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Improvement of the catalytic performance of CuMnOx catalysts for CO oxidation by the addition of Au

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***Received** (in Montpellier, France) 26th November 2003, Accepted 11th February 2004*
First published as an Advance Article on the web 10th May 2004

Highly active Au-containing hopcalite catalysts for ambient temperature CO oxidation have been prepared by a co-precipitation procedure. The addition of Au to the CuO–MnO system resulted in a marked improvement in the catalytic performance, by increasing the rate of CO oxidation and decreasing the extent of catalyst deactivation. The most active catalysts were CuMnOx with 3 wt % Au and these were prepared using a calcination temperature of 300 °C.

Introduction

The catalytic oxidation of CO to CO_2 at ambient temperature and pressure is an important process for respiratory protection. In particular, the process is widely adopted by mining industries and it has also found applications in deep-sea diving and space exploration. Furthermore, new applications for the process, such as reducing the deactivation of CO_2 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 and co-workers demonstrated that Au, highly dispersed on various oxides, forms catalysts active at sub-ambient temperatures.[1] However, the most widely used commercial catalyst is the mixed copper manganese oxide catalyst, $CuMn_2O_4$ (hopcalite), first examined in the 1920s.[2,3] Hopcalite has been widely studied and key investigations have probed the mechanism of deactivation,[4] the role of surface enrichment of Cu and Mn[5] and the influence of ageing time on catalyst structure and activity.[6]

Both the Au-based and hopcalite catalysts are important in terms of their high activity at ambient temperatures. It is the observation of high activity at low temperature that has stimulated significant recent interest in these types of catalysts. Therefore, it is somewhat surprising that there are no studies investigating the addition of Au to hopcalite catalysts. This study has addressed this deficiency and initial results are presented. The CO oxidation activity of a range of hopcalite catalysts prepared with Au by a co-precipitation procedure has been investigated.

Results and discussion

Table 1 details the range of catalysts used and the results of surface area determination. There was a logical decrease of the surface area when the calcination temperature was increased. It was also apparent that the addition of Au decreased the surface area of the calcined catalysts.

Powder XRD patterns of representative catalysts are shown in Fig. 1. It is clear that the calcination temperature had an important influence on the catalyst structure. XRD of uncalcined samples (not shown) confirmed the presence of

Table 1 Surface area and catalytic properties during CO oxidation of Au/CuO–MnO catalysts

			CO oxidation[a]			
Au content/ wt %	Calcination temperature/°C	S_{BET}/ $m^2\ g^{-1}$	Catalytic activity/ 10^2gCO g h^{-1}	Specific catalytic activity[b] / 10^4gCO $m^{-2}h^{-1}$	Increase of activity per gram of gold[c] / gCO $g^{-1}h^{-1}$	% Deactivation after 1000 min[d]
0	200	152	1.8	1.2	—	54
0	300	127	4.0	3.2	—	48
0	400	91	1.6	1.7	—	52
0	500	33	0.83	2.5	—	0
1	300	129	5.9	4.6	1.9	47
3	200	134	5.0	3.7	1.1	32
3	300	121	8.3	6.9	1.4	33
3	400	84	2.9	3.5	0.43	36
3	500	27	0.96	3.6	0.04	0
6	300	91	5.4	5.9	0.23	38

[a] Data for a time on-line of 1000 min. Reaction conditions: $CO:O_2:He = 1:89:10$ (molar ratio), catalyst weight = 100 mg, total flow = 22.5 ml min^{-1}, reaction temperature = 25 °C. [b] Catalytic activity per area of catalyst. [c] Increase of catalytic activity obtained by gold catalysts compared to gold-free catalysts, per gram of gold: [(Catalytic activity Au catalyst − Catalytic activity of Au-free catalyst)/Au content]. [d] (Conversion $t = 0$ − Conversion $t = 1000$)/(Conversion $t = 0$) × 100.

