Cobalt promoted copper manganese oxide catalysts for ambient temperature carbon monoxide oxidation†

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Received (in Cambridge, UK) 2nd January 2008, Accepted 14th January 2008
First published as an Advance Article on the web 1st February 2008
DOI: 10.1039/b800052m

Low levels of cobalt doping (1 wt%) of copper manganese oxide enhances its activity for carbon monoxide oxidation under ambient conditions and the doped catalyst can display higher activity than current commercial catalysts.

The catalytic oxidation of carbon monoxide to carbon dioxide at ambient temperature and pressure is an important process for respiratory protection. Recently, the process has received considerable attention since Haruta *et al.* demonstrated that gold-based catalysts are highly active.[1,2] However, the most widely used catalyst is mixed copper manganese oxide hopcalite, $CuMn_2O_4$.[3] Hopcalite materials remain the catalyst of choice for respiratory protection, but gold-based catalysts may find application in fuel cell technology.[4] Many attempts have been made to improve the performance of hopcalite as a catalyst, in particular by optimizing the preparation conditions.[5] In addition, other materials have been investigated including copper zinc oxide catalysts.[6] Surprisingly, there have been few studies concerning the addition of low levels of promoters to hopcalite, yet this is an approach that has proven beneficial in other oxidation catalysts.[7] Here, we present the first results showing that hopcalite catalysts, prepared by co-precipitation, can be promoted by the addition of low levels of cobalt and these materials can display much higher activity for CO oxidation than the current commercial hopcalite catalysts.

Cobalt was selected as a promoter since the ionic radius of Co^{2+} (83.8 pm) is slightly smaller than Cu^{2+} (87 pm) and substitution in the oxide lattice would be expected. Catalysts were prepared using co-precipitation. Aqueous solutions of $Cu(NO_3)_2{\cdot}3H_2O$ (0.25 mol l^{-1}) and $Mn(NO_3)_2{\cdot}6H_2O$ (0.25 mol l^{-1}) were pre-mixed in a 2 : 1 ratio. For the promoted catalysts, an appropriate amount of the Cu^{2+} solution was replaced by $Co(NO_3)_2.6H_2O$ (0.25 mol l^{-1}). The solution was stirred and heated to 80 °C and fed to a precipitation vessel maintained at 80 °C using a pump. The pH was controlled at 8.3 by the addition of aqueous Na_2CO_3 (2 mol l^{-1}) and the precipitate aged in the liquor for various ageing times (0–12 h). The precipitate was recovered by filtration, washed several times with hot distilled water, dried in air (120 °C for 16 h) and calcined in static air (415 °C for 2 h). The catalysts were tested for CO oxidation at 25 °C using 5000 vppm CO in air and a gas hourly space velocity of 33 000 h^{-1}. Under these conditions the adiabatic temperature rise in the catalyst bed is < 10 °C and consequently the reactor temperature could readily be maintained isothermally at 25 °C.

Catalysts containing 0, 1 and 5 mol% Co were tested for the oxidation of CO and representative data are shown in Fig. 1. One of the most active $CuMnO_x$ catalysts was that aged for 0 h, which gave a CO conversion of *ca.* 40%; the most active was aged for 6 h showing a conversion of *ca.* 65%. Therefore, ageing the precipitate before calcination has a marked effect on the activity of the catalyst. Doping the catalysts with Co promoted the activity for all the different ageing times. The reaction conditions have been selected so that differences in catalytic performance can be readily discerned. On the basis of conversion per unit mass of catalyst, it is apparent that the addition of 1 and 5% Co^{2+}, in place of Cu^{2+}, leads to a significant enhancement in the rate of CO oxidation, with the 1% Co catalyst giving twice the conversion (Fig. 1). Comparison has been made with the activity of a commercial catalyst. The commercial catalyst showed a similar reaction profile with time-on-stream: initial conversion was 65%, decreasing to 42% at the end of the test period. These data demonstrate the significant activity of the Co doped catalysts prepared in

