carbon dioxide converted to all products)/(mol carbon dioxide in feed gas). The methanol selectivity is defined as: (mol methanol)/(mol carbon dioxide converted to all products).

The catalyst samples were characterized by nitrogen physisorption measurements (BET), X-ray powder diffraction (XRD), thermal analysis (TGA/DTA), and X-ray photoelectron spectroscopy, (XPS, Al-anode). Mean crystallite sizes of copper (D_c) in H_2-reduced catalysts were calculated from the half-width of the (111) reflection of Cu metal in XRD patterns using the Scherrer equation after correction of the peak width for the contribution by instrumental broadening [13]. The peak areas of Cu $2p_{3/2}$, Zr 3d, and Cl 2p bands in XPS spectra were used for semiquantitative surface analyses of the samples before and after H_2-reduction. The XPS binding energies were corrected by using the C 1s band at 285.0 eV for adventitious carbon as follows: Zr $3d_{5/2}$: 182.3 eV; Cu $2p_{3/2}$: 934.9 eV for precursor and 932.9 eV for H_2-reduced catalyst; and Cl 2p: 197.5 eV.

3. Results and discussion

Methanol and carbon monoxide were the only carbon-containing products found in this study, except for trace amounts of methane and higher hydrocarbons in the reactions at higher temperatures. Preliminary experiments using catalyst CZ-N (prepared from nitrates) showed that a copper content of around 50 wt% leads to a catalyst with the highest yield of methanol. Fig. 1 shows the effect of the precipitation temperature on the methanol formation rate and selectivity of the resulting catalyst in the hydrogenations at 493 and 513 K. The catalyst prepared at 293 K showed the highest rate of methanol formation, while the methanol selectivity was highest for the catalyst prepared at 333 K. An increase in the precipitation temperature resulted in an increase in the mean crystallite size of copper in the reduced catalysts, which probably explains the decrease in activity and the increase in methanol selectivity as will be seen later.

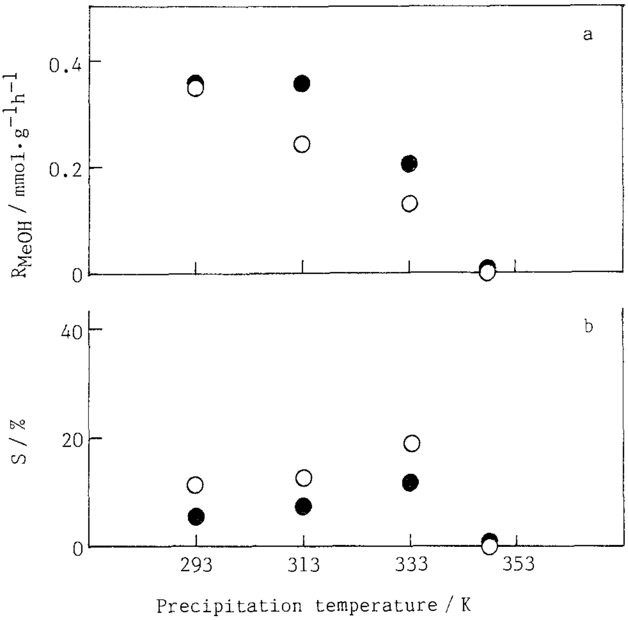

Fig. 1. Carbon dioxide hydrogenation over Cu–ZrO_2 catalysts prepared from copper and zirconyl nitrates by precipitation with 30% excess of Na_2CO_3. Influence of precipitation temperature of precursor on methanol formation rate (a) and selectivity (b) at 493 K (○) and 513 K (●).

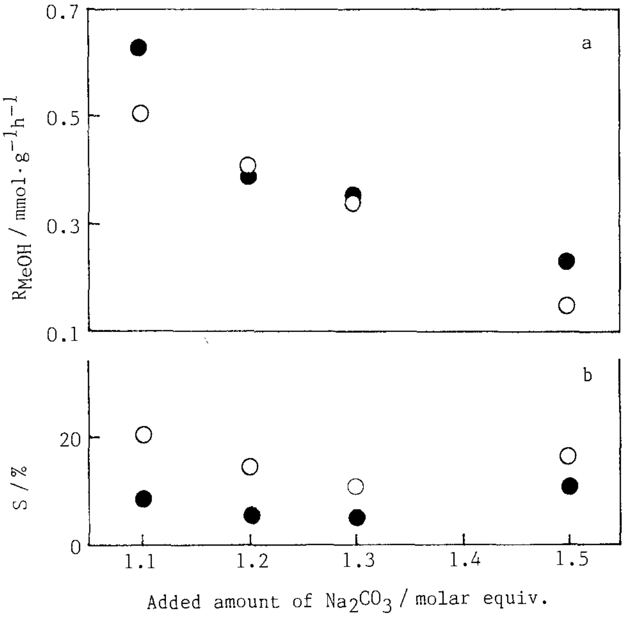

Fig. 2. Carbon dioxide hydrogenation over Cu–ZrO_2 catalysts prepared from copper and zirconyl nitrates by precipitation at 293 K. Influence of added amount of Na_2CO_3 on methanol formation rate (a) and selectivity (b) at 493 K (○) and 513 K (●).