DOI: 10.1039/b315391f

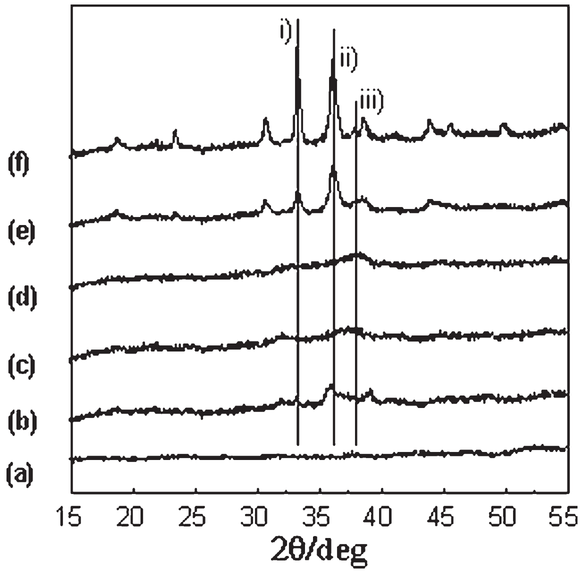

Fig. 1 Powder XRD patterns of CuMnOx and Au/CuMnOx catalysts: (a) 3 wt % Au calcined at 200 °C, (b) Au-free catalyst calcined at 300 °C, (c) 3 wt % Au calcined at 300 °C, (d) 6 wt % Au calcined at 300 °C, (e) 3 wt % Au calcined at 400 °C (f) 3 wt % Au calcined at 500 °C. Note: i and ii correspond to characteristic peaks of Mn_2O_3 and $CuMn_2O_4$ respectively. Peak iii corresponds to the most intense diffraction peak of Au^0.

crystalline $MnCO_3$ and CuO. The catalysts calcined at 200 °C were considerably more amorphous and no crystalline phase could be clearly identified (trace a). The Au-free sample calcined at 300 °C (trace b) presents a low crystallinity but reflections of $CuMn_2O_4$ and Mn_2O_3 were detected, especially those corresponding to the Cu–Mn–O phase. No Mn or Cu–Mn–O crystalline phase could be clearly identified in Au-containing catalysts calcined at 300 °C (traces c and d). However, the presence of metallic Au cannot be ruled out since a peak at 2θ *ca.* 38.2° ($d = 2.357$ Å) was detected. The crystallinity of the catalysts increased as the calcination temperature was increased. Diffraction peaks from $CuMn_2O_4$ and Mn_2O_3 were identified from the more crystalline catalysts produced by calcination at 400 and 500 °C (traces e and f).

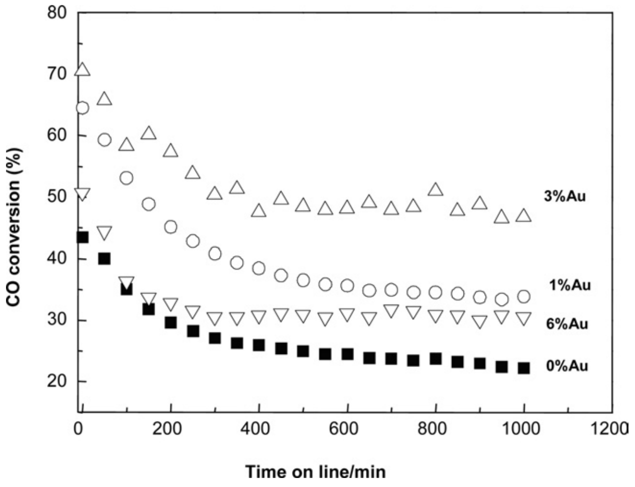

Fig. 2 Variation of the CO conversion with time on-line for representative CuMnOx and Au/CuMnOx catalysts calcined at 300 °C: (■) Au-free catalyst, (○) 1, (△) 3 and (X) 6 wt % Au.

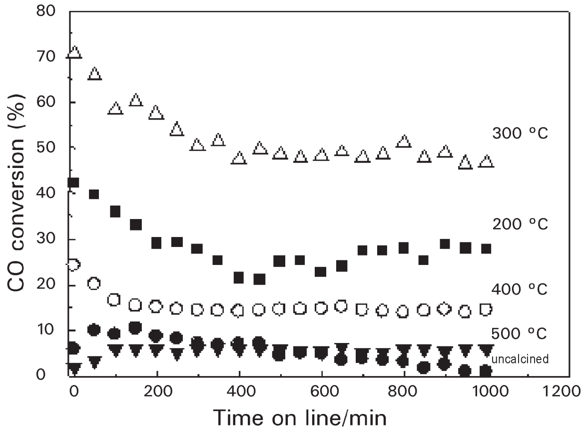

Fig. 3 Variation of the CO conversion with time on-line for Au/CuMnOx catalysts with 3 wt % Au calcined at different temperatures: (●) uncalcined, (■) 200, (△) 300, (○) 400 and (▼) 500 °C.

