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The preparation and activity of copper zinc oxide catalysts for ambient temperature carbon monoxide oxidation

Stuart H. Taylor[a,*], Graham J. Hutchings[a], Ali A. Mirzaei[b]

[a] Department of Chemistry, Cardiff University, P.O. Box 912, Cardiff CF10 3TB, UK
[b] Department of Chemistry, University of Sistan and Baluchistan, Zahedan, Iran

Abstract

A series of copper zinc oxide catalysts have been prepared using a co-precipitation procedure by varying the ageing time in the precipitation liquor. The catalysts were studied for the oxidation of CO at ambient temperature. All the catalysts exhibited ambient temperature CO oxidation activity and the ageing time is important in controlling the catalyst activity. The most active catalysts were aged for 165 min. Characterisation by powder X-ray diffraction showed that the catalyst precursors were sensitive to ageing time. It was also evident that ageing time influenced the precursor morphology. The calcined catalysts were all comprised of CuO and ZnO. The origin of the high activity for the CuO/ZnO catalysts prepared with short ageing times is not fully understood, 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.

Keywords: Ambient temperature CO oxidation; Co-precipitation; Mixed metal oxides

1. Introduction

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 15 years low temperature carbon monoxide oxidation has received renewed attention since Haruta et al. [1] demonstrated that gold, highly dispersed on various oxides, forms catalysts active at sub-ambient temperatures. However, the most widely used catalyst is the mixed copper manganese oxide hopcalite, $CuMn_2O_4$, first examined in 1921 [2,3]. We have shown that the preparation of $CuMn_2O_4$ by co-precipitation is influenced by many variables, but the most important in controlling the carbon monoxide oxidation activity was ageing time in the co-precipitation liquor [4,5].

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. It is interesting to consider whether other catalysts are capable of sustaining carbon monoxide oxidation at ambient temperature. This study presents the results investigating the carbon monoxide oxidation activity of CuO/ZnO catalysts prepared by co-precipitation.

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* Corresponding author.
E-mail address: taylorsh@cardiff.ac.uk (S.H. Taylor).

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Catalysts based on CuO/ZnO mixed oxides are of considerable industrial interest due to their activity for the low temperature and pressure methanol synthesis and the water–gas shift reaction [6,7]. Mechanistic studies of the water–gas shift reaction [8] and methanol synthesis [9] using CuO/ZnO based catalysts have indicated that carbon monoxide oxidation can be an integral step in these processes. The current study was initiated against this background to investigate the potential of copper zinc oxide catalysts for ambient temperature carbon monoxide oxidation. In particular we have concentrated on the effect of catalyst ageing time during preparation. Previously, it has been shown that it is an important factor influencing the structure of copper zinc oxide catalysts [9–11] and mixed copper manganese oxides for ambient temperature carbon monoxide oxidation.

2. Experimental

2.1. Catalyst preparation

Catalysts were prepared using a co-precipitation technique under an air atmosphere. Aqueous solutions of $Cu(NO_3)_2\cdot 3H_2O$ (0.25 mol l^{-1} Aldrich 99.999%) and $Zn(NO_3)_2\cdot 6H_2O$ (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. The solution was allowed to equilibrate under a gas flow of 20 ml min^{-1} air 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 for a specified time. After ageing the precipitate was recovered by filtration, washed several times with hot distilled water and dried in air (120 °C for 16 h). This material was the catalyst precursor and subsequently the catalyst was produced by calcination in static air (550 °C for 6 h).

2.2. Catalyst and precursor characterisation

The surface areas of the catalysts were measured using N_2 adsorption at 77 K in accordance with the BET method, after the samples were degassed for 16 h at 300 °C. Powder X-ray diffraction patterns were obtained using a Philips 1050 W system modified by Hiltonbrooks. Data were collected with a 2θ step size of 0.01° and a counting time of 1.0 s per interval with a Cu Kα radiation source operated at 30 keV and 20 mA. Matching the experimental diffraction patterns to entries in the JCPDS powder diffraction file identified phases.

Temperature programmed reduction measurements were carried out using a Micromeritics TPD/TPR 2900 system. A known mass of catalyst (12–25 mg) was used for analysis with a temperature programmed regime from ambient to 800 °C at 10 °C min^{-1}. The reducing gas was 10% H_2 in Ar with a flow rate of 50 ml min^{-1}.

