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Evidence of a metal–support interaction in sol–gel derived Cu–ZrO_2 catalysts for CO hydrogenation

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Sol–gel derived Cu/ZrO_2 catalysts have recently been shown to have high activity and selectivity toward methanol synthesis. TPR, TEM, in situ XRD and N_2O decomposition have now been used to characterize the active sites in such catalysts over a wide range of Cu concentration. Copper is shown to be in two forms: surface aggregates (or particulate) and dispersed copper in the ZrO_2 substitutional sites. The proportion of the former increases with an increasing Cu content, while the overall strength of the Cu–ZrO_2 interaction simultaneously decreases. The activity in CO/CO_2 hydrogenation showed no evident correlation with the total Cu surface area, but rather with the concentration of highly-dispersed form of copper. This is taken to indicate that the copper in the substitutional sites of ZrO_2 is predominantly responsible for and associated with the active sites on Cu/ZrO_2 for CO/CO_2 hydrogenation.

Keywords: metal–support interactions; sol–gels; Cu–ZrO_2; CO hydrogenation

1. Introduction

Cu/ZrO_2 catalysts have been found to be very active in CO/CO_2 hydrogenation [1–5]; a fact which was attributed to some special interaction of an "inverse" SMSI type [6]. With samples derived from Cu–Zr alloys [7,8], the copper was shown to be incorporated into the ZrO_2 and the interfacial area between Cu and ZrO_2 was proposed to be the active site. Certainly, crystallization of the amorphous zirconia sharply decreased the rate of methanol synthesis. With ZrO_2-supported Cu [9], similar phenomena were observed and were also taken to show the importance of the metal-to-zirconia contact area in methanol synthesis. However, more evidence is needed to clarify the precise role of the concentration between Cu and ZrO_2 in this hydrogenation reaction.

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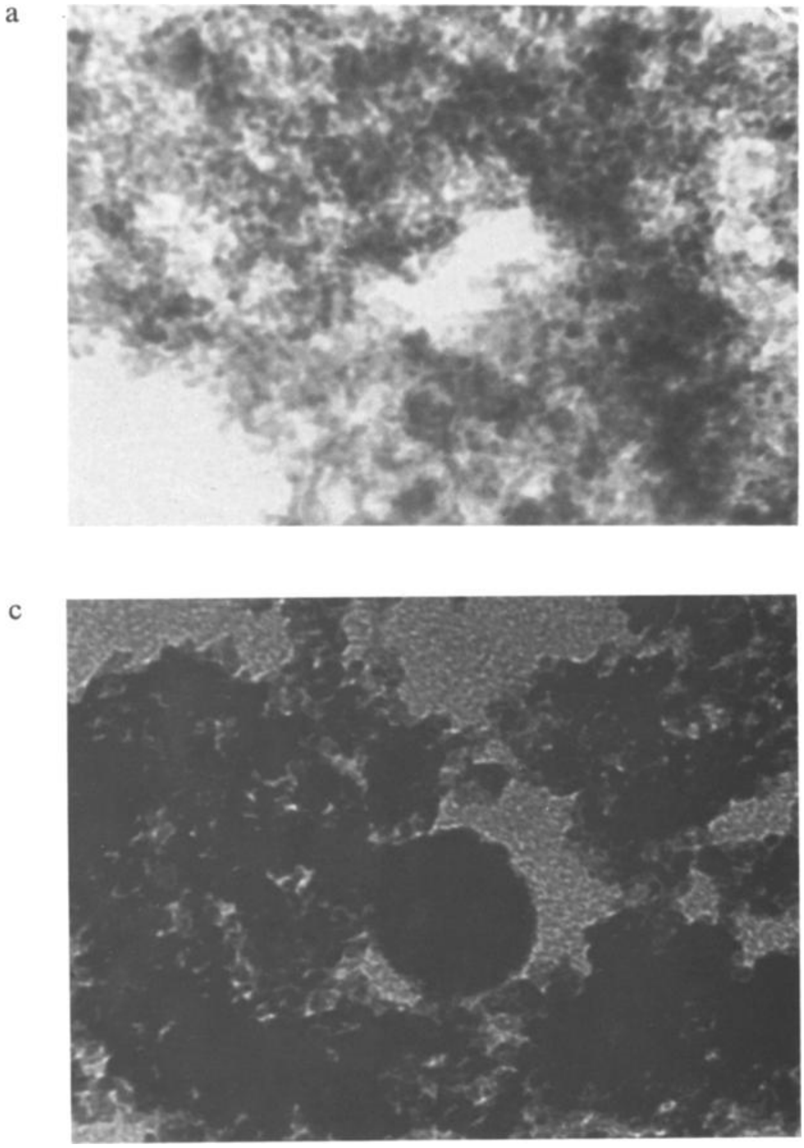

Fig. 1. Transmission electron micrographs and electron diffraction of sample CZ3 before and after evacuation at 703 K (1 cm = 20 nm). (a) and (b) indicate the primary aerogel, (c) and (d) the sample evacuated.

