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Ambient temperature oxidation of carbon monoxide using a $Cu_2Ag_2O_3$ catalyst

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The mixed copper–silver oxide, $Cu_2Ag_2O_3$, has been prepared by co-precipitation and tested for ambient temperature carbon monoxide oxidation. The catalyst demonstrated appreciable low temperature oxidation activity and the catalyst aged for 4 h was the most active. Carbon monoxide conversion increased with time-on-stream, reaching steady state after ca. 1000 min. 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.

KEY WORDS: carbon monoxide, oxidation, ambient 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 it is also used for deep-sea diving, military and space exploration applications. Furthermore, new applications such as reducing the deactivation of carbon dioxide lasers and their use for new sensors have been explored. Recently, interest in low temperature carbon monoxide oxidation has been considerable, since Haruta and co-workers demonstrated that gold, highly dispersed on various metal oxides, forms catalysts active at sub-ambient temperatures [1]. However, the most widely used commercial catalyst is the mixed copper manganese oxide hopcalite, $CuMn_2O_4$, first examined in 1921 [2,3]. Both the gold based and the copper manganese oxide catalysts are important in terms of their 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 [4]. It is interesting to consider whether other catalysts are capable of sustaining carbon monoxide oxidation at ambient temperature. In 1999 the first synthesis of the mixed silver copper oxide ($Cu_2Ag_2O_3$) was described [5]. 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 mixed silver copper oxide has been probed for the ambient temperature oxidation of carbon monoxide. In this communication we present the first results showing that a mixed silver copper oxide catalysts, prepared by precipitation, can display appreciable activity for the CO oxidation reaction when compared with a hopcalite catalyst.

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2. Experimental

The catalysts were prepared from solutions of $Cu(NO_3)_2 \cdot 3H_2O$ (3.85 g in 5.0 g H_2O) and $AgNO_3$ (2.60 g in 5.0 g H_2O) stirred together in a flask. About 20.0 ml of NaOH solution (3M) 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 catalysts were characterised by powder X-ray diffraction and thermogravimetric analysis performed under a 5% H_2/Ar atmosphere with a heating rate of 2 °C min^{-1}. Catalyst surface areas were determined by multi point N_2 adsorption at 77 K, and data were treated in accordance with the BET method.

The catalysts were tested for CO oxidation using a fixed bed laboratory micro reactor. 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 were 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 <ca. 7 °C and consequently the reactor temperature could readily be maintained isothermally at 25 °C.

Results and discussion

The powder XRD patterns of the catalysts prepared by drying at 90 °C and aged for 1 h, 2 h and 4 h are shown in figure 1. The phases identified for the catalysts were $Cu_2Ag_2O_3$ [5]. Thermogravimetric analysis under a 5% H_2/Ar atmosphere provided an excellent tool for distinguishing between a $Cu_2Ag_2O_3$ phase and a mixture of the oxides AgO and CuO [5]. The TGA profile for the catalyst prepared by heating in air at 90 °C showed weight loss from a single feature centred at ca. 260 °C. The single feature is indicative of the $Cu_2Ag_2O_3$ phase [5]. The TGA profile for a mixture of CuO and AgO indicated separate weight losses due to reduction of the two oxides. Therefore, TGA data confirms the presence of the mixed $Cu_2Ag_2O_3$ phase identified by powder XRD.

The CO conversion of the aged catalysts is shown in figure 2. 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.

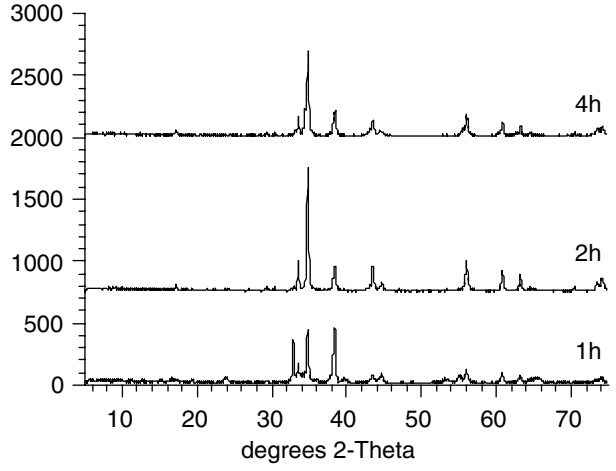

Figure 1. Powder X-ray diffraction patterns of catalysts prepared by ageing for 1, 2 and 4 h.