The variation of CO conversion with time on-line for catalysts calcined at 300 °C and for catalysts with 3 wt % Au calcined at different temperatures are shown in Figs. 2 and 3, respectively. It can be concluded that the catalytic performance was influenced by the addition of Au to the Cu/Mn oxide. The addition of Au promoted CO conversion relative to the catalyst that did not contain Au. The catalysts showed a gradual deactivation with time on-line but after prolonged testing (500 min) no further deactivation was observed. The temperature of calcination also influenced the activity for CO conversion. The pattern of activity with time on-line was more complex and the catalysts calcined at 300 and 400 °C showed deactivation to a steady state. On the other hand, the catalyst calcined at 200 °C showed an initial deactivation followed by a gradual increase in CO conversion, eventually reaching a steady state around 1000 min.

The steady-state activity of the catalysts is summarised in Fig. 4. The optimum calcination temperature for catalyst preparation was 300 °C. For catalysts prepared at this temperature, all the samples containing Au were more active than those that did not contain Au. The catalyst with 3 wt % Au added was more active than the Au-free samples at every calcination temperature. Decreasing the Au content to 1 wt % resulted in a decrease of activity compared to the 3 wt % catalyst and the same effect was also observed when the Au loading was increased to 6 wt %. These data clearly demonstrate the beneficial effect of adding Au to promote CO oxidation activity.

In addition to increasing the rate of CO oxidation, a further advantage of incorporating Au into the hopcalite-type materials was that lower levels of deactivation were observed when compared to the equivalent catalyst without Au (Table 1). Typically the deactivation over the initial 1000 min period was *ca.* 50% for the hopcalite catalyst and this was decreased to *ca.* 35% by the addition of 3 and 6 wt % Au. The addition of 1 wt % Au did not demonstrate such a marked decrease in deactivation.

The effect of calcination temperature on hopcalite catalysts has been studied previously.[7] The optimum temperature of 300 °C observed in this study is due to two main factors. There is a correlation between the calcination temperature and the surface area and, as expected, the surface area decreased as the calcination temperature was increased. Conversely, the formation of Mn_2CuO_4, the most active phase of the CuO–MnO system, has to occur by the thermal reaction of the precursor phases during calcination. The catalysts calcined at 200 °C do not fully react to form the active mixed oxide phase. Consequently, there is a necessity to attain a sufficiently high calcination temperature to form the active phase by solid-state reactions, whilst calcination at a higher temperature results in a detrimental loss of catalyst surface area. Additionally, the catalysts calcined at 500 °C have a highly crystalline structure and it has been established that more amorphous hopcalite catalysts are more active for CO oxidation.[7]

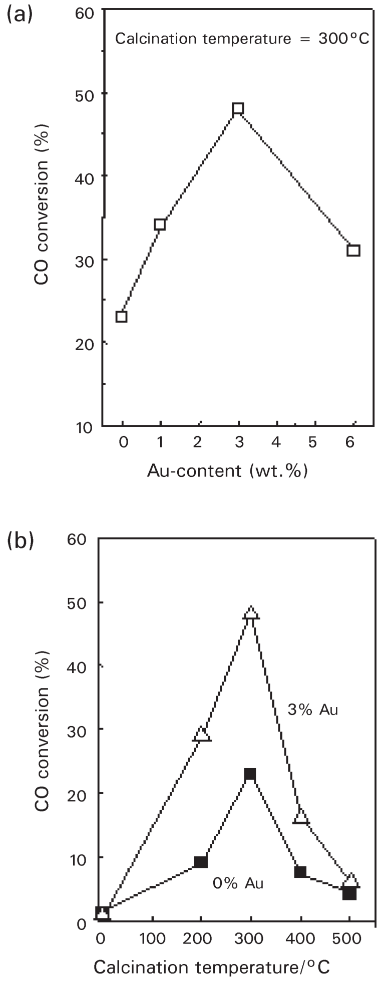

Fig. 4 Summary of the influence of calcination temperature and Au loading on CO oxidation activity after 1000 min time on-line. (a) Effect of Au loading, (b) effect of calcination temperature on (■) CuMnOx and (△) Au/CuMnOx (3 wt % Au).

