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The oxidation of carbon monoxide at ambient temperature over mixed copper–silver oxide catalysts

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Abstract

$Cu_2Ag_2O_3$ has been prepared by a precipitation method and evaluated for ambient temperature carbon monoxide oxidation. The $Cu_2Ag_2O_3$ catalyst demonstrated appreciable activity and a relationship with preparation ageing time was observed. An ageing time of 4 h produced a catalyst with the highest oxidation performance. The catalyst precursor materials, prepared by drying at room temperature, displayed initial high activity, which decreased with time on line. The precursors were transformed during CO oxidation to form the mixed oxide $Cu_2Ag_2O_3$ as the material was dried in situ. A comparison of the catalytic activity has been made with a representative sample of a high activity hopcalite, mixed copper/manganese oxide catalyst. On the basis of CO oxidation rate data corrected for the effect of catalyst surface area the $Cu_2Ag_2O_3$, aged for 4 h was at least as active as the hopcalite catalyst.

Keywords: CO; Oxidation low temperature; $Cu_2Ag_2O_3$

1. Introduction

The catalytic oxidation of carbon monoxide to carbon dioxide at ambient temperature is an important process for respiratory protection and life support. 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 such as reducing the deactivation of carbon dioxide lasers and applications for new sensors have been explored. In the last few years low temperature carbon monoxide oxidation has received renewed attention since Haruta and co-workers demonstrated that gold, highly dispersed on various oxides, forms catalysts active at sub-ambient temperatures [1]. In subsequent years interest in gold-based catalysts has increased significantly for low temperature CO oxidation and a wide range of active supports have been investigated [2]. Other catalysts, such as CuO/ZnO [3] and supported Pt/Sn alloys [4] have also been identified for their low temperature CO oxidation activity. However, the most widely used commercial catalyst is the mixed copper manganese oxide hopcalite, $CuMn_2O_4$, first examined in 1921 [5,6]. Both the gold based and the copper manganese oxide catalysts are important in terms of their oxidation 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 [7]. It is interesting to consider whether other catalysts are capable of sustaining carbon monoxide oxidation at ambient temperature.

In 1999, a communication was published by Gomez et al. describing the synthesis of the first mixed silver–copper oxide ($Cu_2Ag_2O_3$) [8]. The structure and chemistry of $Cu_2Ag_2O_3$ suggests that the material is potentially an interesting catalyst for oxidation reactions. Against this background the activity of mixed silver–copper oxide has been probed for the ambient temperature oxidation of carbon monoxide. In this work we present results showing that mixed silver–copper oxide catalysts, prepared by precipitation, can display high activity for CO oxidation at ambient temperature.

2. Experimental

2.1. Catalyst preparation

The catalyst was prepared by the procedure described by Gomez et al. [8]. Solutions of $Cu(NO_3)_2{\cdot}3H_2O$ (3.85 g in 5.0 g

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H_2O) and $AgNO_3$ (2.60 g in 5.0 g H_2O) were prepared with deionized water and stirred together in a flask. 20.0 ml of NaOH solution (3 M) was added drop-wise to the stirred solution of Cu and Ag nitrates. The resulting precipitate was aged in the flask under an atmosphere of air with continuous stirring for 1, 2 and 4 h. The dark green precipitate was collected by filtration and washed with deionised water until the pH of the washings were neutral. The precipitate was allowed to dry at room temperature and the material formed was denoted as the precursor. The catalyst was produced by heating the precursor to 90 °C in air for 24 h.

The hopcalite catalyst was prepared by co-precipitation from a 2/1 solution of manganese and copper nitrate by a solution of sodium carbonate. The resulting precipitate was collected by filtration, washed, dried and calcined to form the catalyst. The detailed method of preparation has been described elsewhere, and these previous studies have optimised the synthesis of hopcalite using the co-precipitation method [9].