More recently, a systematic study on sol–gel derived pure and doped-zirconia has been carried out for alcohol synthesis by CO/CO_2 hydrogenation by the present authors [10,11]; significantly, copper-doped amorphous zirconia *aerogels* were found to have very high activity and selectivity to methanol synthesis. Evidently, their catalytic performance could not be simply attributed to high total surface area

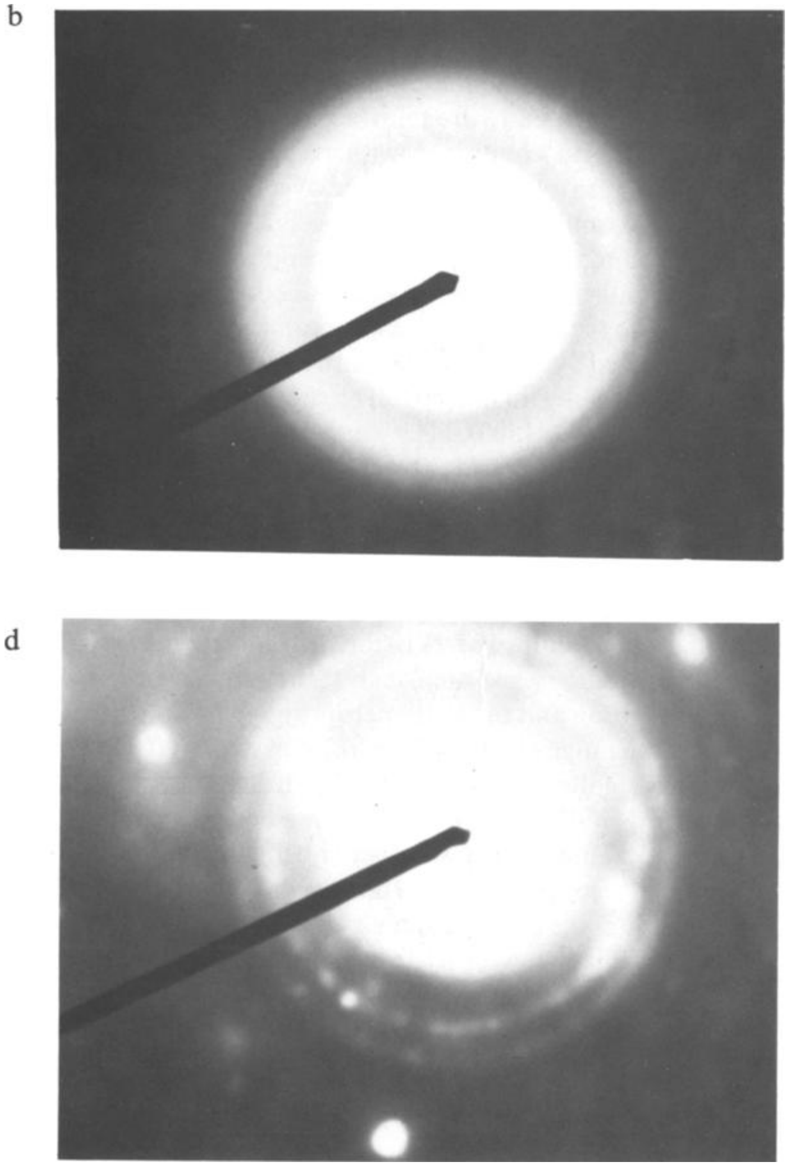

Fig. 1. Continued.

of these aerogels but rather appeared to be related to the nature of the interaction between copper and zirconia [12]. Previous work [12] indicates that the incorporation of copper into zirconia leads to highly-dispersed and homogeneous Cu clusters and suggests that evacuation at 703 K *weakens* the interaction between Cu and ZrO_2. This was the background of the present work on Cu/ZrO_2 in which the samples were expected to contain possibly two forms of copper; its aim was to illustrate the nature of the active sites in such catalysts.