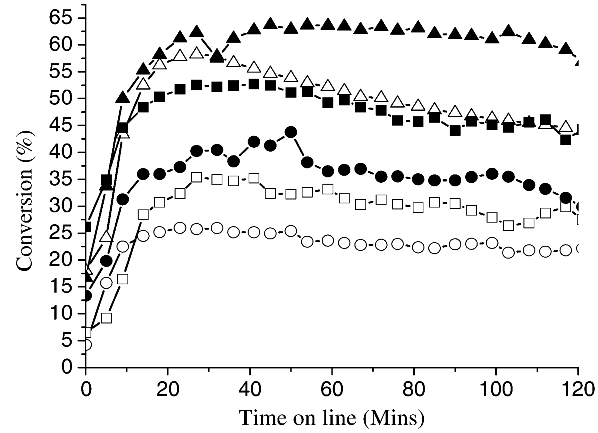

Fig. 1 Catalytic performance of Co-doped catalysts aged for 0 h: (● $CuMnO_x$, ▲ 1% Co/$CuMnO_x$, ■ 5% Co/$CuMnO_x$) and 12 h (○ $CuMnO_x$, △ 1% Co/$CuMnO_x$, □ 5% Co/$CuMnO_x$).

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† Electronic supplementary information (ESI) available: Powder X-ray diffraction studies of prepared catalyst precursors. See DOI: 10.1039/b800052m

Table 1 CO oxidation over Co-promoted $CuMnO_x$ catalysts

$CuMnO_x$			1% Co/$CuMnO_x$			5% Co/$CuMnO_x$		
Ageing time/h	Surface area/$m^2\ g^{-1}$	Rate[a]	Surface area/$m^2\ g^{-1}$	Co : Cu mol ratio[b]	Rate[a]	Surface area/$m^2\ g^{-1}$	Co : Cu mol ratio[b]	Rate[a]
0	74	6.5	127	0.010	7.5	82	0.50	8.7
0.5	87	3.5	84	0.010	8.5	67	0.50	4.2
1.0	72	5.0	65	0.010	6.2	55	0.050	3.5
2.0	110	3.0	73	0.013	10.2	85	0.55	5.0
4.0	121	5.6	92	0.009	7.2	104	0.056	4.5
12.0	88	4.0	100	0.010	7.2	120	0.050	5.0

[a] Rate measured at 120 min time on stream: 10^{-9} mol m^{-2} s^{-1}. [b] Measured by atomic absorption spectroscopy.

this study. All catalysts show an increase in conversion with time-on-stream, and in most cases a small degree of deactivation. The reason for this behaviour is not clear, but it is most likely due to the surface concentration of hydroxyl and carbonate species attaining steady state. The catalyst temperature is maintained isothermally at 25 °C and consequently some irreversible adsorption of CO_2 will occur. For application in air filters a considerably larger catalyst bed is employed and the less efficient heat removal from the catalyst bed minimises irreversible adsorption of water and products.

The promotion of the CO oxidation activity could be due to two factors, as has been described previously for other oxidation catalysts.[7] First, the effect could be structural/textural in nature. In particular if the surface area is affected this could strongly influence the catalytic activity. This is indeed the case, since the addition of Co to $CuMnO_x$ leads to an increase in surface area for both the unaged and the 12 h aged materials (Table 1). It is therefore important to normalise the CO conversion data taking into account the surface area. When this is done, it is apparent that the promotion in activity observed on addition of 1% Co in the unaged catalyst is wholly associated with an enhancement in surface area (Fig. 2); however, the promotion observed with the 5% Co doping cannot be wholly explained by this structural effect, suggesting that there is a second factor involved. For the 12 h aged materials, the 1% Co doped material shows a significant enhancement in the surface area normalised rate (Fig. 2); whereas, the enhanced catalyst performance at the higher doping level is found to correlate with the observed increase in surface area. Ageing of the precipitate, prior to calcination, therefore has a marked effect on the catalytic activity. We, therefore, carried out a study of intermediate ageing times and the surface area normalised data are summarised in Table 1. Ageing clearly has a complex effect on the surface area, and hence it is important that surface area normalised rates are compared. Ageing does not particularly affect the Co : Cu molar ratio and in all cases this is close to the expected value. For the undoped and 5% Co-doped $CuMnO_x$ catalysts the highest rates are observed for the unaged materials; whereas, for the 1% Co-doped catalyst the highest rate was found for the material aged for 2 h.

