Ambient temperature CO oxidation using copper manganese oxide catalysts prepared by coprecipitation: effect of ageing on catalyst performance

Graham J. Hutchings [a], Ali A. Mirzaei [a], Richard W. Joyner [b], M. Rafiq H. Siddiqui [a] and Stuart H. Taylor [a]

[a] *Leverhulme Centre for Innovative Catalysis, Department of Chemistry, University of Liverpool, Liverpool L69 3BX, UK*
[b] *Catalysis Research Centre, Department of Chemistry, University of Nottingham at Trent, Nottingham NG11 7NS, UK*

Received 22 July 1996; accepted 13 August 1996

Copper manganese oxides are prepared using a coprecipitation procedure and studied for the oxidation of CO at ambient temperature. In particular, the effect of the ageing time, i.e. the time that the precipitate remains in contact with the precipitating medium, is investigated. It is shown that this parameter is of crucial importance in controlling the catalytic performance and that catalysts which are aged for $\leqslant 30$ min or $\geqslant 300$ min give the best performance. Preliminary characterisation using powder X-ray diffraction indicates that a combination between CuO and copper manganese oxide may be responsible for the enhanced activity observed with these samples.

Keywords: catalyst preparation; coprecipitation; effect of ageing; copper manganese oxide; CO oxidation

1. Introduction

Mixed oxide catalyst precursors containing copper are typically prepared using the coprecipitation procedure in which suitable metal salts, typically the nitrates, are premixed and then a precursor is precipitated using sodium carbonate. This process has been well studied in the case of the $CuO/ZnO/Al_2O_3$ precursor for the methanol synthesis catalyst [1]. In this case a complex mixture of hydroxy carbonates is formed as the precipitate which on subsequent calcination forms the mixed oxide precursor [2,3]. Recently, there has been considerable interest in this precipitation process [4] and it is known that an important controlling parameter with respect to the activity of the final catalyst is the ageing time of the precipitate in the precipitation medium [3]. During this ageing process the initial hydroxy carbonate species formed gradually crystallise and the subsequent catalytic performance can be correlated to the nature of the phases that are formed [3]. Although the effect of ageing has been studied in this one well researched example other copper catalysts of commercial importance have not been studied. The oxidation of CO at ambient temperatures over amorphous manganese oxide promoted with transition metals has long been established [5,6]. The mixed copper manganese oxide in the form of hopcalite, $CuMn_2O_4$, is used as a catalyst for the oxidation of CO at ambient temperature and is important in respiratory protection, particularly in the mining industry. The low temperature oxidation of CO has received renewed attention since Haruta et al. [7] demonstrated that supported Au catalysts could be active at subambient temperatures. Hopcalite, however, is still the catalyst of choice for respiratory protection. Recently, detailed characterisation studies of copper–manganese, cobalt–manganese and high surface area cobalt–copper–manganese systems using X-ray diffraction, X-ray absorption and electron microscopy have been correlated with the catalytic activity of these systems [8]. Other aspects of the hopcalite catalyst have been studied and these include the mechanism of deactivation [9], the effect of surface enrichment of Cu and Mn [10], in addition to being used as a model system for the design of oxidation catalysts [11]. The effect of precipitate ageing has not been addressed in these previous studies. In this paper we present our initial results concerning the effect of ageing in the coprecipitation preparation method and demonstrate that this is an important factor influencing activity for this catalyst system.