2.3. Catalyst testing

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 passed over the powdered catalyst (100 mg) in a Pyrex reactor 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. Carbon monoxide conversion was calculated on the vol.% of CO_2 in the reactor effluent and carbon balances were $100 \pm 1\%$ in all cases.

3. Results and discussion

3.1. Catalyst precursor characterisation

Many previous studies of the copper zinc oxide system have established the importance of the structure of the catalyst precursor in controlling the structure of the final catalyst and consequently activity. Therefore, in addition to the catalysts we have also concentrated on characterising the catalyst precursor in these studies. Powder XRD results for the aged precursors are shown in Fig. 1. The unaged precursor was clearly amorphous to X-rays, whilst increasing the ageing time resulted in

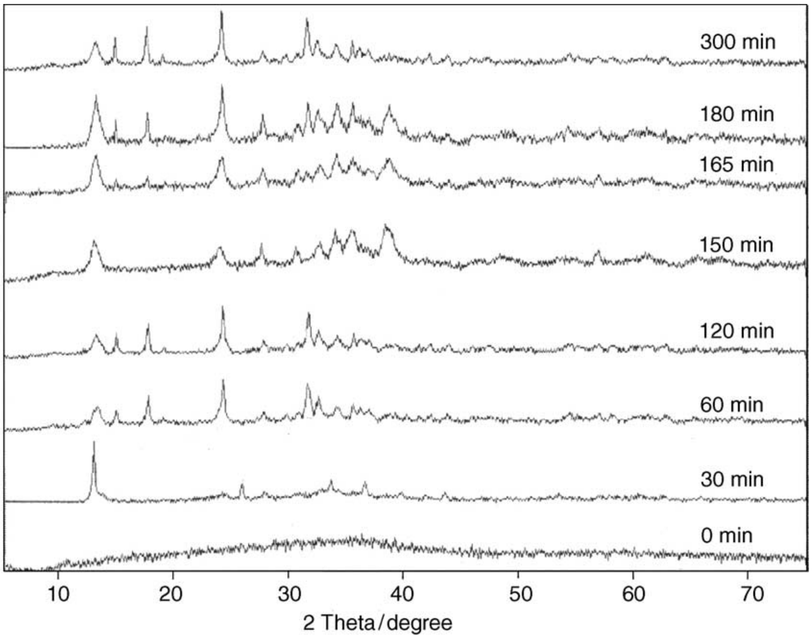

Fig. 1. Powder XRD pattern of aged catalyst precursors.

the observation of crystalline diffracting phases. The diffraction pattern of the precursor aged for 30 min showed reflections attributed to the presence of a rosasite phase. Ageing for 60 min did result in a change of the precursor phases as aurichalcite was also detected. It must be noted that although the reflections are identified as rosasite, the diffraction pattern is very similar to other common hydroxycarbonate phases such as malachite and assignment cannot be made unequivocally. Rosasite and malachite are crystallographically identical structures [12,13]. The phases only differ chemically in that the mineral malachite is a pure copper hydroxycarbonate, whilst rosasite is a mixed copper zinc hydroxycarbonate. Comparing the diffraction pattern from the longer aged samples, a trend appeared to develop. All the diffraction patterns of the samples aged for over 60 min showed reflections characteristic of rosasite and aurichalcite. The sample aged for 165 min was slightly different as the rosasite reflections were reduced, and tenorite (CuO) peaks were observed. The CuO phase is identified primarily by the strong (1 1 1) 2.33 Å and (2 0 2) 1.57 Å reflections. The same peaks were not identified in the samples aged for 180 and 300 min. A summary of the bulk phases identified by XRD is presented in Table 1.

The catalyst precursors and catalysts have been characterised in detail using scanning transmission electron microscopy and high resolution EDX. The results of these studies are not reported here, a detailed microscopy study of the systems is reported elsewhere [14]. Electron diffraction experiments confirmed that the unaged precursor was amorphous. Studies also showed that once the catalyst ageing time was increased to 30 min and higher two distinct morphologies were present. The morphologies were platelets and needles, and both showed an increase

Table 1
Precursor phases identified from powder XRD[a]

Ageing time (min)	Precursor bulk phases
0	Amorphous
30	Rossasite
60	Aurichalcite, rossasite
120	Aurichalcite; rossasite
150	Aurichalcite; rossasite
165	Aurichalcite; rossasite, tenorit
180	Aurichalcite; rossasite
300	Aurichalcite; rossasite

[a] Rossasite, $(Cu/Zn)_2CO_3(OH)_2$; Aurichalcite, $(Cu/Zn)_5(CO_3)_2(OH)_6$; Tenorite, CuO.