Fig. 2 shows the effect of added amount of alkali in the precipitation at 293 K with nitrates. Both methanol formation rate and selectivity were highest at 10% excess of alkali; the rate decreased with increasing amount of added alkali, while the selectivity showed a minimum at 30% excess. Accordingly, further experiments to clarify the effect of starting salts were carried out with the catalysts prepared by precipitations at 293 K and with 10% excess of alkali unless otherwise stated.

Figs. 3 and 4 show the reaction temperature dependences of the rates of CO and methanol formation, respectively. As the reaction temperature increased, the CO_2 conversions and CO formation rates increased remarkably for all the catalysts examined, while the methanol formation reached maximum rates at different temperatures, depending on the starting salt. The maximum rate of methanol formation decreased in the order: CZ-S > CZ-N > CZ-A > CZ-C. It is noteworthy that the yields of both products at a given temperature are strongly dependent on the starting salts employed for the catalyst preparation: the use of sulfates enhances the activity and the use of chlorides depresses it markedly. Moreover, the choice of the starting salts had a greater influence on CO formation than on methanol formation. The CZ-C catalyst almost inhibited the formation of CO, leading to a high selectivity toward methanol as shown in fig. 5. The methanol selectivity decreased in the opposite order of activity: CZ-C > CZ-A > CZ-N > CZ-S. These findings suggest that the use of chlorides is

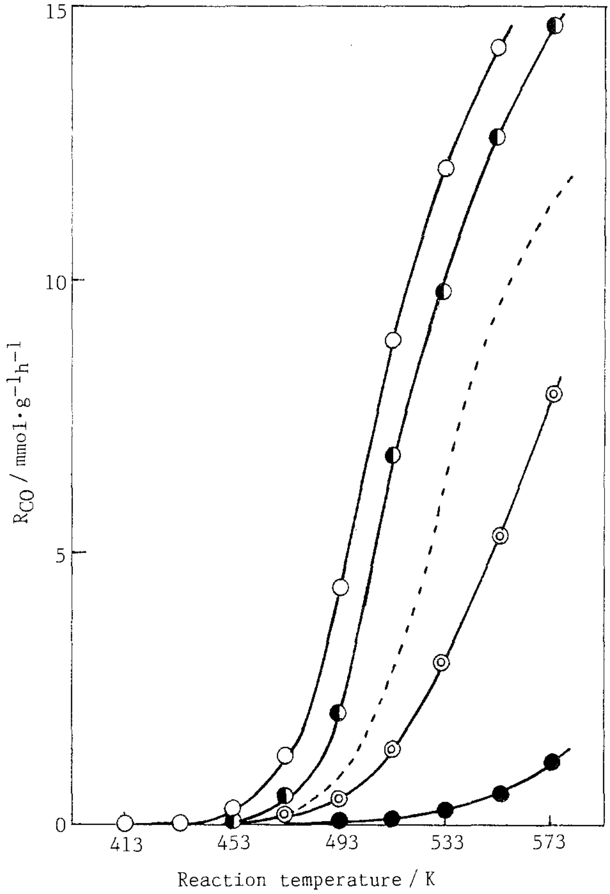

Fig. 3. Reaction temperature dependence of CO formation rate over Cu–ZrO_2 catalyst prepared by a precipitation at 293 K from various starting salts. (○) CZ-S, (◐) CZ-N, (◎) CZ-A, (●) CZ-C, and (- - -) CZ-CS.

favourable for selectivity and the use of sulfates, on the other hand, for activity. Therefore, we examined a catalyst prepared from a mixture of copper chloride and zirconium sulfate (CZ-CS) under the same reaction conditions as described above. As is clearly shown in fig. 4, this catalyst exhibited the highest yield of methanol of all the catalysts examined here at around 500 K. The catalyst prepared from copper sulfate and zirconyl chloride (CZ-SC), however, had only a similar activity and selectivity to CZ-S.

