Characterization of Copper-Manganese Oxide Catalysts and Their Precursors: Effect of Precipitate Aging upon the Structure and Morphology of Precursors and Catalysts

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Abstract
Copper-manganese oxide catalysts are prepared with an atomic ratio of Cu/Mn=2/1 using a coprecipitation procedure under air atmosphere. The time of aging, i.e., the time that precipitate remains in contact with the precipitating medium, has been varied from 0 (for unaged precursor) to 300 minutes and the effect of precipitate aging time in each atmosphere upon the structure and morphology of different catalysts and their precursors is investigated. The precursors and catalysts were characterized by powder X-ray diffraction (XRD), temperature programmed reduction (TPR) and transmission electron microscopy (TEM). X-ray diffraction and electron microscopy showed that aging of the initial precursor altered the structure of the precursor. The TPR reduction profiles of the copper – manganese mixed oxide catalysts showed a dramatic change of shape on aging. In all catalysts, CuO was completely reduced to metal while the MnO did not reduce under the experimental conditions.

Keywords: *Catalyst, Copper-Manganese Oxide, XRD, Precipitation Method*

Introduction

Catalysts based on copper-manganese mixed oxides are of a considerable industrial importance owing to their activity as powerful oxidation catalysts [1-3]. It is known that these materials can catalyze near room temperature, the oxidation of CO to CO_2 and at higher temperatures, 473-773 K, the combustion of several organic com-pounds including hydrocarbon, halide-and nitrogen-containing compounds [4,5]. It has also been reported that in the reduced state, copper- manganese mixed oxides are active catalysts for methanol synthesis from $CO/CO_2/H_2$ or for light hydrocarbons synthesis from CO/H_2, depending on reaction pressure and temperature [6]. The catalysts are of high activity in the amorphous state but it has generally been observed that they lose activity at temperatures above 773 K where crystallization of the spinal Cu/MnO_4 occurs [7-9]. However, crystalline $CuMnO_4$ has also been reported to be active [10]. The success of the copper-manganese mixed oxide catalyst has prompted a great deal of fundamental work devoted to clarifying either the role played by each component and the nature of the active sites. This is well documented in several reviews [11-13], which indicates that controversial issues are

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remaining that are yet to be resolved. The activity of copper- manganese oxide is known to depend upon the structure/ preparation of the catalyst precursor. This is the aspect on which the present work is focused. The significance of characterizing the hydroxy carbonate precursor phases of copper-manganese oxide catalysts was first high lighted by Porta, *et al*. [14], and particular attention has since been accorded to malachite, $Cu_2CO_3(OH)_2$, and rhodochrosite, $MnCO_3$, compound. The occurrence of the individual phases and their quantitative proportions depend not only on the precipitation conditions such as temperature, pH and concentrations of the reactant solutions, but also on the way the precipitate is aged. Aging of the precipitate in the mother liquor is a common procedure in the preparation method. Aging of the precipitates obtained by coprecipitation leads to phase changes and forms that are more stable. However, the first systematic study of the effects of precipitate aging was not reported until 1989 by Waller, *et al*. [15] for the case of CuO/ZnO mixed oxide catalysts. The study of Cu/Zn catalyst, for which the precursors were aged for 205 minutes, utilized various physical characterization techniques such as XRD, TEM, XPS and DTA, as well as surface area and catalytic activity measurements. The purpose of the present work was to study the effects of precipitate aging on the phase structural characterization and morphology of the precursors and catalysts. In this paper, we present our initial results concerning the effect of aging in the coprecipitation preparation method and demonstrate that aging is an important factor influencing the structure and morphology of these precursors and catalysts. Also, all samples are char-acterized by means of different methods.

Experimental

Sample Preparation

Catalyst precursors were prepared using the coprecipitation procedure. Aqueous solutions of $Cu(NO_3)_2$. $3H_2O$ (0.25 mol/L) and $Mn(NO_3)_2.6H_2O$ were premixed to give a molar Cu/Mn ratio of 2/1 and the resulting solution was heated at 80 °C. Aqueous Na_2CO_3 (0.25 mol/L) was added dropwise to the nitrate solution, which was continuously stirred at 150 rpm whilst the temperature was maintained at 80 °C until a pH between 8.0 and 8.3 was achieved. This procedure took approximately 10 to 15 minutes to complete. The resulting precipitate was aged in this medium from 0 to 300 minutes. The precipitate was then filtered, washed several times with hot and cold distilled water until the observed sodium content by atomic absorption was less than approximately 150 ppm. The precipitate was dried at 120 °C for 16 hr to give a material denoted as the catalyst precursor, which was then calcined (550 °C, 6 hr) to give the final catalyst.

