Copper zinc oxide catalysts for ambient temperature carbon monoxide oxidation

S. H. Taylor,[a] G. J. Hutchings[a] and A. A. Mirzaei[b]

[a] *Cardiff University, Department of Chemistry, PO Box 912, Cardiff, UK CF10 3TB. E-mail: taylorsh@cf.ac.uk*
[b] *Leverhulme Centre for Innovative Catalysis, University of Liverpool, Department of Chemistry, Liverpool, UK L69 3BX*

Received (in Cambridge, UK) 29th April 1999, Accepted 16th June 1999

Copper zinc oxide catalysts are effective for the ambient temperature carbon monoxide oxidation and display higher specific activity than the current commercial hopcalite catalyst.

The catalytic oxidation of carbon monoxide to carbon dioxide at ambient temperature and pressure is an important process for respiratory protection. In particular, the process is widely adopted by mining industries and has also found applications in deep sea diving and space exploration. Furthermore, new applications for the process such as reducing the deactivation of carbon dioxide lasers and applications for new sensors have been explored. In the last 10 years low temperature carbon monoxide oxidation has received renewed attention since Haruta *et al.* demonstrated that gold, highly dispersed on various oxides, forms catalysts active at sub-ambient temperatures.[1] However, the most widely used catalyst is the mixed copper manganese oxide hopcalite catalyst, $CuMn_2O_4$, first examined in 1921.[2,3] Both the gold based and the copper manganese oxide catalysts are important in terms of their high activity at ambient temperatures. It is the observation of high activity at low temperature which has stimulated significant recent interest in these types of catalysts.[4,5] It is interesting to consider whether other catalysts are capable of sustaining carbon monoxide oxidation at ambient temperature. Here, we present the first results showing that copper zinc oxide catalysts, prepared by co-precipitation, can display much higher activity for reaction than the current commercial hopcalite catalysts.

Catalysts were prepared using a co-precipitation technique under different atmospheres, including air, nitrogen, hydrogen and carbon dioxide. Aqueous solutions of $Cu(NO_3)_2\cdot3H_2O$ (0.25 mol l^{-1} Aldrich 99.999%) and $Zn(NO_3)_2\cdot6H_2O$ (0.25 mol l^{-1} Aldrich 99.999%) were pre-mixed in a 2:1 ratio. The resulting solution was stirred and heated to 80 °C in a round bottomed flask fitted with a condenser and equilibrated under a gas flow of 20 ml min^{-1} for 5 min. An aqueous solution of Na_2CO_3 (0.25 mol l^{-1} Aldrich 99.999%) was added to the continuously stirred flask until a pH in the range 6.8–7.0 was attained. At this stage the gas flow was passed through the solution and the precipitate allowed to age between 60 and 300 min. After ageing the precipitate was recovered by filtration, washed several times with hot distilled water and dried in air (120 °C for 16 h) and subsequently calcined in static air (550 °C for 6 h) to produce the catalyst. The hopcalite catalyst was also prepared in a similar manner using co-precipitation. The catalysts were characterised by powder X-ray diffraction. and nitrogen adsorption to determine the BET surface area.

The catalysts were tested for CO oxidation using a fixed bed laboratory microreactor. Typically CO (5% CO in He, 5 ml min^{-1}) and O_2 (50 ml min^{-1}) were fed to the reactor at controlled rates using mass flow controllers and passed over the catalyst (100 mg) at 20 °C. The products were analysed using on-line gas chromatography with a 3 m packed Carbosieve column. These conditions are equivalent to a total gas hourly space velocity of 33 000 h^{-1} and CO concentration of 0.45 vol%. Under these conditions the adiabatic temperature rise is $<$ 7 °C and consequently the reactor temperature could readily be maintained isothermally at 20 °C.

All the copper zinc oxide catalysts, irrespective of the preparation atmosphere, showed appreciable activity for the oxidation of carbon monoxide at 20 °C. Blank reactions under the same conditions demonstrated no conversion. All the copper zinc oxide catalysts showed an initial decrease in activity over the first 30 min on line, but after this initial period steady state activity was maintained over the 500 min test period. Representative data for the catalysts prepared in an air atmosphere are shown in Fig. 1. The steady state activity of the aged copper zinc oxide catalysts derived from different atmospheres, and comparison with a copper manganese oxide catalyst are shown in Table 1.

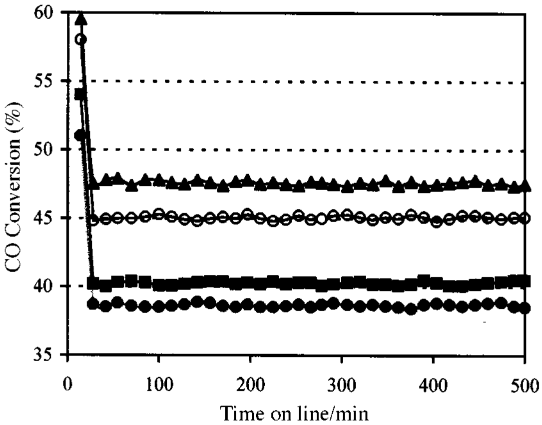

Fig. 1 Carbon monoxide conversion at 20 °C for aged catalysts prepared using air *vs.* time on line (GHSV = 33 000 h^{-1}, 100 mg catalyst, 0.45 vol% CO: Ageing time: (●) 60, (■) 120, (▲) 180 (○) 300 min.

