

Carbon Monoxide Hydrogenation over ZrO_2 and Cu/ZrO_2

Yuhan Sun*† and Paul A. Sermon

Solids and Surface Research Group, Department of Chemistry, Brunel University, Uxbridge, Middlesex, UK UB8 3PH

Sol-gel-derived ZrO_2 with a high surface area ($> 250 \text{ m}^2 \text{ g}^{-1}$) is found to be very active in CO hydrogenation and unexpectedly produces propan-2-ol with high selectivity; after incorporation of Cu, a methanol synthesis catalyst is produced not only with a higher activity per unit area than Cu/ZnO , but also with an even lower tendency to produce alkanes at higher temperature.

There has been a great deal of work on Cu/ZnO samples, which act as models for methanol synthesis catalysts;¹ thus 9% Cu/ZnO (prepared by precipitation, calcination and reduction) shows the expected activity and selectivity in CO hydrogenation at 523 K, 1.7 MPa and $180 \text{ cm}^3 \text{ min}^{-1}$, producing 161 nmol of methanol per m^2 of the total surface area per min. The support itself has long been known to show

activity in the reaction² and interestingly, the copper is not entirely reduced in such a catalyst because in temperature-programmed reduction to 613 K only 0.76 mol H_2 are consumed per mol Cu.

Cu/ZrO_2 (derived from CuZr alloy precursors as well as those prepared by impregnation or ion-exchange of ZrO_2) is already known to be active in CO hydrogenation. The interface between Cu and ZrO_2 has been proposed as the location of the active sites,^{3,4} although the structure of the ZrO_2 remains uncertain.^{5,6} As with Cu/ZnO , the support

† *Permanent address:* Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001 P.R. China.

Table 1 CO Hydrogenation over ZrO₂^a and 10 mol% Cu/ZrO₂^b

Catal.	Time /min	Conv. ^c (%)	MeOH rates		Selectivity (mol%)				
			/μmol g ⁻¹ min ⁻¹	/nmol m ⁻² min ⁻¹	MeOH/CH ₄	MeOH	EtOH	PrOH	Alk ^d
ZrO ₂ ^a	30	2.00	0.8	2.9	1.1	6.0	14.4	73.4	6.2
	60	1.93	0.7	2.6	1.0	5.6	14.1	73.9	6.4
	120	1.87	0.6	2.4	1.0	5.4	14.6	73.8	6.2
	240	1.83	0.6	2.4	1.0	5.4	14.3	73.9	6.4
Cu/ZrO ₂ ^b	10	10.72	79.6	287.1	74.3	65.1	24.2	8.4	1.7
	60	13.04	165.1	595.4	87.0	92.6	3.1	2.7	1.2
	120	12.46	160.3	578.3	132.4	95.0	1.9	2.0	0.9
	180	11.67	155.0	558.9	147.3	95.0	1.8	1.6	0.7
	240	10.34	138.2	498.4	147.5	96.0	1.4	1.3	0.7

^a Catalyst contained about 0.82 wt% K. ^b Catalyst contained about 0.73 wt% K. ^c CO₂ and water were not considered in the calculation of activity and selectivities, and conversions were based on carbon number. ^d Alk denotes hydrocarbon products.

Table 2 Effect of the operation parameters on catalytic performance of Cu/ZrO₂^a

T/K	Total pressure /MPa	Flow rate /cm ³ min ⁻¹	MeOH rates	
			/μmol g ⁻¹ min ⁻¹	/nmol m ² min ⁻¹
523	2.0	30	109.8	424.9
523	2.0	60	83.5	332.8
523	2.0	120	59.8	231.5
523	2.0	180	40.0	154.9
523	1.6	60	66.1	255.8
523	2.4	60	96.7	373.9
523	3.0	60	108.9	421.1
508	2.0	60	54.5	211.0
538	2.0	60	114.8	444.2
553	2.0	60	150.1	580.5
568	2.0	60	157.6	609.8

^a Data were collected after 24 h running, $S_{\text{BET}} = 259 \text{ m}^2 \text{ g}^{-1}$.

ZrO₂ alone also produces methanol, ethers and alkanes,^{7,8} but only at a modest level.