2.2. Catalyst characterisation

Catalysts were characterised by powder X-ray diffraction using an Enraf Nonius PSD120 diffractometer with a monochromatic Cu Kα1 source operated at 40 keV and 30 mA. Surface areas were determined by multi point N_2 adsorption at 77 K, and data were treated in accordance with the BET method. Scanning electron microscopy was performed using a Jeol 5600 instrument.

2.3. Catalyst testing

Catalysts were tested for CO oxidation using a fixed bed laboratory microreactor. Typically CO (5% CO in He, 0.5 ml min^{-1}) and O_2 (5.0 ml min^{-1}) were fed to the reactor at controlled rates using mass flow controllers, and passed over the catalyst (100 mg) at 25 °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 3000 h^{-1} and CO concentration of 0.45 vol.%. Under these conditions the maximum adiabatic temperature rise is <7 °C and consequently the reactor temperature could readily be maintained isothermally at 25 °C.

3. Results and discussion

The powder X-ray diffraction patterns of the precursors aged for varying times are shown in Fig. 1. The diffraction patterns of the samples were broadly similar, indicating that the same bulk phases were produced at the various ageing times. It was not possible to identify the precursor phases by XRD, but it was most likely that they were composed of mixed hydroxide phases. There was a variation of the relative intensities as the ageing time was extended. The variations of relative intensities indicated that there was a change of the precursor morphology with ageing time. It was also evident that the diffraction peaks from the precursor aged for 1 h was broader than the precursors aged for longer times. This is consistent with the catalyst prepared with the shortest ageing time having the smallest crystallite size.

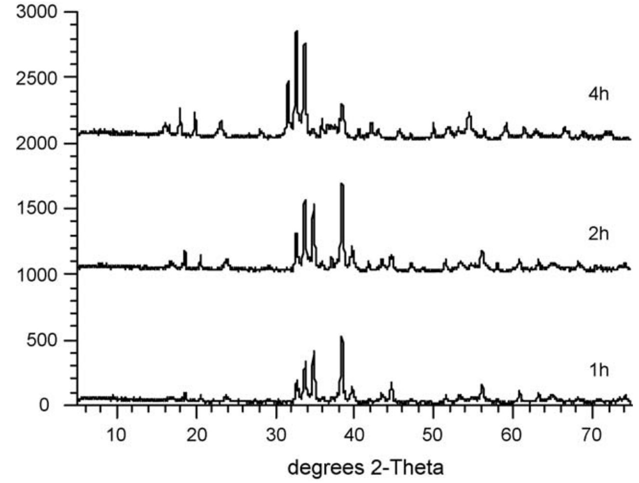

Fig. 1. Powder X-ray diffraction patterns of precursors aged for 1, 2 and 4 h.

The CO oxidation activity of the precursor materials dried at room temperature is presented in Fig. 2. Ageing for 1 h produced a catalyst with the lowest activity of the materials. CO conversion increased marginally with time on line before slowly decreasing to a value slightly below the initial rate of oxidation. Catalysts aged for 2 and 4 h demonstrated similar rates of CO conversion. Initial CO conversion was ca. 12% for the 2 h aged material and it was ca. 16% once ageing was increased to 4 h (not shown). Both catalysts showed a marked decrease of CO conversion over the first 1500 min on stream. After approximately 2000 min on stream the CO conversion for both the 2 and 4 h aged materials was equivalent and remained constant for the duration of the test period. The BET surface areas of the dried precursors were all similar, with values measured in the range of 20–23 $m^2 g^{-1}$.