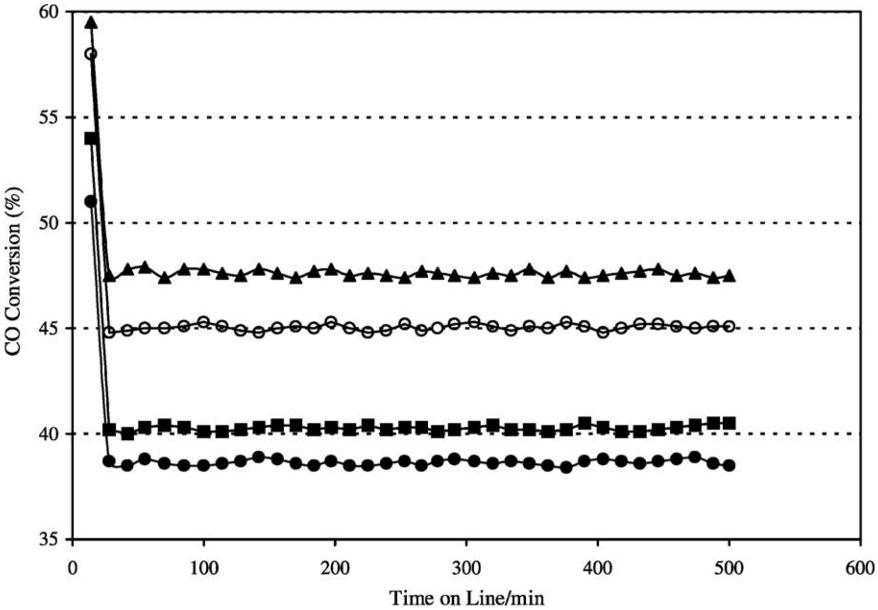

Fig. 2. CO oxidation activity as a function of time on line for aged catalysts.

in their dimension as the precursor ageing time increased. TEM also showed the presence of supported nanoparticles in the 165 min aged precursor. Analysis of the nanoparticles with EDX revealed a copper rich structure and this might explain the observation of tenorite from the XRD analysis.

3.2. Catalyst CO oxidation activity

The mixed copper/zinc oxide catalysts prepared by co-precipitation were all active for ambient temperature CO oxidation. The representative activity of catalysts aged for varying times is shown in Fig. 2. Catalyst activity remained stable throughout the test period and the steady state CO conversion is summarised in Fig. 3. In general, increasing the catalyst ageing time up to 165 min was accompanied by an increase in CO conversion. A further increase of the ageing time from 165 to 300 min resulted in a slight decrease of CO conversion. The catalyst surface areas are summarised in Table 2. Data shows that there is a general increase in surface area as a result of increased ageing time. Although, the overall conversion increases with ageing time, the activity normalised for surface area effects shows a gradual decrease (Fig. 4).

Table 2
BET surface areas of copper/zinc oxide catalysts

	Ageing time (min)							
	0	30	60	120	150	165	180	300
Surface area ($m^2 g^{-1}$)	14	26	29	36	38	49	46	42

3.3. Characterisation of calcined catalysts

Catalyst precursors were calcined at 550 °C for 6 h in static air to produce the active metal oxide catalysts. Catalysts were characterised using powder XRD and the resulting patterns are presented in Fig. 5. The XRD patterns of the catalysts were all similar. The phases identified were CuO and ZnO with no other crystalline phases present. The only significant difference identified from the diffraction data was associated with the broadening of the diffraction peaks. It was observed that broader diffraction peaks were produced from the catalysts with increased ageing time. X-ray line broadening was treated in accordance with the Scherrer equation, and the resulting crystallite sizes were calculated (Table 3).

The unaged and 30 min aged catalysts showed the largest crystallite sizes, with CuO crystallites