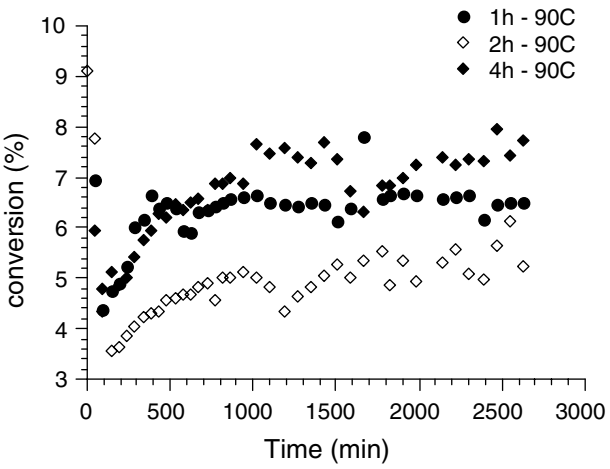

Figure 2. CO oxidation activity of the aged catalysts. (0.45% CO, 25 °C, GHSV = 3000 h^{-1}).

Comparison of the CO oxidation activity of the $Cu_2Ag_2O_3$ catalysts aged for varying times has been made with a representative sample of the commercially used $CuMnO_X$ catalyst (table 1). 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 considerably higher. Comparing the rate of CO oxidation normalised for the influence of surface area demonstrated that the $Cu_2Ag_2O_3$ catalysts were of a similar order of magnitude to the $CuMnO_X$ catalyst. The catalyst aged for 4 h had a higher specific activity and it was at least as active as $CuMn_2O_4$. 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 synthesis of these materials with higher surface areas would result in further improvements of catalyst activity when normalised on a weight basis.

It is interesting to consider why the $Cu_2Ag_2O_3$ mixed oxide catalysts are effective for low temperature CO oxidation. The TGA profiles carried out under a reducing atmosphere demonstrate that reducible species

Table 1
Comparison of the CO oxidation activity of aged $Cu_2Ag_2O_3$ catalysts dried at 90 °C with a $CuMnO_X$ hopcalite catalyst

Catalyt	Ageing time (h)	Steady state CO conversion (%)	S_{BET} (m^2 g^{-1})	S_{BET} normalised CO oxidation rate(10^{-9}) (mol s^{-1} mss^{-2})
$Cu_2Ag_2O_3$	1	6.5	7.6	1.63
$Cu_2Ag_2O_3$	2	5.1	7.1	1.33
$Cu_2Ag_2O_3$	4	7.2	7.0	1.97
$CuMnO_X$	2	60.1	69	1.66

existed at relatively low temperatures. The $Cu_2Ag_2O_3$ catalyst showed a gradual consumption of H_2 from 25 to 200 °C. This observation indicated that labile oxygen species, capable of performing oxidation, were present on $Cu_2Ag_2O_3$. AgO has long been recognised as an effective promoter for low temperature CO oxidation catalysts [6]. These early studies identified that the combination of AgO with CuO and Mn_2O_3 increased the catalytic activity. It has been postulated 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 [7]. Similarly, 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 low temperature mechanism of activity on metal oxide catalysts remains a subject of debate, as oxidation may take place via lattice oxygen or adsorbed species.

Conclusions

$Cu_2Ag_2O_3$ prepared by precipitation displayed long-term activity at ambient temperatures 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. Comparison of the catalytic activity of $Cu_2Ag_2O_3$ with hopcalite, mixed copper/manganese oxide, demonstrated that on the basis of CO oxidation rate 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. At this stage no attempt has been made to optimise the activity of the $Cu_2Ag_2O_3$ catalysts, but it is clear that these catalysts show promising performance for the oxidation of CO under ambient conditions. To the best of our knowledge this is the first reported study of a $Cu_2Ag_2O_3$ catalyst for the oxidation of CO at low temperatures and these systems are now worthy of further investigation.

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