The atmosphere used during co-precipitation has a marked influence on the activity of the copper zinc oxide catalysts. Regardless of ageing time, the general trend in terms of carbon monoxide conversion is air $>$ hydrogen $\approx$ nitrogen $>$ carbon dioxide. Increasing the catalyst ageing time up to 180 min increased the carbon monoxide conversion over all the copper zinc oxide catalysts. Increasing the ageing time to 300 min resulted in a slight decrease in conversion for the catalyst prepared in an air atmosphere, however, the catalysts prepared under the other atmospheres continued to show an increase in conversion. The catalyst surface areas were of similar magnitude regardless of the preparation atmosphere, however, there is a general increase in surface area as a result of increased ageing time. Although the overall conversion increases with ageing time the specific activity shows a gradual decrease.

Under our reaction conditions comparison of the copper zinc oxide catalyst has been made with the highly active copper manganese oxide catalyst.[6] The copper zinc oxide catalysts aged for <180 min are all considerably more active than the copper manganese oxide catalysts. For example, the specific activity of copper zinc oxide aged for 60 min is greater than the

Table 1 Steady state activity for ambient temperature carbon monoxide oxidation (GHSV = 33 000 h^{-1}, 100 mg catalyst, 0.45 vol% CO)

Catalyst	Ageing time/min	Preparation atmosphere	Surface area/ $m^2\ g^{-1}$	CO conversion 10^{-16} (%)	Rate/molecules m^{-2}
CuO/ZnO	60	Air	29	38.8	1.50
CuO/ZnO	60	CO_2	26	20.5	0.88
CuO/ZnO	60	H_2	25	29.8	1.33
CuO/ZnO	60	N_2	27	30.4	1.26
Cu/Mn_xO_y	60	Air	28	9.9	0.39
CuO/ZnO	120	Air	36	40.2	1.35
CuO/ZnO	120	CO_2	28	21.5	0.86
CuO/ZnO	120	H_2	34	34.8	1.14
CuO/ZnO	120	N_2	32	33.2	1.16
$CuMn_xO_y$	120	Air	26	11.8	0.51
CuO/ZnO	180	Air	46	47.5	1.16
CuO/ZnO	180	CO_2	38	25.6	0.76
CuO/ZnO	180	H_2	41	40.2	1.10
CuO/ZnO	180	N_2	40	38.6	1.08
$CuMn_x/O_y$	180	Air	27	20.4	0.84
CuO/ZnO	300	Air	42	45.0	1.20
CuO/ZnO	300	CO_2	40	28.8	0.81
CuO/ZnO	300	H_2	45	42.4	1.06
CuO/ZnO	300	N_2	43	41.4	1.08
$CuMn_xO_y$	300	Air	30	49.5	1.85

corresponding copper manganese oxide catalyst by a factor >3.8. It is only once the copper manganese oxide catalyst has been aged for 300 min that it demonstrates higher activity. The optimum ageing time for the copper manganese oxide catalyst is 720 min showing a specific oxidation rate greater than the best copper zinc oxide by a factor of *ca.* 2.2.

Characterisation of the catalysts by powder X-ray diffraction showed that the preparation atmosphere and ageing process strongly influence the structure of the catalyst precursor. Hydrozincite [$Zn_5(CO_3)_2(OH)_6$], gerhardite [$Cu_2(OH)_3NO_3$], malachite [$Cu_2CO_3(OH)_2$], aurichalcite [$(Cu,Zn)_5(CO_3)_2(OH)_6$] and rosasite]$(Cu,Zn)_2CO_3(OH)_2$], were all determined and the relationship between preparation conditions and structure is considered to be complex. However, after calcination all the catalysts consisted of CuO and ZnO. The particle sizes of the oxides determined by X-ray line broadening decreased with increased ageing time, this effect was most marked with the catalyst prepared under air and carbon dioxide atmospheres, whilst under nitrogen and hydrogen atmospheres the effect was relatively minor. Temperature programmed reduction using hydrogen indicates that there may be some mixed oxide formation in the calcined catalyst. The catalysts were all similar by transmission electron microscopy, but subtle differences indicate that copper/zinc oxide solid solutions were formed and this is consistent with the evidence from temperature programmed reduction. The origin of the low temperature oxidation activity is unclear, but it appears that the highly dispersed CuO and ZnO, and the presence of solid solution phases formed during the controlled precipitation and ageing process are important.

At this stage no attempt has been made to optimise the activity of the copper zinc oxide catalysts, but it is clear that these catalysts show promising performance for the oxidation of carbon monoxide under ambient conditions. To the best of our knowledge this is the first reported study of copper zinc oxide catalyst prepared by co-precipitation under different atmospheres for the oxidation of carbon monoxide at low temperatures and these systems are now worthy of further investigation.

We thank Chris Kiely and Dave Whittle (University of Liverpool) for electron microscopy and Richard Joyner (Nottingham Trent) for useful discussion.

Notes and references

1 Haruta, N. Yamada, T. Kobayashi and S. Iijima, *J. Catal.*, 1989, **115**, 301.

2 T. H. Rogers, C. S. Piggot, W. H. Bahlke and J. M. Jennings, *J. Am. Chem. Soc.*, 1921, **43**, 1973.

3 H. A. Jones and H. S. Taylor, *J. Phys. Chem.*, 1923, **27**, 623.

4 G. J. Hutchings, A. A. Mirzaei, R. W. Joyner, M. R. H. Siddiqui and S. H. Taylor, *Catal. Lett.*, 1996, **42**, 21.

5 G. Fierro, S. Morpurgo, M. LoJacono and M. Inversi, *Appl. Catal. A*, 1988, **166**, 407.

6 E. J. Trimble, *Toxicology*, 1996, **115**, 41.

Communication 9/03426I