The powder XRD patterns of the materials dried at 90 °C and aged for 1, 2 and 4 h are shown in Fig. 3. The phases identified for the 2 and 4 h aged materials were $Cu_2Ag_2O_3$ [8]. Thermogravimetric analysis under a 5% H_2/Ar atmosphere provided a clear indication of the formation of the $Cu_2Ag_2O_3$ phase [8,10], and confirms the results from characterisation by powder XRD. TGA analysis of the precursor materials also

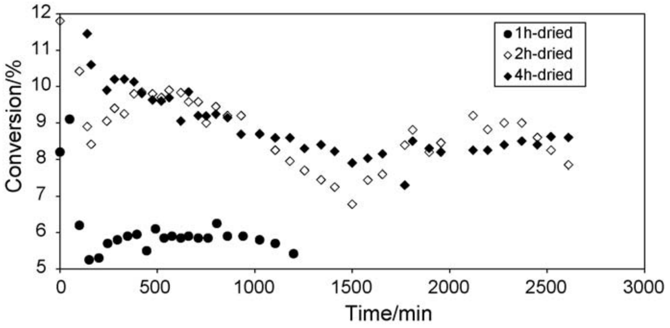

Fig. 2. CO oxidation activity of the precursor materials dried at room temperature (0.45% Co, 25 °C, GHSV = 3000 h^{-1}).

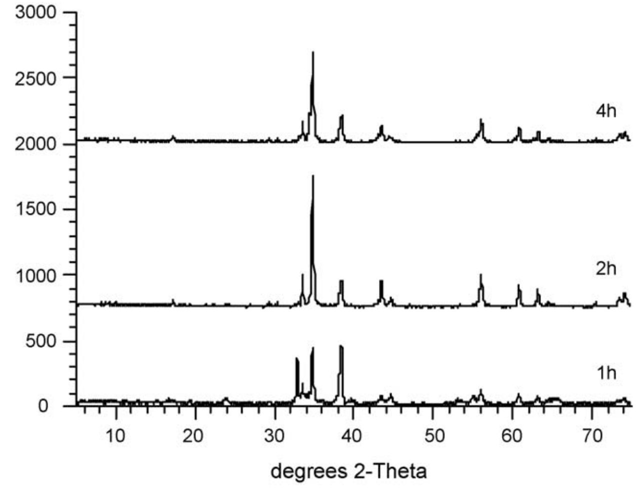

Fig. 3. Powder X-ray diffraction patterns of precursors heated at 90 °C for 24 h and aged for 1, 2 and 4 h.

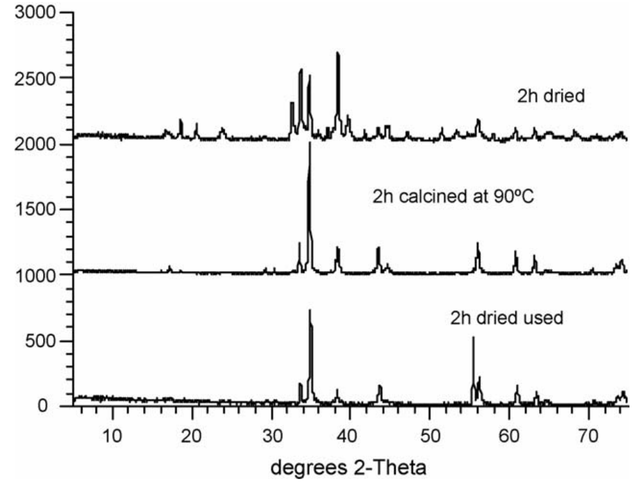

Fig. 5. Comparison of the powder X-ray diffraction patterns of the 2 h precursor before and after use for CO oxidation and the 2 h aged catalyst dried at 90 °C.

demonstrated that the mixed oxide phase was only formed from the precursor after heating to 90 °C.

The activity of the aged catalysts prepared by heating at 90 °C for 24 h are shown in Fig. 4. Initial activity for the catalysts was very low. However, the rate of CO oxidation increased with time on line. After approximately 1000 min time on stream the rate of CO conversion reached steady state. The CO conversion ranged from ca. 5% for the 2 h aged catalyst to ca. 8% for the 4 h aged catalysts. The catalyst aged for 1 h showed intermediate activity. The surface areas of the catalysts were very similar; as they were all in the range 7–8 $m^2 g^{-1}$. Materials prepared using the same preparation procedure but containing only copper or silver were not active under the test conditions.