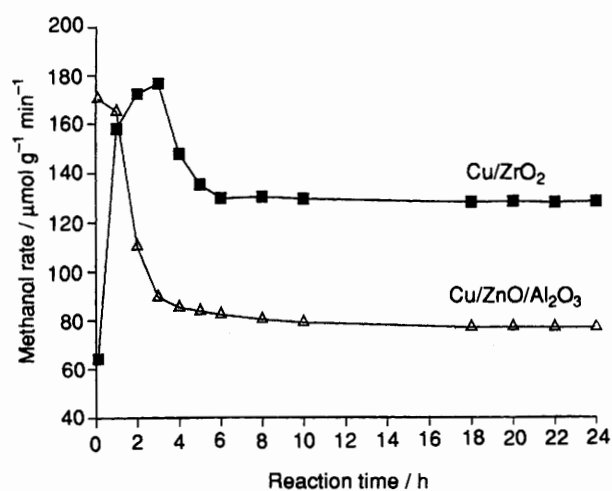
Recently, sol-gel chemistry has been attracting more attention from those interested in the preparation of supported metal catalysts since it may produce homogeneous materials of high dispersion with lower levels of deactivation.⁹⁻¹²

Here, doped and pure zirconia aerogels have been prepared by such sol-gel routes with subsequent supercritical drying. These have been considered in CO hydrogenation.

ZrO₂ and 10% Cu/ZrO₂ have been prepared as hydrogels and then aerogels as follows, using Aldrich reagents. Zirconyl nitrate (in the presence or absence of copper(II) nitrate) was first transformed into the sol and then the hydrogel by adjusting and raising the final solution pH to ca. 10 by KOH addition. The precipitate was aged in the mother liquor for 40 min and was then filtered off and washed with doubly distilled water (until the pH remained constant) and then with ethanol. Finally, the gel was dried supercritically (at 533 K and 8.1 MPa).

After reduction at 573 K the ZrO₂ had a total surface area of 259 m² g⁻¹, and this increased a little in the presence of the Cu (*i.e.* was 277 for 10 mol% Cu/ZrO₂). TPR (temperature-programmed reduction) indicated that the ZrO₂ itself was not significantly reduced below 573 K, but that the Cu seemed to be almost entirely reduced under the same conditions [and the total surface area of the reduced sample had decreased marginally (*i.e.* to 259 m² g⁻¹)].

X-Ray diffraction and transmission electron microscopy revealed that reduced catalysts were X-ray amorphous but with a narrow distribution of particle size centred at below 5 nm.

**Fig. 1** CO Hydrogenation over Cu/ZrO₂ and Cu/ZnO/Al₂O₃ at 523 K

Samples (0.1 g) of these were tested in CO/H₂ = 2 at 2 MPa at a reactant flow of 60 m³ min⁻¹ at 523 K and the results for ZrO₂ are those shown in Table 1. Although conversions of CO were not very high, these results are interesting in that the oxygenates (oxy) produced were predominantly of one C₃ higher alcohol (which was not expected in the light of the results of others on ZrO₂^{7,8}), and this situation did not deteriorate with increasing reaction time. This selectivity is certainly closely related to the nature of surface sites in the amorphous aerogel and the presence of residual K in the catalyst. Methanol formation over ZrO₂ can be understood through a formate-to-methoxide mechanism, subsequent hydrolysis and then K-promoted chain growth.^{8,13} Surface anion vacancies may of course be important.¹⁴ In this context, amorphous aerogels have high surface area and more surface vacancies than more poorly dispersed and more crystalline samples, but a full understanding of the mechanism is at present being pursued.

With 10 mol% Cu/ZrO₂ (see Table 1), the overall conversion of CO is much higher than that seen for ZrO₂ alone, but the balance of products is towards MeOH. Nevertheless, the rate of methanol synthesis (in μmol g⁻¹ min⁻¹ or nmol m⁻² min⁻¹) over Cu/ZrO₂ per unit area of catalyst is three times that seen for Cu/ZnO.¹ After 24 h running, the catalyst was still active. As expected its activity at 523 K (see Table 2) decreased as the molecular residence time decreased from 3.0–0.5 s. However, it is noteworthy that as the temperature was increased, alkane production did not begin to dominate over alcohol formation in the way it does for some catalysts. The relevant activation energy was 123 kJ mol⁻¹. Furthermore, activity at 538 K and 2 MPa (*i.e.* 128 μmol

methanol $\text{g}^{-1} \text{min}^{-1}$ after 24 h) was rather stable (*i.e.* was 124 μmol methanol $\text{g}^{-1} \text{min}^{-1}$ after 48 h) when compared with a commercial catalyst (*i.e.* Cu/ZnO/Al₂O₃ (KAT/93/29, ICI) (see Fig. 1). This was true despite the fact that Cu/ZrO₂ had a lower Cu surface area (23.1 $\text{m}^2 \text{g}^{-1}$, as estimated by N₂O decomposition) than the Cu/ZnO/Al₂O₃ (54.3 $\text{m}^2 \text{g}^{-1}$).

ZrO₂ prepared as described appears very selective in CO hydrogenation to propan-2-ol. After incorporation of Cu, a methanol synthesis catalyst is produced with an activity per unit area which is much higher than Cu/ZnO/Al₂O₃. These results then highlight the excellent potential of sol-gel catalysts derived supercritically for the synthesis of methanol or higher alcohols.

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