Analytical Techniques for Sample Characterization

(a) Powder X-ray diffraction (XRD): The diffractometer that was used to obtain the data presented in this investigation was a Philips 1050W modified by Hilton Brooks. Scans were taken with a 2θ step size of 0.01 and a counting time of 1.0 second using CuK$_{radiation}$ generated at 40 kV and 20 mA. The peak intensities were monitored and recorded by a computer, which was equipped with JCPDS indexing system.

(b) Temperature programmed reduction (TPR): The chromatographic software and control module interface board is supplied with the TPD/TPR 2900. A known mass of the calcined sample (between 12-25 mg) was heated to 800°C under flowing hydrogen. The flow rate of gas over the catalyst was 50 cm^3/min and the ramp rate of the furnace was 10 °C/min. The system was calibrated using a known mass of copper oxide. Copper oxide is assumed to reduce directly and completely to copper metal.

(c) Transmission electron microscopy and probe microanalysis: The electron micrographs were taken from catalysts and their

precursors using a JEOL 2000 EX high-resolution electron microscope. Illumination was achieved using a LaB_6 filament. The instrument used to carry out the energy-disp. X-ray analysis (EDAX) was a high-performance VC HB601 UX microscope.

Results and Discussion

The structure and morphology of the precursors and calcined catalysts.

(A) X-ray diffraction measurement: The X-ray diffraction results for the different aged precursors are shown in Figure 1.
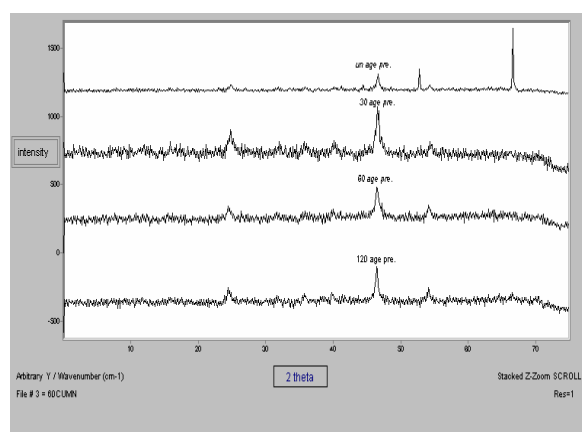

Figure 1. Powder X-ray diffraction patterns for aged catalyst precursors.

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 aging, the copper hydroxy nitrate redissolved and poorly crystalline manganese carbonate was identified by X-ray diffraction in all the aged precursors. 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 X-ray diffraction results for calcined catalysts show more variation (Figure 2) with aging time although all these material were less crystalline than the precursors.
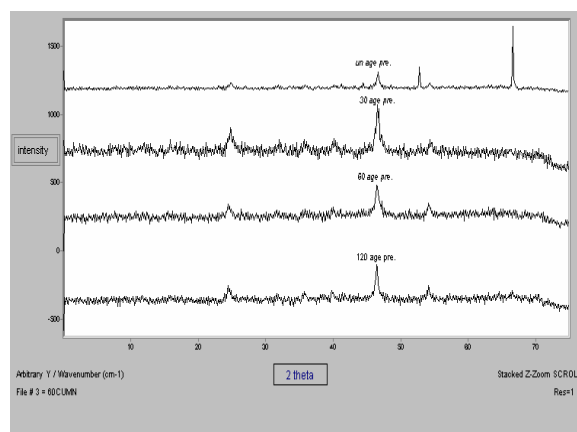

Figure 2. Powder X-ray diffraction patterns for aged catalyst precursors.

The unaged catalyst comprises copper manganese oxide ($Cu_{1.4}Mn_{1.6}O_4$), Mn_2O_3 together with 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 less. The catalysts aged for 60 to 180 min comprise copper manganese oxide ($Cu_{1.4}Mn_{1.6}O_4$), Mn_2O_3 and CuO characteristic of the catalyst aged for shorter times; however, the intensity of the CuO diffraction lines and Mn_2O_3 decreased with aging time. The major phase identified after aging for 30 mins was $Cu_{1.2}Mn_{1.8}O_4$ with Mn_2O_4 and Cu_2O as minor phases.