Table 1 lists the results of catalyst characterization together with the hydrogenation properties and preparation conditions. It was found from XPS measurements that the catalysts prepared by using copper chloride contain residual chlorine both in the precursors and in the reduced catalysts. The addition of an increased amount of alkali in the precipitation of CZ-C catalysts led to a decrease in the relative amount of residual chlorine as well as in the methanol

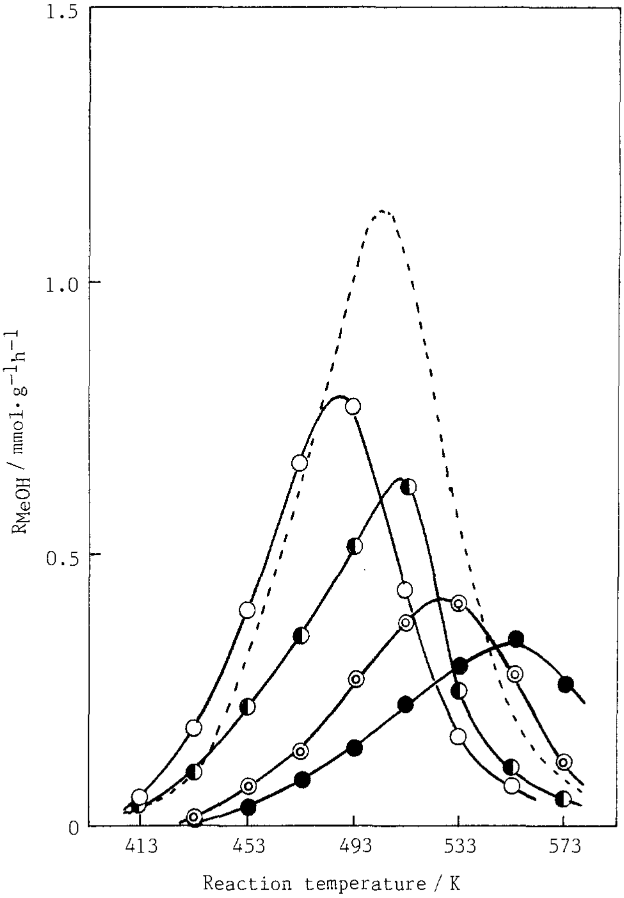

Fig. 4. Reaction temperature dependence of methanol formation rate over Cu–ZrO_2 catalyst prepared from various starting salts. Conditions and symbols are same as in fig. 2.

selectivity and to an increase in the activity (CZ-C-2 and CZ-C-3 in table 1). Therefore, it can be said that the residual chlorine plays an important role in determining the methanol selectivity in CO_2 hydrogenation over Cu–ZrO_2 catalysts. The increased selectivity of CZ-C catalyst may be explained as follows: residual chlorine in the precursor increases the crystallite size of copper after H_2 reduction and chlorine remaining in the reduced catalyst blocks nonselective reaction sites (e.g., edges and corners), thus inhibiting undesired reaction toward CO. In other words, the high selectivity of CZ-C catalyst may suggest that methanol synthesis from CO_2 on Cu–ZrO_2 catalysts is a structure-sensitive reaction: methanol formation is favoured on larger crystallites of Cu. The marked decrease in BET surface area during H_2 reduction and the relatively large D_c of CZ-C catalyst support this idea. The favourable effects of residual chlorine on selectivities in structure-sensitive hydrogenations have also been reported with supported Co and Ni catalysts [10,14]. The low selectivity of

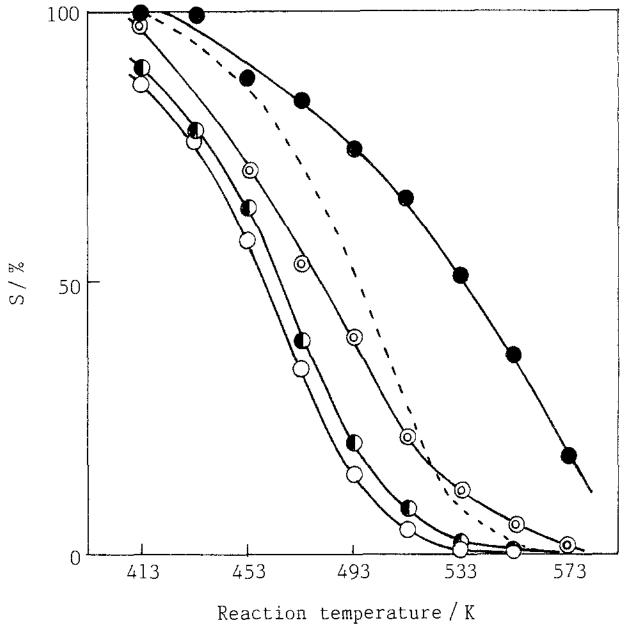

Fig. 5. Reaction temperature dependence of methanol selectivity of Cu–ZrO_2 catalyst prepared from various starting salts. Conditions and symbols are same as in fig. 2.