2. Experimental

Catalyst preparation. Catalysts were prepared using a coprecipitation procedure. Aqueous solutions of $Cu(NO_3)_2{\cdot}3H_2O$ (0.25 mol/ℓ) and $Mn(NO_3)_2{\cdot}6H_2O$ (0.25 mol/ℓ) were mixed in a 1 : 2 ratio and the mixed solution was heated to 80°C. Aqueous Na_2CO_3 (0.25 mol/ℓ) was added to the mixed nitrate solution with stirring while the temperature was maintained at 80°C until pH = 8.9 was achieved. This procedure took approximately 10 min to complete. The resulting precipitate was then left in this medium (80°C, pH = 8.9 ± 0.1) for times ranging from 0 to 12 h. The precipitate was then filtered, washed several times with warm distilled water until no further Na^+ was observed in the

© J.C. Baltzer AG, Science Publishers

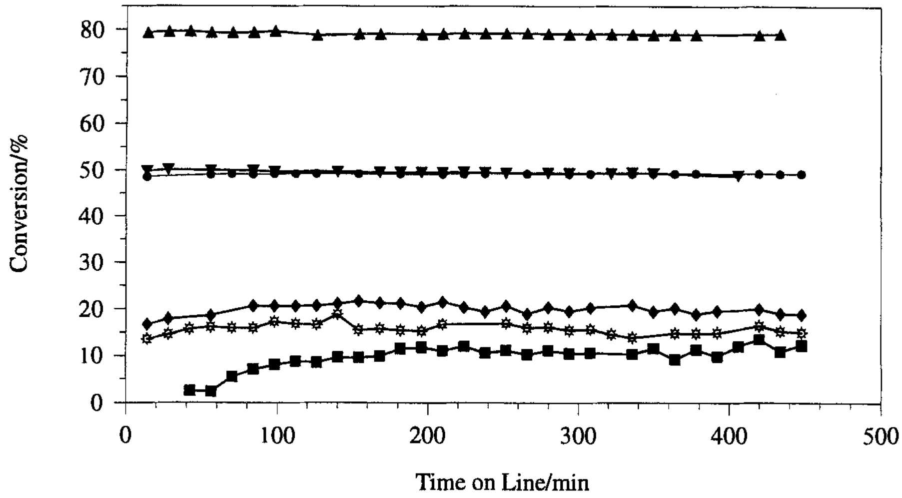

Fig. 1. Catalytic performance for CO oxidation at 20°C versus time on line; ageing time: (●) 30 min, (■) 60 min, (○) 150 min, (◆) 165 min, (▼) 300 min, (▲) 12 h.

washings. The precipitate was then dried (120°C, 16 h) to give a material denoted as the catalyst precursor which was then calcined (500°C, 17 h) to give the final catalyst.

Catalyst testing. The catalysts were tested for CO oxidation using a fixed bed laboratory microreactor. Typically CO (5% CO in He, 5 ml/min) and O_2 (50 ml/min) were fed to the reactor in controlled feed rates using mass flow controllers and passed over the catalyst (100 mg) at 20°C; the products were analysed using on-line gas chromatography. These conditions are equivalent to a total gas hourly space velocity of 33000 h^{-1} and CO concentration of 0.45 mol%. Under these conditions the adiabatic temperature rise is < 7°C and, consequently, the reactor temperature could readily be maintained isothermally at 20°C.

3. Results and discussion

A series of $CuMn_2O_x$ catalysts were prepared with a range of ageing times for the precipitate (0–12 h) and the catalytic activity for the oxidation of CO was investigated for the materials following calcination. The activity with respect to time on line is shown in fig. 1 for CO oxidation (0.45% CO in air, GHSV = 33000 h^{-1}). There are two features that require comment. First, there is considerable variation in the catalytic activity. Second, all the catalysts require a short period for steady state activity to be achieved and the catalysts with the poorest steady state performance require the longest stabilisation period. The variation in catalytic activity is, however, apparent for the initial time on line results. Fig. 2 shows a plot of steady state conversion at 200 min time on line for the different ageing times used in this study. The CO conversion is observed to be ca. 50% for the