(B) Temperature programmed reduction (TPR): The TPR profiles of calcined catalysts derived from the differently aged precursors were used in identifying the reducible species present. The TPR profiles of CuO obtained from the precipitation of copper nitrate by Na_2CO_3 following 180 min showed a reduction peak at 250 °C; originating from the reduction of the Cu^{+2} ion. Fierro, *etal*. [16], reported that TPR profiles of CuO exhibit the typical peak with a shoulder at higher temperature originating from two step reduction of the Cu^{+2} ion to metallic copper: Cu^{+2} Cu^{+1}. . Cu. They also reported that CuO reduces only in one step and the second signal, respectively the shoulder, is an artifact originating from sublimation of metallic copper on the unreduced CuO particles. The TPR profiles of manganese oxide catalyst, prepared by precipitation of manganese nitrate under similar conditions, showed reduction peaks entered at about 300 and 405 ^{o}C. The first peak entered at 300 ^{o}C is attributed to the reduction of Mn_2O_3 to MnO and the other peak at 405 ^{o}C shows that reduction of Mn_5O_8 to MnO does not occur under experimental conditions applied [17]. This result is supported by the existence of Mn_2O_3 and Mn_5O_8 as main phases. The TPR profiles of the mixed compounds are difficult to interpret because of the large number of possible combinations of different oxidation states of copper and manganese. Hence, it is possible to attribute individual peaks to well-defined redox reactions, but only some trends can be recognized. Figure 3 gives the TPR profiles obtained for the different aged samples.
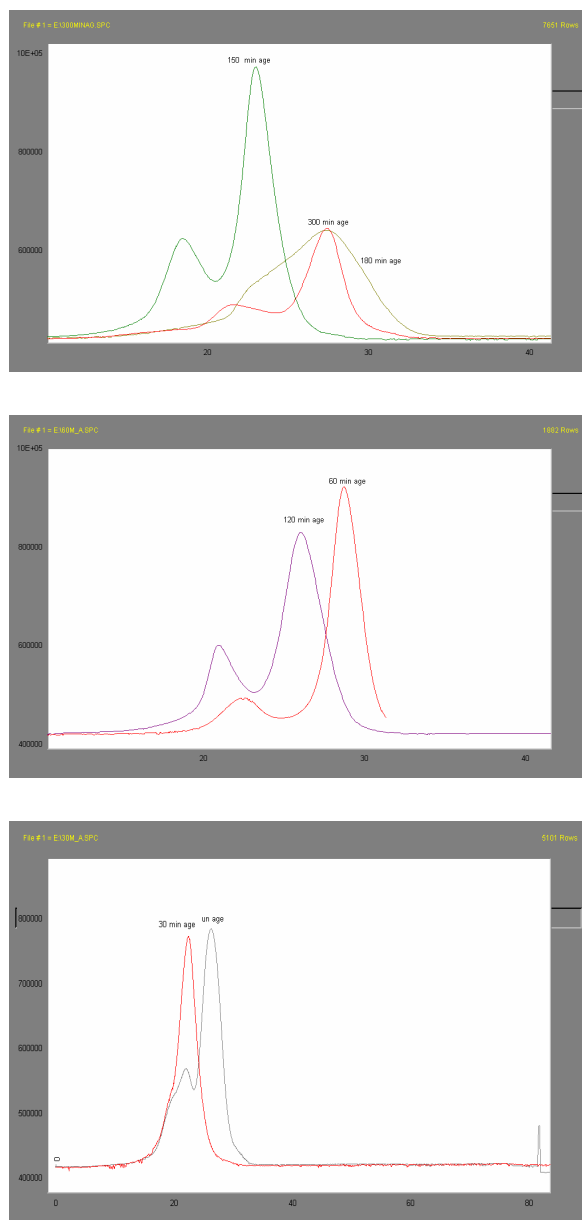

Figure 3. TPR profiles of catalysts prepared with varying aging times.

The low temperature peaks seem to correspond to the reduction of Cu^{+2}. Copper also has a higher reducibility than manganese in mixed compounds. This is due to the more negative free energy of formation of the manganese oxides as compared to copper oxide [18]. Manganese oxides are therefore not expected to reduce at temperatures lower than that of CuO [19]. However, manganese retards the reduction of copper as indicated by the shift of the corresponding peak to

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higher temperatures with increasing manganese content [17].

The high temperature peaks can be attributed to a reduction of manganese because it becomes more intensive with increasing manganese content and nearly disappears if the content of copper is high. The middle-temperature peaks correspond to the reduction of copper-manganese mixed oxides with the formula $Cu_{1+x}Mn_{2-x}O_4$ (X=0.54±0.04) as determined by X-ray diffraction. The TPR pattern of unaged catalyst has shown Reduction profiles with three peaks. The XRD pattern for this catalyst also has shown the existence of three phases (Table 1) and showed higher peak intensity arising from CuO.

