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DECOMPOSITION OF HYDROGEN PEROXIDE OVER PURE AND MIXED COPPER OXIDE AND MANGANESE OXIDE PREPARED FROM CARBONATES

By

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ABSTRACT

Thermal decomposition of pure and mixed copper and manganese carbonate 1.0: 0.225, 1.0: 0.50 and 1.0: 1.0 with respect to CuO: MnO_2 was studied. The products at different temperatures were characterized by x-ray diffraction analysis. The catalytic activity of the thermal products of pure and mixed oxides was tested in H_2O_2 decomposition.

Thermal treatment of copper carbonate produced CuO at temperature as low as 200°C the increase of temperature of treatment increased the degree of crystallinity of CuO. Manganese carbonate starts to decompose at temperatures higher than 300°C yielding MnO_2 whereas at 500°C a mixture of cubic and tetragonal Mn_2O_3 was detected. At temperatures higher than 500°C, the major crystalline form of Mn_2O_3 was cubic. On the other hand, Cu-Mn-mixed carbonates produced only $MnCO_3$ crystalline form at low temperatures. At 500°C CuO and other compounds such as Mn_2O_3 or $CuMn_2O_4$ were detected depending on the composition of mixtures. The increase of temperature of treatment was found to be accompanied by an increase in the degree of crystallinity of $CuMn_2O_4$.

The catalytic activity of these solids in hydrogen peroxide decomposition was found to increase as the activation temperature was increased passing through a maximum when the catalysts were preheated at 500°C. The increase of calcination temperature higher than 500°C was accompanined by a marked decrease in the activity in H_2O_2 decomposition. This may be attributed to sintering and/or formation of inactive form of $CuMn_2O_4$.

INTRODUCTION

The decomposition of hydrogen peroxide was studied in many reports$^{(1-6)}$. This process takes place in homogeneous as well as in heterogeneous systems. The transition metal oxides are imjortant catalysts in this reaction due to their higher activity. These metals can be used as catalysts for the production of oxygen from H_2O_2 instead of the expensive silver oxide or metallic platinum or palladium black(7).

Manganese oxide is considered as an active catalyst for the decomposition of H_2O_2(6,8,9). The combination of this oxide with other transition metal oxides may produce solids with new and important properties in the field of catalysis(10,12).

The present investigation describes the thermal treatment of individual and mixed oxides. The structure and composition of the thermal products have been considered. Catalytic activity for the decomposition of H_2O_2 have been worked out.

EXPERIMENTAL

Materials:

The starting materials were $CuCO_3$. Cu (OH_2) and $MnCO_3$. Three mixtures of copper and manganese carbonates, with the molar ratios of I (1.0: 0.25), II (1.0: 0.5) and III (1.0: 1.0) with respect to CuO: MnO_2, were obtained by mixing these carbonates. The catalyst mixtures were prepared by heating the mixtures at 200°C, 500°C and 800°C for 4 hours.

Techniques:

The thermal analysis of Cu–carbonate and Mn–carbonate was carried out in DuPont 900 thermal analyzer with a differential scanning calorimeter cell. The rate of heating was 5°C min^{-1}.

X–ray diffractograms of the samples were taken on a diffractometer Phillips (Holland) with a scintillation counter and puls height analysis at 35 Kv, 14 mA using Cu–Kα radiation. The scanning speed used was $2°min^{-1}$ at 2 x 10^3 cps.

The activity of all samples for the decomposition of H_2O_2 was evaluated by the method suggested by Deren J. et al(13) in which the rate of production of oxygen gas was used as a measure. The reaction was studied at 313°K.

RESULTS AND DISCUSSION

Solid state properties:

The DTA of pure copper carbonate, Fig. 1, shows an endotherm between 90 and 200°C due to the loss of water, and carbon dioxide, and an exotherm around 220°C, which is attributed to the crystallization of copper oxide.