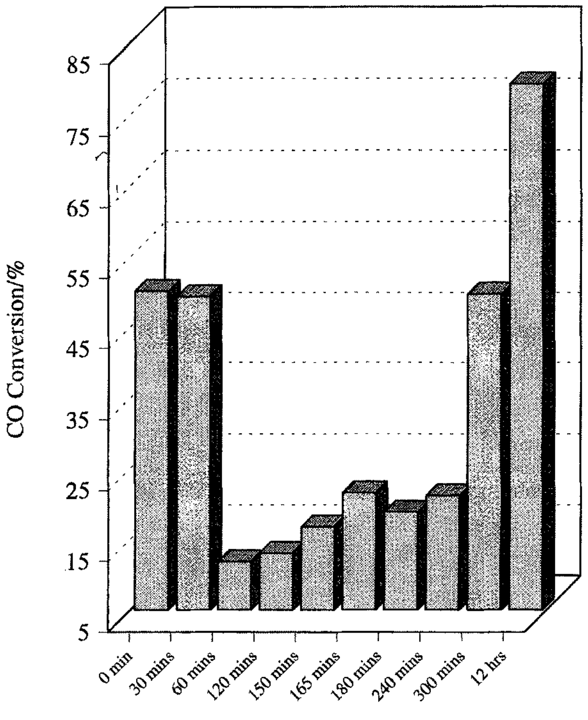

Fig. 2. Steady state activity after 200 min on line versus ageing time.

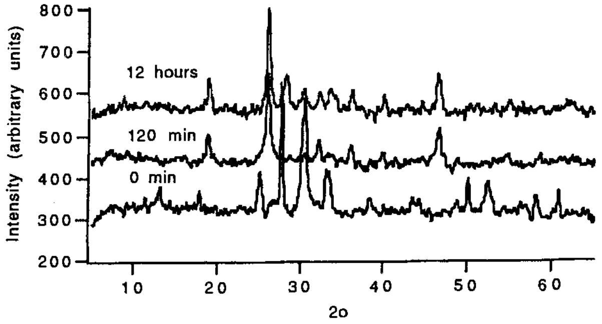

Fig. 3. Powder X-ray diffraction patterns for aged catalyst precursors.