The TPR spectra of catalysts aged between 30 to 300 min have shown reduction profiles with two peaks and the XRD patterns for these catalysts (except the catalyst aged for 300 min) show the existence of three phases (Table 1). However, with the 300 min, the intensity of the CuO diffraction lines of Mn_2O_3 decreased with aging time. The reduction in intensity of the diffraction lines may indicate that the amount of these phases is reduced.

(C) Transmission electron microscopy (TEM):

The effect of aging on the morphology of the both precursors and catalysts was studied using TEM technique. The electron micrographs of the differently aged precursors showed different shapes (Figure 4).
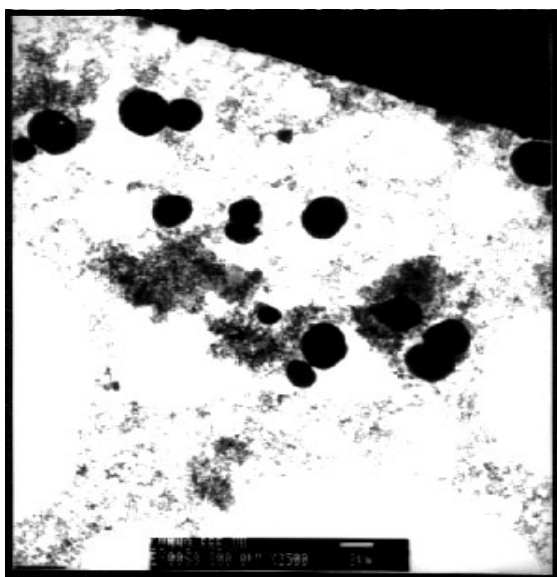
The electron micrographs of the catalysts derived from calcinations of these precursors also showed significant differences.

Figure 5 shows the electron micrographs for the calcined catalysts derived from the precursors aged for a) 0, b) 30 and c) 120 min.

The unaged catalyst showed the presence of amorphous irregularly-shaped aggregates. On aging for 30 min, these aggregates gradually disappear and the appearance of CuO-like aggregates together with copper-manganese oxide mixture was observed. Further aging led to growth of these aggregates, so that on ageing for 120 min, the amorphous aggregates completely disappeared and the flat more regularly-shaped aggregates formed perhaps due to the presence of CuO, and the needle- like aggregates in the 120 min aged sample appeared to be indicative of the copper- manganese oxide material.

**Table 1.** TPR and XRD results for catalysts prepared with varying ageing times

| Ageing time (min)	XRD phases	TPR peaks ($^{\circ}C$)
0	$CuO, Cu_{1.4}Mn_{1.6}O_4, Mn_2O_3$	208,238,280
30	$CuO, Cu_{1.4}Mn_{1.6}O_4, Mn_2O_3$	212,248
60	$CuO, Cu_{1.4}Mn_{1.6}O_4, Mn_2O_3$	230,295
120	$CuO, Cu_{1.4}Mn_{1.6}O_4, Mn_2O_3$	217,269
150	$CuO, Cu_{1.4}Mn_{1.6}O_4, Mn_2O_3$	221,264
165	$CuO, Cu_{1.4}Mn_{1.6}O_4, Mn_2O_3$	217,265
180	$CuO, Cu_{1.4}Mn_{1.6}O_4, Mn_2O_3$	238,286
300	$Cu_2O, Cu_{1.2}Mn_{1.8}O_4$	216,276