Determination of the CO oxidation activity for the materials dried at room temperature and those heated in air at 90 °C demonstrated that once steady state was attained the precursors and 90 °C dried catalysts with ageing times of 2 and 4 h showed similar CO conversions. The steady state activity of the precursor aged for 1 h was very different from the catalyst aged for the same time. It is interesting to note that the catalysts aged for 2 and 4 h showed only diffraction from a $Cu_2Ag_2O_3$ phase, whilst the 1 h aged catalysts also showed diffraction from another minor phase diffracting at 32.8° 2θ. The presence of the additional phase for the 1 h aged catalyst may help to explain he intermediate activity as the impurity phase may also catalyse CO oxidation in combination with the $Cu_2Ag_2O_3$ phase.

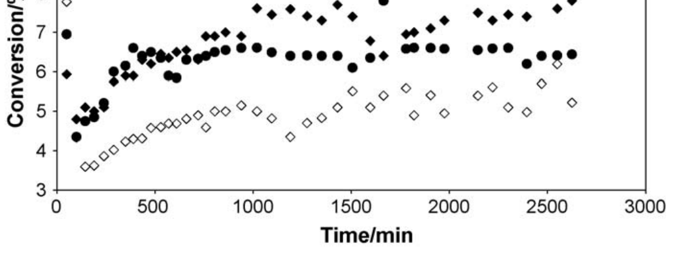

Fig. 4. CO oxidation activity of the precursor materials prepared by heating at 90 °C for 24 h (0.45% CO, 25 °C, GHSV = 3000 h^{-1}).

Powder XRD of the room temperature dried precursors aged for 2 and 4 h following the test period for CO oxidation showed that the diffraction profiles were modified. Representative data are presented in Fig. 5 for the 2 h material, the same trend was also observed for the 4 h material. The diffraction patterns after use were similar to the patterns for the materials heated at 90 °C and the phase identified was $Cu_2Ag_2O_3$. In addition, after use the TGA profiles of the same samples (not shown) displayed a single feature around 260 °C and not the two features that were observed initially. These data demonstrate that the $Cu_2Ag_2O_3$ phase was formed from the precursor in situ during the CO oxidation reaction. Scanning electron microscopy (Fig. 6) also showed that after use the morphology of the catalyst precursor transformed from a morphology with a relatively smooth surface to larger particles with a more irregular surface.

Although the adiabatic temperature rise was minimal for the reaction conditions used in this study the gas streams were relatively dry and the continuous flow will aid the removal of water from the sample. The removal of water from the sample may initiate the formation of $Cu_2Ag_2O_3$. The loss of water may also explain why there is a decrease in activity, as it has been reported recently that adsorbed hydroxyl species have an important role in sustaining CO oxidation over other low temperature CO oxidation catalysts [11].

Comparison of the CO oxidation activity of the $Cu_2Ag_2O_3$ catalysts aged for varying times and dried at 90 °C has been made with a representative sample of the commercially used $CuMnO_x$ catalyst (Fig. 7). The hopcalite catalyst reached steady state conversion after approximately 90 min time on stream and this was considerably quicker than the $Cu_2Ag_2O_3$ catalysts. The steady state CO conversion for the hopcalite was 60.1%, which was greater than the $Cu_2Ag_2O_3$ catalysts. However the BET surface area of the $CuMnO_x$ catalyst was