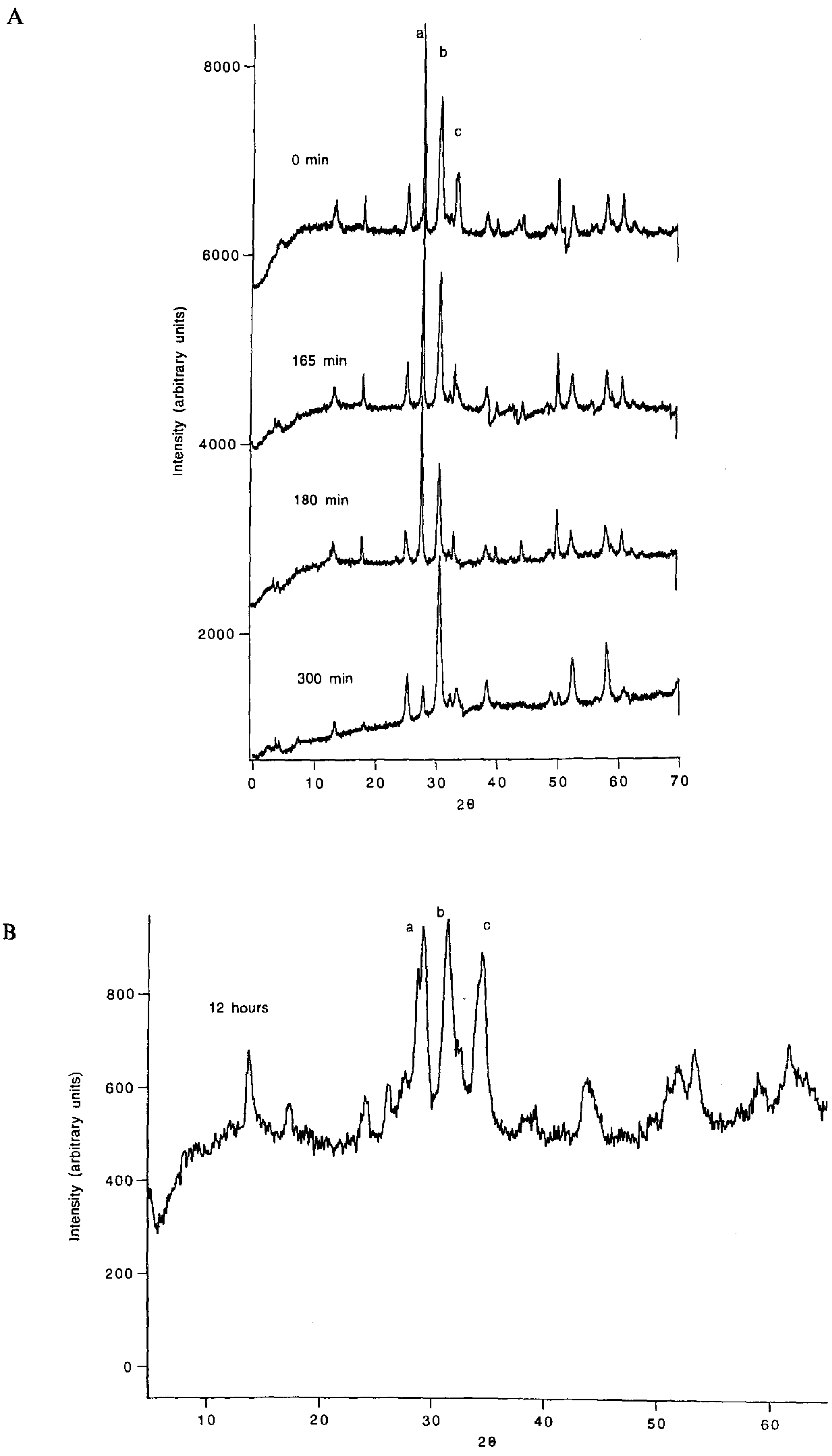

Fig. 4. Powder X-ray diffraction patterns for catalyst aged (A) 0–300 min (B) 12 h.

unaged catalyst and the sample aged for 30 min. The samples aged for longer periods up to 240 min all show much lower CO conversion; however, increased ageing time then restores the catalytic performance and also leads to an enhancement for a sample aged for 12 h. The catalyst surface areas as determined by BET were found to be similar, in the range 25–31 m^2 g^{-1} and therfore the variation in catalyst performance cannot be attributed to surface area effects.