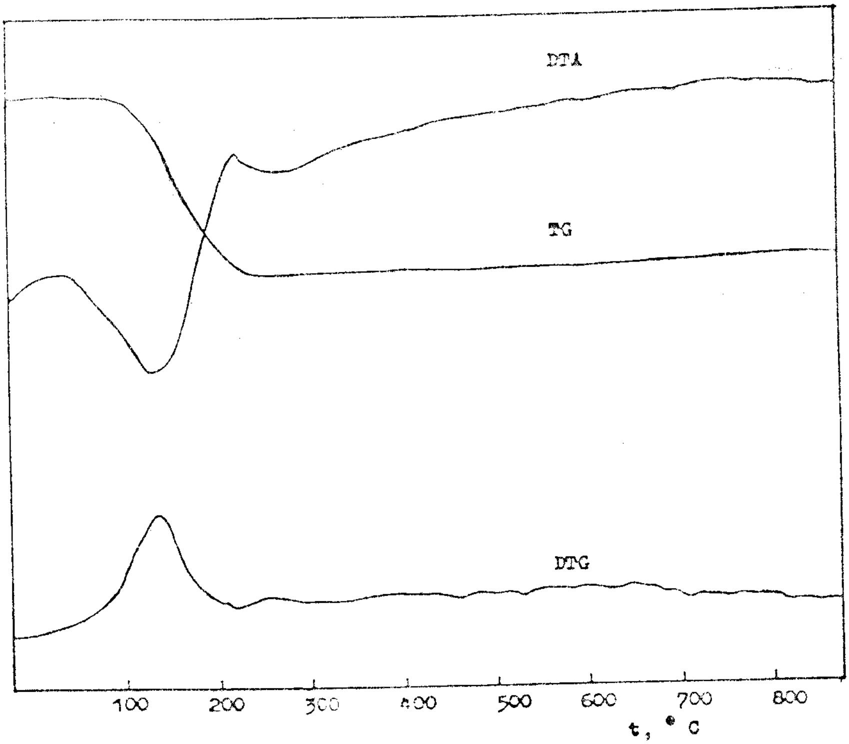

Fig. 1. Thermal analysis (DTA, TG and DTG) of Cu–basic carbonate.

$$CuCO_2.\ Cu\ (OH)_2 —— 2\ CuO + H_2O + CO_2$$

The DTA of pure manganese carbonate shows a broad endotherm up to 300°C due to slow decomposition of the carbonate into MnO_2 which formed at a temperature around 400°C. The transformation of MnO_2 into Mn_2O_3 takes place at about 450–500°C. The decomposition of $MnCO_3$ can be represented as follows(10):

$$1\text{- } MnCO_2.\ 0.5\ H_2O \xrightarrow{100\text{–}300^\circ C} MnCO_3 + 0.5\ H_2O$$

$$2\text{- } MnCO_3 \xrightarrow{300\text{–}450^\circ C} MnO_2 + CO_2$$

$$3\text{- } MnO_3 \xrightarrow{> 450^\circ C} Mn_2O_3 + 0.5\ O_2$$

Interaction between copper carbonate and manganese carbonate:

The solid–solid interaction between Cu–carbonate and Mn–carbonate mixtures of the ratios (I) 1.0: 0.25, (II) 1.0: 0.5 and (III) 1.0: 1.0 with respect to CuO: MnO_2 was studied at temperatures 200°C, 500° and 800°C.

From results of DTA and TG of the individual salts, it can be concluded that at temperatures up to 200°C, $CuCO_3$. $Cu(OH)_2$ started to decompose and at 200°C mainly crystalline $MnCO_3$ phase was detected (Fig. 2). The appearance of poorly crystalline CuO can be attributed to that the process of crystallization is not complete. The increase of temperature of treatment up to 500°C (Fig. 3) was accompanied by an increase in the crystallization of CuO and the appearance of cubic

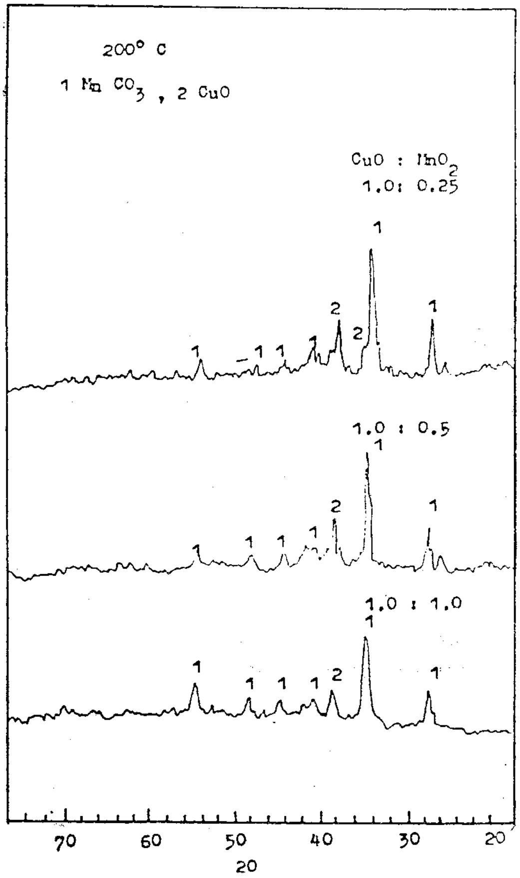

Fig. 2. X–ray diffraction patterns of mixed catalysts preheated at 200°C.