2. Experimental

Cu/ZrO_2 catalysts were prepared via the sol–gel route used previously [11,12] at 295 K; this produced at first a hydrogel which was redispersed in ethanol and evacuated under supercritical conditions with respect to ethanol at 531 K ($T_c = 519$ K, $p_e = 6.4$ MPa). Samples were prepared over the range of copper concentration $0 \leqslant \text{mol\% Cu} \leqslant 50$, and the resulting aerogels were evacuated at 703 K in vacuum (100 mPa; 4 h) and then cooled to room temperature. Such aerogels (with their different Cu concentrations) were expected to contain both mono-dispersed copper (incorporated into the support framework) and aggregated copper clusters, and were then characterized by TPR, TEM, in situ XRD, XRF and N_2O decomposition. Total surface area was evaluated by full nitrogen adsorption–desorption isotherms at 77 K (Carlo Erba 1800) after outgassing for 4 h at 523 K. N_2O decomposition at 333 K was employed to estimate Cu surface areas after reduction (0.25 g, 573 K) and outgassing for 4 h at 573 K; measurements were carried out at 333 K and 0.1 mPa. A Jeol 2000FX transmission electron microscope (TEM) was used to observe the shape and size of primary particles (as well as allowing electron diffraction before and after CO/CO_2 hydrogenation). X-ray diffraction patterns were recorded using a Philips PW 1710 diffractometer with nickel-filtered Cu Kα radiation. Both continuous and step-scan techniques were used, the former allowing phase identification and the latter permitting quantitative analysis. Step-scans were taken over the range of 2θ from 25° to 35° in steps of 0.02°, where intensities for each point were collected over 10 s. TPR measurement was carried out using 5% H_2/Ar flowing at 40 cm^3 min^{-1} through a bed containing 0.03 g of catalyst during heating at 5 K min^{-1}; produced water being removed at 195 K.

Catalytic activity and selectivity for CO/CO_2 hydrogenation were measured by using a fixed-bed reactor made of 4 mm quartz-lined stainless steel tube. Catalysts (0.1 g) were pre-reduced in a flow of hydrogen (60 cm^3 min^{-1}) at 573 K for 1 h and were then tested at 523 K in $CO/CO_2/H_2$ (65/2/33) at 2 MPa with reactants flowing at 60 m^3 min^{-1}. The product composition was analysed by gas chromatography (Perkin Elmer 8401 with an FID detector).

3. Results

3.1. CHARACTERIZATION

As shown in figs. 1a and 1b, the primary aerogels consisted of clusters of cross-linked particles smaller than 5 nm. Evacuation at 703 K caused an agglomeration which led to a bimodal distribution in size. Electron diffraction (see figs. 1c and 1d) revealed that the particles were a mixture of crystalline copper and amorphous zirconia after being evacuated at 703 K. The average size of these particles was somewhat dependent on the Cu loading and was up to 40 nm for 20 mol% Cu/ZrO_2. A fraction of the copper was apparently segregated from the support oxide frame-

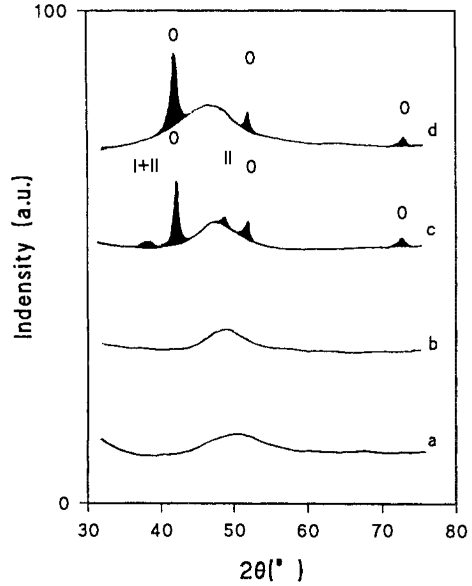

Fig. 2. X-ray diffractograph of ZrO_2 and Cu/ZrO_2 aerogels. (a) ZrO_2, (b) the primary aerogel of Cu/ZrO_2, (c) sample (b) evacuated at 703 K in vacuo, (d) sample (b) reduced at 503 K in H_2.

work, due to its lower entropy of formation, which partially destroyed the structure of homogeneous clusters in the aerogels. Thus, the copper co-existed in the highly-dispersed and particulate states, occupying substitutional sites and surface sites, respectively.