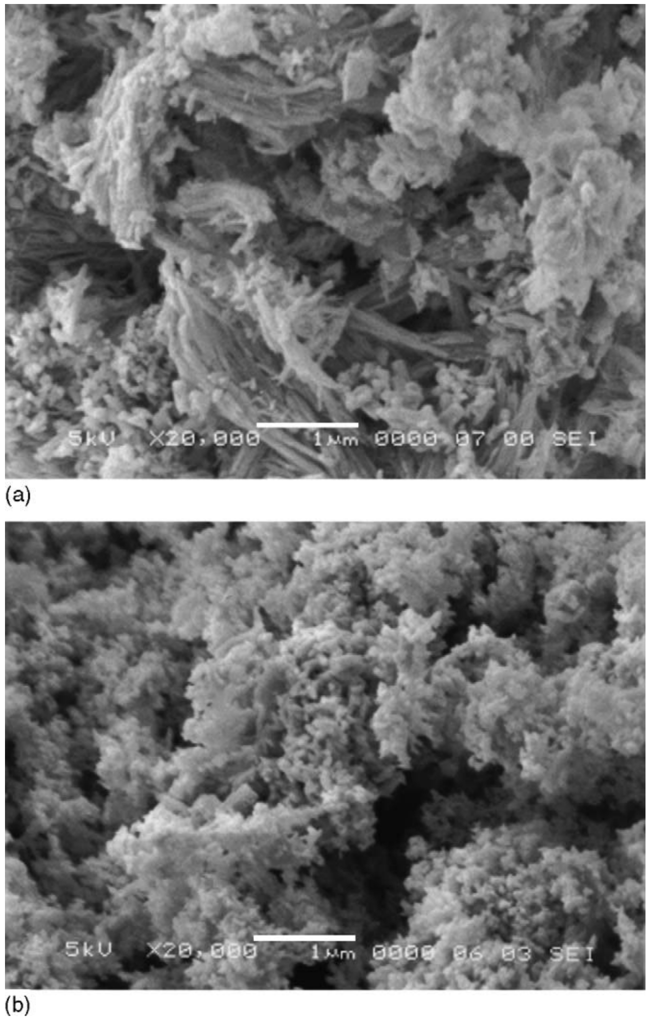

Fig. 6. Scanning electron microscopy images of (a) $Cu_2Ag_2O_3$ catalyst precursor as prepared and (b) after use for CO oxidation a 25 °C.

considerably higher (69 $m^2\ g^{-1}$) when compared with the $Cu_2Ag_2O_3$ catalysts (7.0–7.6 $m^2\ g^{-1}$). Comparing the rate of CO oxidation normalised for the influence of surface area demonstrated that the $Cu_2Ag_2O_3$ catalysts were very similar in activity to the $CuMnO_x$ catalyst. The catalyst aged for 4 h had a higher specific activity, but due to this parameter being highly dependent on the surface area of $Cu_2Ag_2O_3$ a significant conclusion is not possible. The surface area normalised rate for the 4 h aged $Cu_2Ag_2O_3$ catalyst clearly demonstrates that these new materials are effective oxidation catalysts for CO at ambient temperatures. Furthermore, it is expected that if it were possible to synthesise these materials with higher surface areas this would result in further improvements of catalyst activity when normalised on a weight basis.

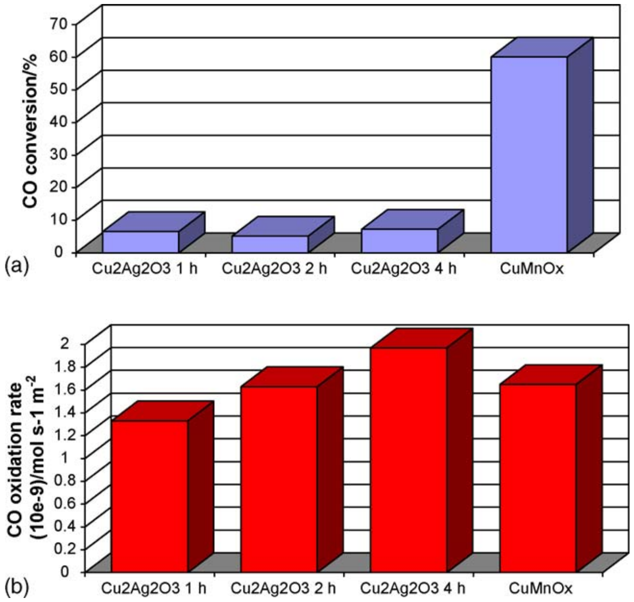

Fig. 7. Comparison of ambient temperature CO oxidation activity between the aged $Cu_2Ag_2O_3$ catalysts and a mixed copper manganese hopcalite catalyst: (a) steady state CO conversion; (b) surface area normalised CO oxidation rate.