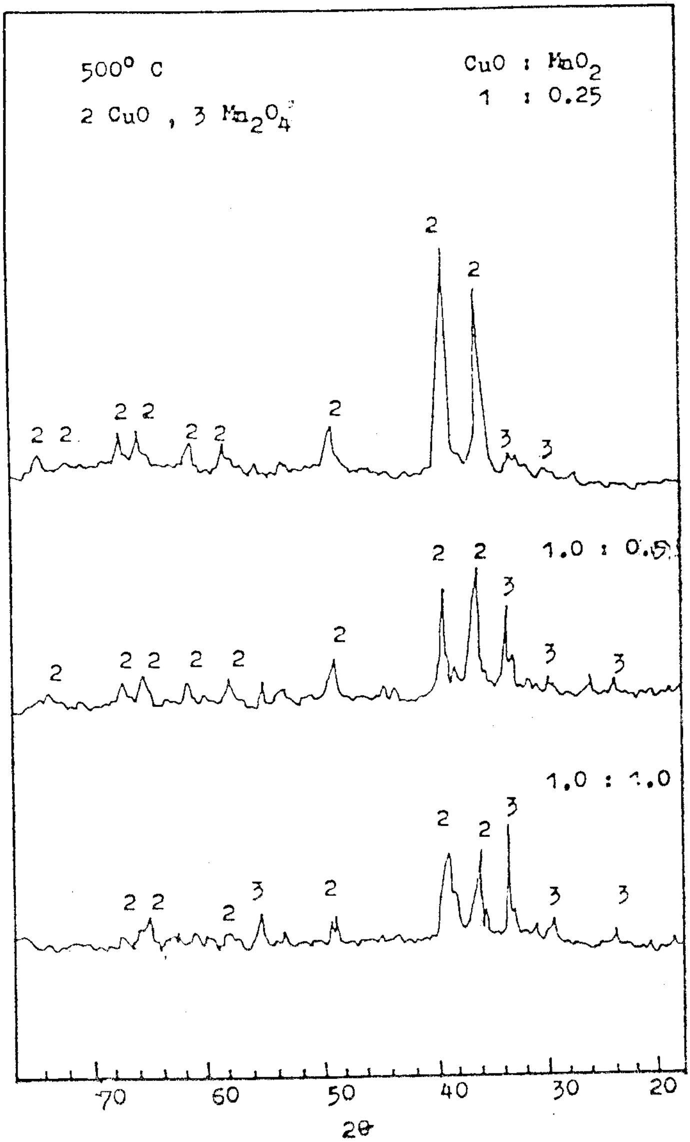

Fig. 3. X-ray diffraction patterns of mixed catalysts preheated at 500°C.

Mn_2O_3 crystalline phase. The increase of manganese content showed an increase of the intensity of the patterns of cubic Mn_2O_3 with a decrease of the lines of CuO. Further increase of the thermal treatment up to 800°C (Fig. 4) was accompanied by a detectable solid–solid inte-