(a) unaged
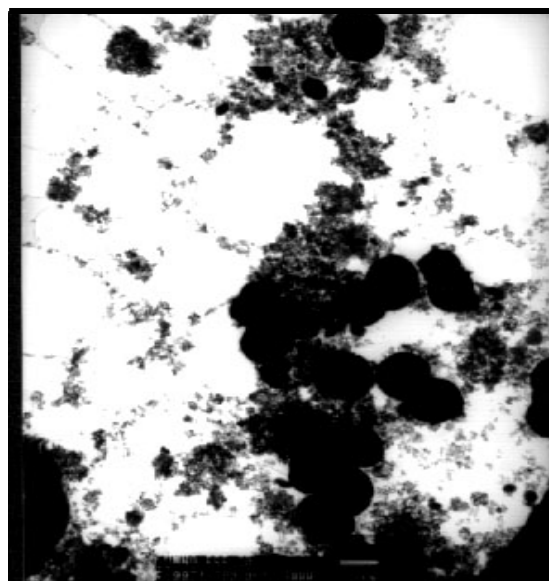
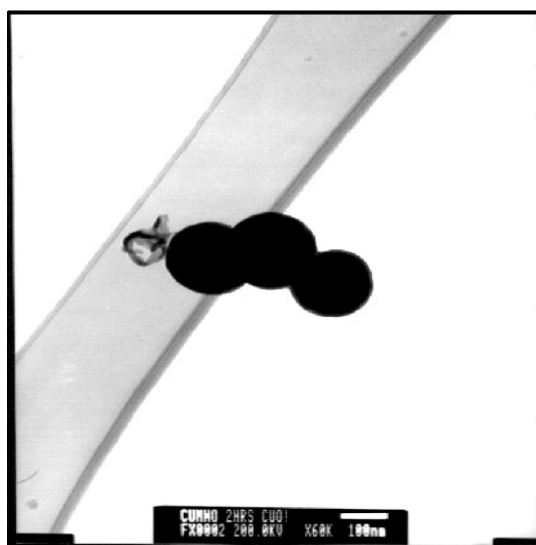(b) 30 min aged
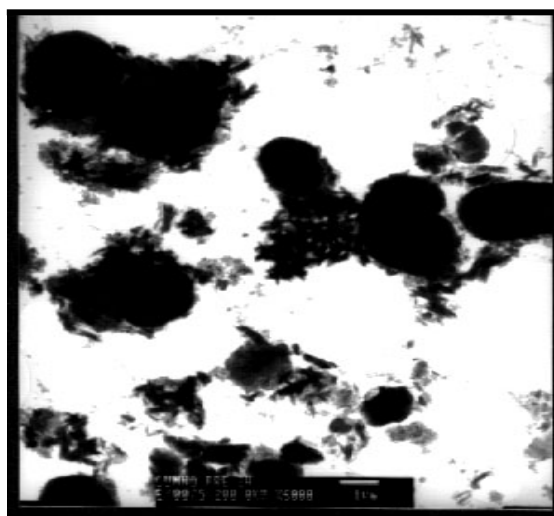
(c) 120 min aged

Figure 4. Electron micrographs of the differently aged precursors: (a) unaged (b) 30 min aged, (c) 120 min aged samples
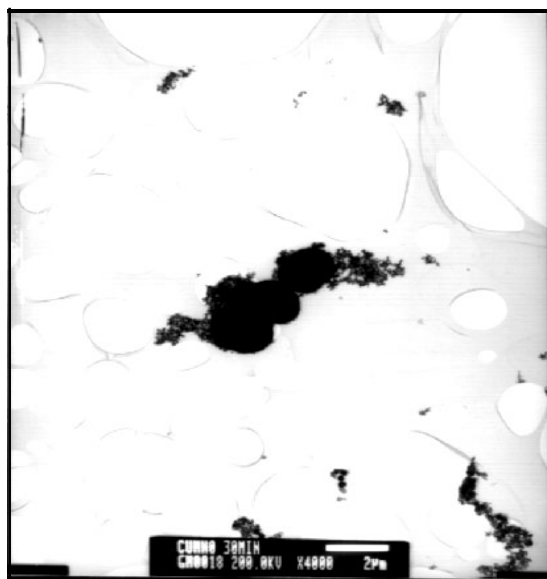
(a) unaged

(b) 30 min aged

(c) 120 min aged

Figure 5. Electron micrographs of the calcined precursors, (a) unaged (b) 30 min aged, (c) 120 min aged samples.

Conclusion

X-ray diffraction studies for the unaged precursor showed the well-crystalline copper hydroxy nitrate together with manganese carbonate. On aging the copper hydroxy nitrate, poorly crystalline manganese carbonate was identified by X-ray diffraction in all of the aged precursors. The X-ray diffraction results for calcined catalysts showed more variation with aging time,

although all these materials were less crystalline than the precursors. Catalyst phases were dependent on aging time. The TPR investigation showed that the copper oxides can be reduced at lower temperatures compared to manganese oxides and so reducibility of copper oxides is higher than that of the manganese oxides. However, manganese retards the reduction of copper, as indicated by the shift of the corresponding peak to higher temperatures compared to the TPR profile of manganese oxide catalyst prepared under similar condition. Unfortunately, the TPR signals of the mixed compounds cannot unequivocally, be attributed to well-defined reduction steps because of the complexity of the systems due to the large number of possible combinations of different oxidation states of copper and manganese. Transmission electron mic-roscopy (TEM) has shown that aging the precipitates leads to profound changes in morphology. The electron micrographs of the aged precursors showed different shapes. The electron micrographs of the calcined catalysts showed significant differences with the increase of aging time. It appears that the aggregates formed in the unaged catalyst, lead to the flat more regularly-shaped aggregates at 120 min aged sample.

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