While we have compared the effect of cobalt promotion with an undoped hopcalite material prepared in an equivalent manner, it is, perhaps, more important to assess the catalytic performance in relation to a current industrial catalyst. In view of this we have evaluated a commercial hopcalite[8] (100 m^{-2} g^{-1}) which exhibits a surface area normalised rate of 6.0 × 10^{-9} mol m^{-2} s^{-1} under the standard reaction conditions. On this basis it is apparent that the 1% Co doped catalyst is more active than the commercial formulation.

Characterisation of the catalyst precursors, prior to calcination at 415 °C, using powder X-ray diffraction† showed that the materials were either poorly crystalline or nanocrystalline. The precursor materials showed no differences by XRD on the addition of Co. X-Ray photoelectron spectroscopy of the 1% doped precursors did not reveal a Co signal indicating the Co

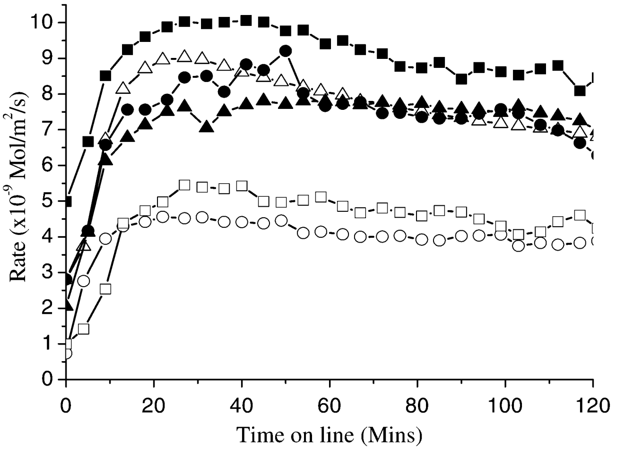

Fig. 2 Surface area normalised catalytic performance of Co-doped $CuMnO_x$ catalysts, CO conversion over zero (● $CuMnO_x$, ▲ 1% Co/$CuMnO_x$, ■ 5% Co/$CuMnO_x$) and 12 h (○ $CuMnO_x$, △ 1% Co/$CuMnO_x$, □ 5% Co/$CuMnO_x$) aged catalysts.

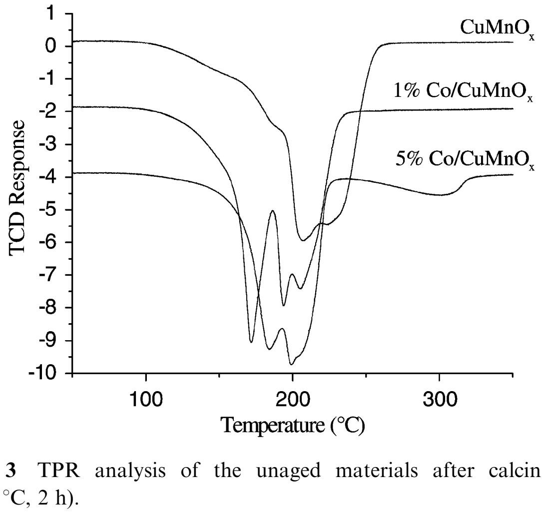

Fig. 3 TPR analysis of the unaged materials after calcination (415 °C, 2 h).