XRD (see fig. 2) revealed structural changes in the catalyst after the evacuation. Broad reflections in the range $20° \leqslant 2\theta \leqslant 60°$ were noted for the primary aerogels which indicated no long-range crystallinity. Data in table 1 clearly show the concentration-dependence of the average crystallite size of the Cu in the catalysts. It is likely that catalysts with higher Cu loadings exhibit more severe segregation of

Table 1
Properties of Cu/ZrO_2 catalysts[a]

Catalyst code	Atomic ratio $Cu : ZrO_2$	S_{BET}[b] ($m^2 g^{-1}$)	d_{Cu} (nm)			Reducibility (TPR, %)
			TEM	XRD		
				unreduced	reduced	
CZ1	0 : 100	253	–	–	–	0
CZ2	10 : 90	268	14.2	16.8	17.3	61.5
CZ3	20 : 80	241	35.8	36.6	36.9	83.8
CZ4	30 : 70	234	43.4	44.5	44.8	73.2
CZ5	45 : 55	225	56.3	59.7	60.1	61.6

[a] All catalysts had K levels of about 0.64 wt%, and were evacuated at 703 K.
[b] Reduced at 573 K for 1 h.

Cu and ZrO_2. More interestingly, it was noted by in situ XRD that reduction at 503 K only led to a slight increase in the average size of the crystallite copper (i.e. from 16.8 to 17.3 nm for sample CZ2). This indicated that the residual copper in the support framework was still in a highly-dispersed state.

TPR indicated (see fig. 3) a change in the Cu–ZrO_2 interaction; clearly their reducibility was concentration-dependent (see table 1), with the T_{max} shifting to lower temperature as the Cu concentration increased (see fig. 3). It seems from this that an increase in the Cu loading also leads to the weakening in the interaction between Cu and Zr oxides. TPR (see table 1) also showed that the relative reducibility of the copper (estimated by the H_2 consumption in terms of a H/Cu) was much less than that expected for complete reduction of the Cu and showed a maximum value at a concentration of 20 mol% of Cu. Obviously this was due to the formation of metallic copper during evacuation. Presumably the H_2 consumed in TPR was mainly attributable to the reduction of the highly-dispersed copper oxides which were strongly interacting with (or incorporated into) the oxide support framework. As a result, the fraction of this type of copper, could, it is believed, be estimated by the H_2 consumption in TPR experiments. If so then this extends the value of TPR for such catalysts.

3.2. SURFACE AREA AND REACTIVITY

The total surface area of copper-doped zirconia aerogels was very high (i.e. up to 290 $m^2\ g^{-1}$ [12] even after evacuation at 703 K and reduction at 573 K (see table 1)). It is therefore safe to assume that the Cu-doped ZrO_2 aerogels had textural stability and would avoid sintering during the pre- and post-treatments. How-

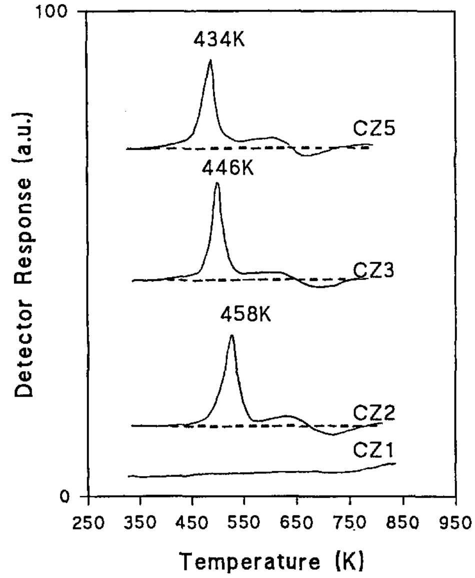

Fig. 3. TPR of Cu/ZrO_2 aerogels after evacuation at 703 K.

Table 2
Activities and selectivities in CO/CO_2 hydrogenation[a]

Catalyst code	Conv.[b] (%)	CH_3OH rates (μmol g^{-1} min^{-1})	CH_3OH/CH_4	Surface area of copper (m^2 g^{-1})
CZ1	1.83	0.6	1.1	–
CZ2	2.01	34.7	24.1	17.8
CZ3	5.81	78.9	28.5	28.5
CZ4	6.04	81.2	30.4	31.3
CZ5	4.88	63.6	22.6	41.2

[a] All data were collected after 6 h running.

[b] CO_2 and water were not considered.

ever, the Cu surface area estimated by N_2O decomposition showed a not unexpected concentration-dependence in that the metal surface area increased with an increase in Cu loadings (see table 2), indicating that the catalysts with higher Cu content had more *metallic* copper occupying the surface of the ZrO_2. However, the activity of the catalysts in CO/CO_2 hydrogenation appeared *not* to be related to these surface areas (see table 2) although the rate of methanol synthesis (as well as the methanol/methane ratio) was strongly dependent on the Cu content (see fig. 4). The activity is shown to parallel the change in the %Cu reduction. These deductions indicate that the metallic surface did not play a crucial role in the reaction for the present catalysts.