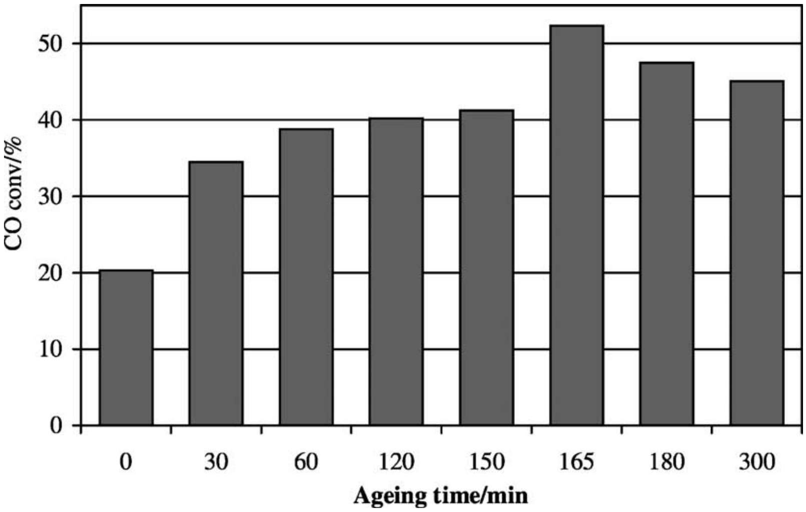

Fig. 3. Steady state CO conversion for differently aged catalysts.

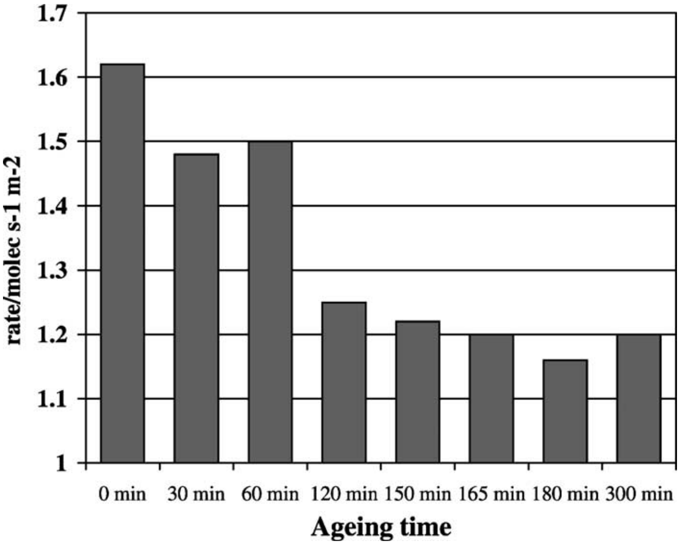

Fig. 4. Catalyst activity normalised for the effect of surface area for aged catalysts.

Table 3
Copper and zinc oxide crystallite size as a function of ageing time, determined from X-ray line broadening

	Ageing time (min)							
	0	30	60	120	150	165	180	300
CuO (nm)	189	143	79	51	38	37	32	27
ZnO (nm)	76	69	69	57	56	35	33	28

significantly larger than ZnO. The catalysts aged for 60 min and above showed broadly similar crystallite sizes for CuO and ZnO. However, as the ageing time was increased the copper and zinc crystallite sizes decreased further. These observations are consistent with the increase in surface area measured by the BET method. Similar relationships between crystallite size and ageing time have also been observed previously for the production of copper zinc oxide catalysts by

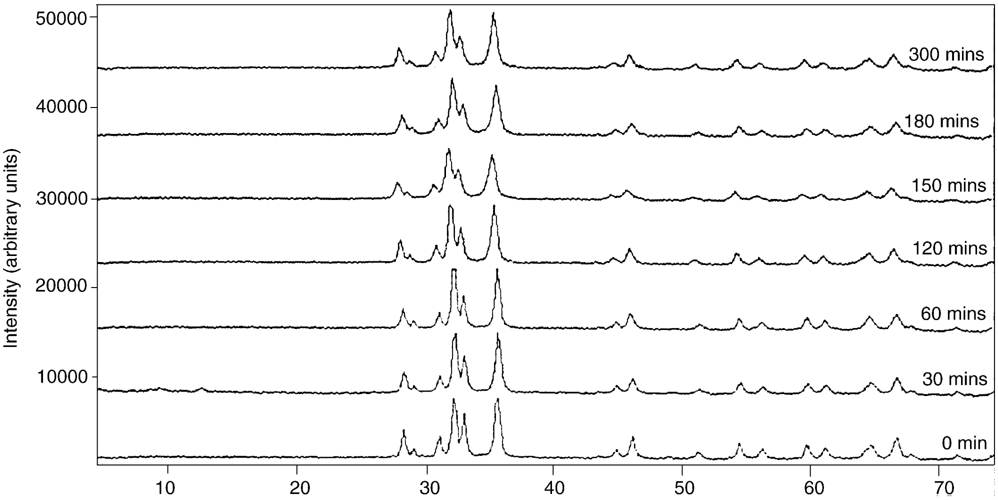

Fig. 5. Powder XRD pattern for aged catalysts.

co-precipitation [9]. However, the decrease in the crystallite size of the catalyst is in clear contrast to the precursor, which showed an increase in crystallite size as the ageing time was extended.