It is interesting to consider why the mixed Cu/Ag mixed oxide demonstrates ambient temperature activity for CO oxidation, as the range of catalysts that display this behaviour is limited. Gomez et al. have determined the structure of $Cu_2Ag_2O_3$ via Rietveld analysis of powder X-ray diffraction data [8]. The $Cu_2Ag_2O_3$ has a three-dimensional array of hexagonal tunnels with a minimum Ag–Cu distance of 2.9429 Å. Therefore, the dimensions of these tunnels are more than adequate for the effective diffusion of oxygen species that can readily access the metal cations of the lattice. Indeed, Gomez et al. predicted that the possibility of oxidation of Ag^{1+} to Ag^{2+} and the reduction of Cu^{2+} to Cu^{1+} will give the compound rich redox chemistry.

TGA carried out under H_2 provides an indication of the reducibility of the $Ag_2Cu_2O_3$ and the lability of reactive oxygen. The physical mixtures of AgO and CuO showed major reduction features at 100 and 240 °C [10], these were identified as the reduction of AgO and CuO. The formation of the mixed oxide phase decreased the ease of bulk reduction as the major reduction feature was at 260 °C. This increase in temperature indicated that the lattice oxygen of the $Ag_2Cu_2O_3$ phase was less labile than AgO, which along with CuO did not demonstrate any low temperature CO oxidation activity. However, the profile for the $Ag_2Cu_2O_3$ catalyst showed that hydrogen was consumed from 25 to 200 °C [10], indicating that there were labile oxygen species available to carry out oxidation at low temperatures.

AgO has long been recognised as an effective promoter for low temperature CO oxidation catalysts [12]. These early studies identified that the addition of AgO to CuO and Mn_2O_3 increased the catalytic activity. Later work has also confirmed that the CO oxidation activity of Mn_2O_3 was promoted by the addition of AgO [13]. The combination of the Mn and Ag oxides demonstrated a clear synergy over the oxides alone and studies using thermal gravimetric analysis and temperature programmed desorption showed that the combined oxides had active lattice oxygen associated with the Ag component. Ag remained in the oxidised state even after the desorption of active lattice oxygen, but reduction of Mn occurred. These findings were interpreted in terms that the active oxygen on Ag was mainly consumed in the oxidation of CO, and Mn oxide acted as an oxygen supplier by activating molecular O_2. This concerted action of Mn and Ag in the composite catalyst provided high activity in the oxidation of CO.

In the present study the formation of the mixed oxide phase modified the redox properties when compared to Ag and Cu oxides and this is an important factor in the promotion of the low temperature oxidation activity. The active oxygen species may be O^{2-} lattice anions, with the catalyst operating by a Mars van Krevelen mechanism, or by adsorbed oxygen species on the catalyst surface. Both of these suggestions have been postulated as the active species for low temperature CO oxidation on the hopcalite mixed oxide catalyst and there still remains a degree of debate.

4. Conclusions

$Cu_2Ag_2O_3$ prepared by precipitation displayed long-term activity at ambient temperature for the oxidation of carbon monoxide to carbon dioxide. A relationship between ageing time and activity was observed. An ageing time of 4 h produced a catalyst with superior performance while shorter ageing times were also active. The precursor materials, prepared by drying at room temperature, displayed initial high activity, which decreased with time on line. The precursors were transformed during CO oxidation to form the mixed oxide $Cu_2Ag_2O_3$, as the material was dried in situ. The higher activity of the precursor indicated that this system is tolerant to the presence of water and that the introduction of water into the feed stream may prove beneficial.

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