4. Discussion

Copper incorporated into the oxide support framework in Cu/ZrO_2 exists in two forms after the evacuation at 703 K: one is highly-dispersed in the substitu-

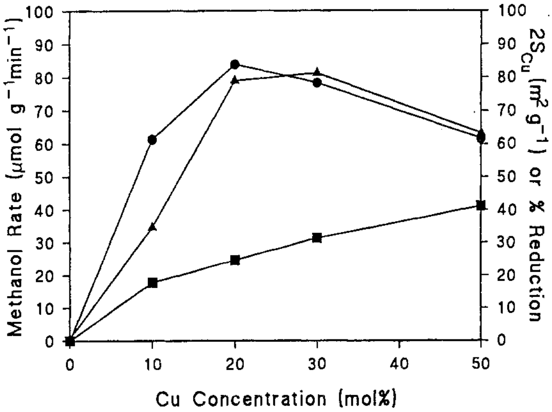

Fig. 4. The change in the percent Cu reduction on heating in 5% H_2/Ar to 773 K (●), the Cu surface area determined by N_2O decomposition at 33 K (■) and the activity in CO/CO_2 hydrogenation at 2 MPa and 523 K after 6 h reaction (▲) of Cu/ZrO_2 aerogels with varying Cu content after these have been evacuated at 703 K.

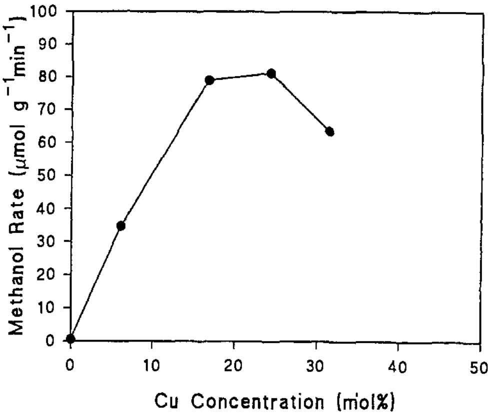

Fig. 5. Correlation between the activity in CO/CO_2 hydrogenation at 2 MPa and 523 K after 6 h reaction and the TPR-estimated concentration of dispersed Cu concentration in Cu/ZrO_2 samples.

tional sites and the other is in the form of metallic particles on the surface (whose concentration is enhanced with an increase in the Cu loadings). However, the activity of Cu/ZrO_2 aerogels in CO/CO_2 hydrogenation showed an optimum as the Cu content was increased. This demonstrates that metallic copper particles could not in these samples be predominantly responsible for their high activity. On the other hand, in these Cu/ZrO_2 aerogels, highly-dispersed copper may be the more important active sites for CO/CO_2 hydrogenation, particularly since there is a clear correlation in fig. 4 between the methanol synthesis rate and the relative reducibility which have similar trends with increasing Cu concentration. This illustrates that for Cu/ZrO_2 aerogel catalysts, the active sites were closely related to the dispersed Cu in the substitutional sites of amorphous ZrO_2 aerogel (as proposed by Baiker et al. [3,9]). However, the Cu/ZrO_2 activity does not show a linear increase with increases in the concentration of highly-dispersed copper (see fig. 5) and so the strength and the nature of the interaction between the dispersed Cu and the amorphous ZrO_2 is *very important* (i.e. a strong interaction favors an improvement in the production of methanol (see fig. 3)).

5. Conclusions

Sol–gel derived Cu/ZrO_2 catalysts have high activity and selectivity toward methanol synthesis. After evacuating at 703 K, copper species in such catalysts existed in two forms: particulate and dispersed. The proportion of particulate copper increases with an increase in the Cu content. The activity shows a maximum value at intermediate Cu concentrations. There is no correlation evident between the Cu surface area and the activity of the catalyst, but rather the activity appears to be correlated to the concentration of *highly-dispersed* copper. It can be concluded therefore that the copper in the substitutional sites of the ZrO_2 are associated with the active sites in Cu/ZrO_2 responsible for CO/CO_2 hydrogenation. However, the nonlinear increase in the activity at high concentrations of dispersed copper demonstrates the importance of the specific interaction between dispersed copper and amorphous zirconia. A detailed investigation of the nature of the interaction is under way.

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