In order to investigate further the catalyst structures, temperature programmed reduction studies were performed using dilute hydrogen. The reduction profiles for representative catalysts aged 30, 180, and 300 min are shown in Fig. 6. The catalyst aged for 30 min showed four reduction peaks at 175, 230, 241, and 261 °C. As the ageing time was increased, the reduction peaks shifted to slightly higher temperatures and they also became broader. The catalyst aged for 180 min showed peaks at 188, 238, and 268 °C, whilst the 300 min aged catalyst had peaks at 182 and 239 °C. The reduction profiles of CuO and ZnO both showed single major reduction features that were significantly different from the catalysts in this study [15]. Temperature programmed reduction studies in the literature [16] have reported similar reduction temperatures to ours for copper species, and they have been interpreted in terms of Cu^{2+} species in different environments. Thus the TPR results can be interpreted in terms of the formation of solid solutions containing Cu in ZnO and Zn in CuO. The relatively small CuO and ZnO crystallites, and consequently the broad X-ray diffraction

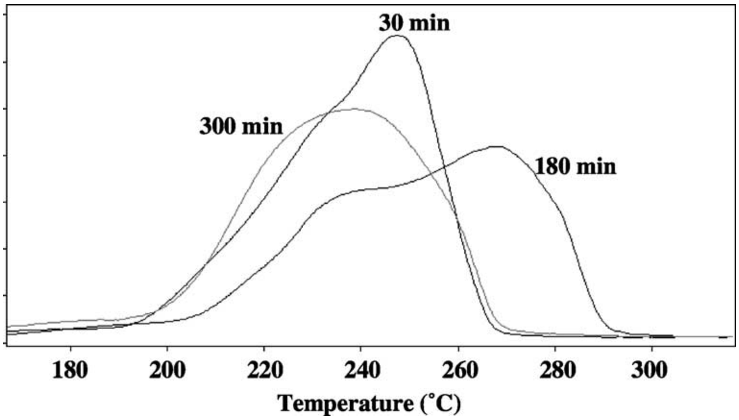

Fig. 6. Temperature programmed reduction profile for representative catalysts.

peaks, make the identification of solid solutions difficult from the XRD data. Detailed high resolution TEM and EDX studies have confirmed that, the CuO and ZnO are indeed present as solid solutions containing considerable concentrations of incorporated Cu and Zn [14]. Furthermore, the most active weight normalised catalyst (165 min) has the highest proportion of Cu dissolved in the ZnO. The formation of solid solutions are not unexpected when the structure of the precursors are considered. The predominant catalyst precursor structures are aurichalcite and rossasite, which are mixed metal hydroxycarbonates. The intimate mix of Cu and Zn in the precursor is an important factor controlling the final catalyst structure and solid solution formation.

The mixed CuO/ZO catalysts prepared by co-precipitation are complex, and the origin of ambient temperature CO oxidation activity is still unclear. It is apparent that normalising the catalyst activities for the effect of surface area results in the materials with the shortest ageing times being the most active. However, normalising activity for total surface area may produce misleading results, as certain catalyst components may be inactive. The formation of solid solutions when the catalysts are prepared by co-precipitation is an important factor, as catalysts prepared by precipitation of copper and zinc alone was inactive. The observation of a relationship between catalyst activity and the degree of solid solution formation is significant and may provide an indication for the origin of the activity of these catalysts.

4. Conclusions

Copper/zinc mixed oxide catalysts have been prepared using co-precipitation by varying the ageing time in the precipitation liquor. The catalysts were studied for the oxidation of CO at ambient temperature. All the catalysts exhibited appreciable CO oxidation activity. It is shown that the ageing time is important in controlling the catalytic activity. The most active catalysts were aged for 165 min. Correcting catalyst activity for the effect of surface area demonstrated that catalysts aged <60 min had the greatest oxidation rates. Characterisation by powder X-ray diffraction showed that the catalyst precursors were sensitive to ageing time. It was also evident that ageing time influenced the precursor morphology. The calcined catalysts were all comprised of CuO and ZnO. The origin of the high activity for the CuO/ZnO catalysts prepared with short ageing times is not clear, 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.

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