The calcination temperature will also influence the dispersion of Au over the CuO–MnO mixed oxides. Several authors have found an increase of Au particle size when increasing the calcination temperature over Au catalysts.[8–10] Therefore, a higher calcination temperature is not expected to be beneficial since the most active Au-based catalysts are those with small particle sizes (*ca.* 3–4 nm diameter). On the other hand, an increase of the Au^0/Au^{+3} ratio has also been reported when increasing the calcination temperature.[10,11] Although it remains a matter of debate, it is thought that an excess of Au^0 is detrimental for CO oxidation.[10] It has also been reported that the presence of moisture absorbed on Au catalysts enhanced the CO oxidation rate.[12]

Therefore, it is logical that increasing the calcination temperature reduced the concentration-adsorbed moisture. However, the CuO–MnO material is not a simple and non-active support for the Au catalysts, as it requires the formation of the active $CuMn_2O_4$ phase for optimum catalyst performance; this is also highly dependent on the calcination temperature.[6] Moreover, the dispersion of Au may also be different depending on the detailed morphology and composition of the Cu/Mn oxide support. Consequently, further detailed structural work is required to understand more fully the catalyst features that are necessary for high CO oxidation activity. Currently high-resolution TEM and scanning TEM studies are under way and it is envisaged that these will further elucidate the important structural synergies of these catalysts.

Conclusions

Highly active Au-containing hopcalite catalysts for ambient temperature CO oxidation have been prepared by a co-precipitation procedure. The addition of Au to the CuO–MnO system resulted in a marked improvement in the catalytic performance, by increasing the rate of CO oxidation and decreasing the extent of catalyst deactivation. The most active catalyst was CuMnOx with 3 wt % Au and this was prepared using a calcination temperature of 300 °C. This study clearly demonstrates that the addition of Au to the well-studied hopcalite catalyst, which is still the catalyst of choice for many commercial applications, has superior activity and resistance to deactivation when compared to hopcalite alone.

Experimental

Catalyst preparation

A range of Au/CuMnOx catalysts were prepared by a co-precipitation method. The two starting solutions [0.25 M $Cu(NO_3)_2$ and $Mn(NO_3)_2$] were mixed to give an Mn/Cu atomic ratio of 2. A controlled aliquot of Au solution (0.05 M $HAuCl_4 \cdot 3H_2O$) was added to the nitrate solution to achieve the desired Au content (0, 1, 3 and 6 wt %). The pH of the solution was adjusted to 9 by the dropwise addition of aqueous sodium carbonate (0.25 M). The resulting solution was stirred and aged for 12 h at 80 °C. The resulting precipitate was collected by filtration and washed with hot and cold distilled water. The solid obtained was dried for 16 h at 100 °C and subsequently calcined at 200, 300, 400 or 500 °C in static air for 16 h.

Catalyst characterisation

Catalysts were characterised by powder X-ray diffraction using an Enraf Nonius PSD120 diffractometer with a monochromatic $CuK_{\alpha 1}$ source operated at 40 keV and 30 mA. Phases were identified by matching experimental patterns to the JCPDS powder diffraction file. Surface areas were determined by multipoint N_2 adsorption at 77 K and data were treated in accordance with the BET method.

Catalyst testing

The catalytic activity was determined in a fixed-bed quartz microreactor, operated at atmospheric pressure. The feed consisted of CO:O_2:He with a molar ratio of 1:89:10. The combined flow rate was maintained at 22.5 ml min^{-1} and a constant catalyst loading of 100 mg was employed. The catalyst temperature was maintained at 25 °C by immersing the quartz bed in a thermostatically controlled water bath. Catalysts were tested for a minimum of 1000 min and analysis of the reaction product was carried out on-line using gas chromatography. Conversion was calculated on the basis of CO_2 concentration in the effluent and carbon balances were $100 \pm 2\%$.

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