CZ-SC catalyst, in spite of the sufficient amount of chlorine existing in the reduced catalyst, suggests that the residual chlorine originating from zirconyl chloride does not block the nonselective sites on copper surface, although it considerably increases D_c of copper.

In contrast with the presence of chlorine on the CZ-C catalyst surface, residual sulfur was not detected at all in any catalysts prepared from sulfates except for CZ-S-5 and CZ-S-6, which were prepared by a precipitation at 333–343 K. A trace amount of sulfur was detected by XPS on these catalysts, explaining considerable decreases in the activity. The CZ-S catalyst prepared at 293 K had relatively large S_a and relatively small D_c, which, at least partly, explains the high activity of the CZ-S catalyst. Moreover, the XPS peak intensity ratios of Cu to Zr for the precursors prepared from sulfates were much smaller than those for the other catalysts (table 1). Taking into account the high activity, large S_a and relatively small D_c of CZ-S catalyst, the small Cu/Zr ratio is attributable to the presence of highly dispersed Zr species in the surface of the CZ-S catalyst. The remarkable increase in the Cu/Zr ratio, the increase in D_c of Cu, and the significant decrease in S_a of reduced catalysts with increasing temperature of precipitation from 293 to 333 K (from CZ-S to CZ-S-4 and CZ-S-5) suggest a steep decrease in the dispersion of Zr species. This is probable because similar observations were reported for the preparation of iron catalysts from iron sulfate [12]. These findings suggest that the dispersion of not

Table 1
Catalytic and physico-chemical properties of $Cu-ZrO_2$ catalysts prepared under different conditions

Catalyst	Preparation conditions			Hydrogenation at 493 K [b]				S_a [c] ($m^2\ g^{-1}$)		D_c [d] (nm)	XPS intensity ratio			
	Starting salt (Cu salt/Zr salt)	f [a]	ppt. temp. (K)	conv. (%)	R_{MeOH}	R_{CO}	S (%)	prec.	red.		Cu/Zr	Cl/Cu		
											prec.	red.	prec.	red.
CZ-N	nitrate/nitrate	1.1	293	4.75	0.510	2.03	20.1	71.6	47.2	23	1.36	1.14		
CZ-C	chloride/chloride	1.1	293	0.36	0.144	0.05	74.8	54.6	24.1	30	1.46	1.82	0.14	0.17
CZ-S	sulfate/sulfate	1.1	293	9.55	0.771	4.34	15.1	39.2	42.9	23	0.66	1.11		
CZ-A	acetate/acetate	1.1	293	1.31	0.279	0.42	39.7	29.8	22.7	24	1.46	–		
CZ-CS	chloride/sulfate	1.1	293	3.67	1.04	0.92	53.1	48.4	48.1	25	0.70	1.30	0.19	0.14
CZ-SC	sulfate/chloride	1.1	293	8.29	0.78	3.66	17.6	37.5	25.2	27	0.59	1.17	0.24	0.14
CZ-C-2	chloride/chloride	1.2	293	0.86	0.254	0.21	55.0	24.3	17.1	24	1.22	1.36	0.13	0.16
CZ-C-3	chloride/chloride	1.3	293	1.46	0.404	0.38	51.7	35.8	18.6	24	1.29	1.37	0.13	0.12
CZ-S-2	sulfate/sulfate	1.2	293	5.31	0.346	2.50	12.2	34.5	33.8	22	0.55	1.13		
CZ-S-3	sulfate/sulfate	1.3	293	2.94	0.248	1.33	15.6	28.6	36.9	27	0.53	1.11		
CZ-S-4	sulfate/sulfate	1.1	313	3.63	0.452	1.49	23.2	42.0	24.2	30	1.33	1.19		
CZ-S-5	sulfate/sulfate	1.1	333	1.00	0.146	0.39	27.4	34.9	13.6	30	1.69	1.26		
CZ-S-6	sulfate/sulfate	1.1	343	1.19	0.129	0.51	20.3	29.3	14.5	31				

[a] Molar equivalent of added alkali (Na_2CO_3).
[b] R_{MeOH}, R_{CO}: methanol and CO formation rates ($mmol\ g^{-1}\ h^{-1}$); S: selectivity to methanol.
[c] BET surface area measured before and after reduction.
[d] Mean crystallite size of Cu in the reduced catalyst.

only Cu but also Zr species is important in determining the activity of $Cu-ZrO_2$ catalyst for CO_2 hydrogenation. Although CZ-CS catalyst contains as much chlorine as CZ-C, it has a smaller D_c and a much higher activity than CZ-C. This is also attributable to the presence of sulfate during the precipitation. Both the presence of chlorine blocking nonselective sites and the higher dispersion of Cu and Zr species explain the highest rate of methanol formation on the CZ-CS catalyst. Further studies on the role of sulfate and Zr species are now in progress.

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