These results indicate that the ageing time is a parameter of crucial importance in the preparation of active $CuMn_2O_4$ catalysts. Preliminary characterisation studies were carried out using powder X-ray diffraction for both the precursors (fig. 3) and calcined catalysts (fig. 4). The unaged precursor was found to be well crystalline copper hydroxy nitrate together with manganese carbonate and, hence, immediately after the initial precipitation the copper and manganese components are present in separate phases. On ageing the copper hydroxy nitrate redissolves and all the aged precursors are comprised poorly crystalline manganese carbonate. The line shapes of the manganese carbonate are very broad and so it is not possible to determine if there are any changes in line spacing that are consistent with copper being in solid solution in the manganese carbonate. The calcined catalysts show more variation (fig. 4) with ageing time although all these materials were less crystalline than the precursors. The unaged catalyst comprises copper manganese oxide ($Cu_{1.4}Mn_{1.6}O_4$), Mn_2O_3 together with CuO. The Mn_2O_3 phase was the most crystalline, producing narrow high intensity diffraction lines; compared to aged catalysts the unaged catalyst also showed significantly higher peak intensities arising from CuO. The X-ray diffraction pattern for the 30 min aged sample was similar to the unaged material, although the relative diffracted intensities from Mn_2O_3 and CuO were decreased. The catalysts aged for between 60 and 240 min comprise copper manganese oxide ($Cu_{1.4}Mn_{1.6}O_4$), Mn_2O_3 and CuO characteristic of the catalysts aged for shorter times; however, the intensity of the CuO diffraction lines were weak and generally the intensity of the diffraction lines of Mn_2O_3 decreased with ageing time. The major phase identified after ageing for 300 min was $Cu_{1.2}Mn_{1.8}O_4$ with Mn_2O_3 and Cu_2O as minor phases. The diffraction pattern of the material aged for 12 h was significantly different, this material was less crystalline and the main phases were $CuMn_2O_4$ and CuO; Mn_2O_3 was not detected by X-ray diffraction. Characterisation of the catalysts by powder X-ray diffraction after use showed that the phases initially present were unchanged. The origin of the activity of the catalysts aged for $\leqslant 30$ min may be related to the detection of crystalline CuO in the catalysts, as the CO oxidation activity decreases as the intensity of the CuO diffraction lines decreased when the catalyst was aged for 60–240 min. It is therefore possible that the high activity associated with catalyst aged for $\leqslant 30$ min is related to CuO in combination with copper manganese oxide. Previous studies have indicated that CO oxidation activity with copper manganese oxide catalysts is related to surface enrichment with Cu [10]. In addition, Kanungo [12] showed that the promoting effect of Cu on manganese oxide was due to the formation of a surface $CuMn_2O_4$ phase through exchange of Cu^{2+} on the hydrated manganese oxide surface. Hence, the indication in the present study that a combination between Cu^{2+} of CuO with copper manganese oxide may be important for high catalytic activity is consistent with theses earlier studies. Increasing the ageing time to 300 min resulted in a decrease in the Cu/Mn ratio from 0.875 for the shorter ageing times to 0.666, approaching the ratio of 0.5 for the stoichiometric hopcalite phase ($CuMn_2O_4$) observed for the catalyst after 12 h ageing. The catalyst aged for 12 h was the most active, followed by the catalyst aged for 300 min; it is therefore considered that activity of catalysts, not comprising CuO that is characteristic of the shorter ageing times, is related to the Cu/Mn ratio of the bulk mixed oxide phase. The increased incorporation of Mn into the mixed oxide is consistent with the decrease in the diffraction intensity of Mn_2O_3 as the ageing time is increased. We now plan to carry out a detailed transmission electron microscopy study of these catalysts. From the results presented in this preliminary study it is clear that ageing of the precipitate in the coprecipitation procedure is of crucial importance and that this parameter should be incorporated into the design of experimental programmes involving precipitation as the method of catalyst preparation.

References

[1] J.C.J. Bart and R.P.A. Sneeden, Catal. Today 2 (1987) 1.

[2] D. Waller, D. Stirling, F.S. Stone and M.S. Spencer, Faraday Discussions Chem. Soc. 87 (1989) 107.

[3] R.W. Joyner, F. King, M.A. Thomas and G. Roberts, Catal. Today 10 (1991) 417.

[4] S. Fujita, A.M. Satriyo, G.C. Shen and N. Takezawa, Catal. Lett. 34 (1995) 85.

[5] T.H. Rogers, C.S. Piggot, W.H. Bahlke and J.M. Jennings, J. Am. Chem. Soc. 43 (1921) 1973.

[6] H.A. Jones and H.S. Taylor, J. Phys. Chem. 27 (1923) 623.

[7] M. Haruta, N. Yamada, T. Kobayashi and S. Iijima, J. Catal. 115 (1989) 301.

[8] P.A. Wright, S. Natarajan, J.M. Thomas and P.L. Gai-Boyes, Chem. Mater. 4 (1992) 1053.

[9] S. Veprek, D.L. Cocke, S. Kehl and H.R. Oswald, J. Catal. 100 (1986) 250.

[10] L. Yang, S.F. Chan, W.S. Chang and Y.Z. Chen, J. Catal. 130 (1991) 52.

[11] C.H. Yoon and D.L. Cocke, J. Catal. 113 (1988) 267.

[12] B. Kanungo, J. Catal. 58 (1979) 419.