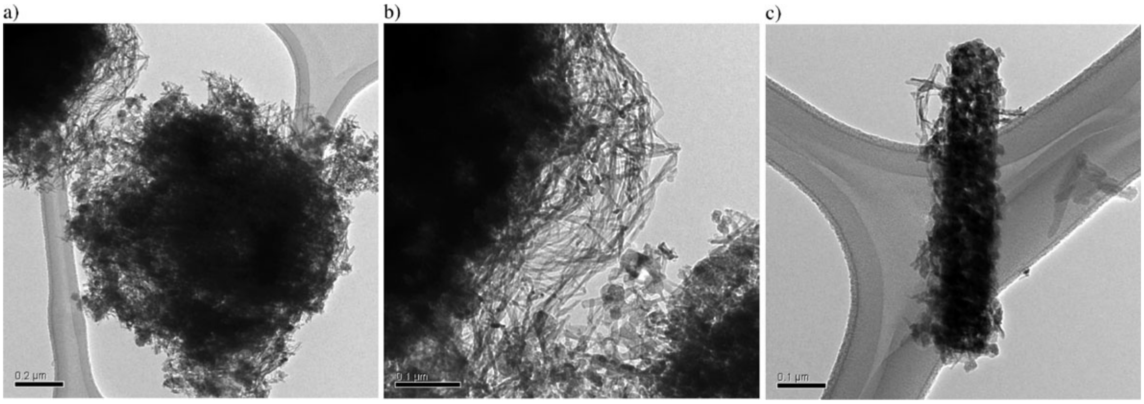

Fig. 4 Bright field TEM micrographs of (a) the spherical agglomerates of hopcalite nanocrystals in the undoped material; (b) the poorly crystalline fibrous bundles in the undoped materials; and (c) the needle type agglomerates wrapped with fibrils in the 1% Co-doped catalysts.

was well dispersed in the materials. The unaged precursors comprised mixtures of copper hydroxy nitrates together with manganese carbonate. However during the ageing process these phases re-dissolved and the materials converted to poorly crystalline manganese carbonate and CuO phases. The absence of a monotonic relationship between ageing time and structure/activity is not surprising considering the complex relationship between ageing time and precipitation of hopcalite catalysts.[5]

The calcined materials were all found to be amorphous or nanocrystalline by powder XRD. Temperature programmed reduction of the calcined materials showed three reduction features at 180, 205 and 230 °C for the undoped $CuMnO_x$ catalyst. On doping with Co, these reduction features shifted to lower temperature (Fig. 3) and this is a general trend. Hence the Co doping decreases the temperature at which the materials react with H_2 and this improvement in the availability of the lattice O^{2-} is considered to be associated with the origin of the increased catalytic activity, as the mechanism of CO oxidation has been proposed to operate *via* a redox mechanism utilising lattice oxygen as the active oxidant.[9]

As a complement to the XRD studies, a sub-set of samples was examined by transmission electron microscopy (TEM). In particular, microstructures of the 12 h aged and calcined undoped and 1% Co-doped catalysts were compared. The undoped material (Fig. 4(a)) was composed of dense 1 µm sized spherical agglomerates of crystalline $CuMn_2O_4$ particles each about 5 nm in diameter. These agglomerates were invariably decorated with bundles of poorly crystalline fibres (5–10 nm in diameter), of similar composition to the hopcalite (Fig. 4(b)). The morphology of the 1% Co doped material (Fig. 4(c)) was distinctly different in that the 5 nm Co-doped $CuMn_2O_4$ primary particles were agglomerated into characteristic needle-like superstructures that were typically 0.1 µm in diameter and 1 µm in length. Once again these superstructures were loosely wrapped with bundles of poorly crystallized fibrils, which energy dispersive X-ray (EDS) analysis confirmed to be cobalt containing. Importantly the observation that no discrete particles of Co or CoO exist in the doped materials suggests that Co had been incorporated substitutionally into the $CuMn_2O_4$ lattice. On the basis of ionic radius comparisons, Co^{2+} is potentially able to substitute for Cu^{2+} in tetrahedral interstices and Co^{3+} can replace Mn^{3+} in octahedral sites of the $CuMn_2O_4$ lattice.

At this stage no attempt has been made to optimise the activity of these cobalt-promoted copper manganese oxide catalysts, and many composition and preparation variables could influence their performance. It is clear that these catalysts show promising performance for the oxidation of carbon monoxide under ambient conditions and these systems are now worthy of further investigation.

We thank Molecular Products and the EPSRC for funding.

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