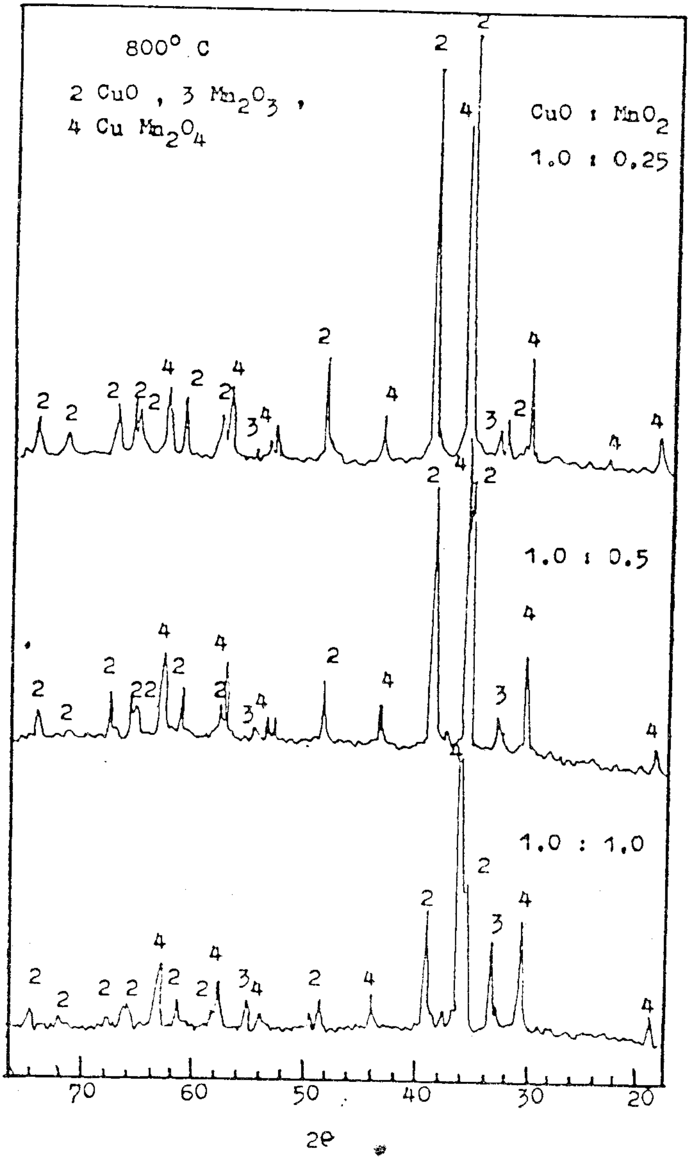

Fig. 4. X–ray diffraction patterns of mixed catalysts preheated at 800°C.

raction between Cu and Mn–oxides forming copper manganite $CuMn_2O_4$. At this temperature beside $CuMn_2O_4$ other compounds; CuO and Mn_2O_3, were also detected on the x–ray diffractograms. This means that the thermal treatment at 800°C for 4 hours is not enough for complete combination of the individual oxides to form the spinel $CuMn_2O_4$.

Catalytic Activity of Thermally Treated Mixed Oxides:

The decomposition of H_2O_2 over the mixed oxides thermally treated at different temperatures are graphically represented on Figures 5–7. It can be seen that all samples thermally treated at 200°C were active in H_2O_2– decomposition. The activity increased as the manganese content increased from 0.25 M to 0.5 M. Further increase in Mn–content showed no more increase in the activity. The calcination of all samples at 500°C produced highly active catalysts with more or less the same trend as catalysts thermally treated at 200°C (with respect to the increase in activity with increasing Mn–content). Further increase in the temperature at which the catalysts were activated i.e. 800°C produced solids with very low activity for H_2O_2 decomposition. The minimum activity may be attributed to sintering or formation of copper manganite.

It is evident from the initial rates of decomposition of H_2O_2 that Mn_2O_3 and MnO are good catalysts(14). Cota(15) observed that MnO_2

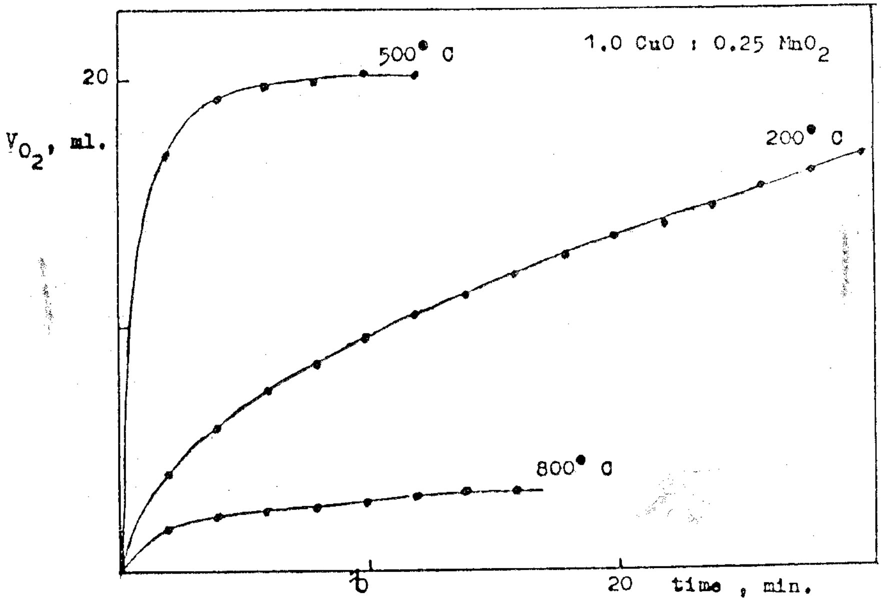

Fig. 5. The activity of catalyst 1CuO: 0.25 MnO_2 preheated at various temperatures.

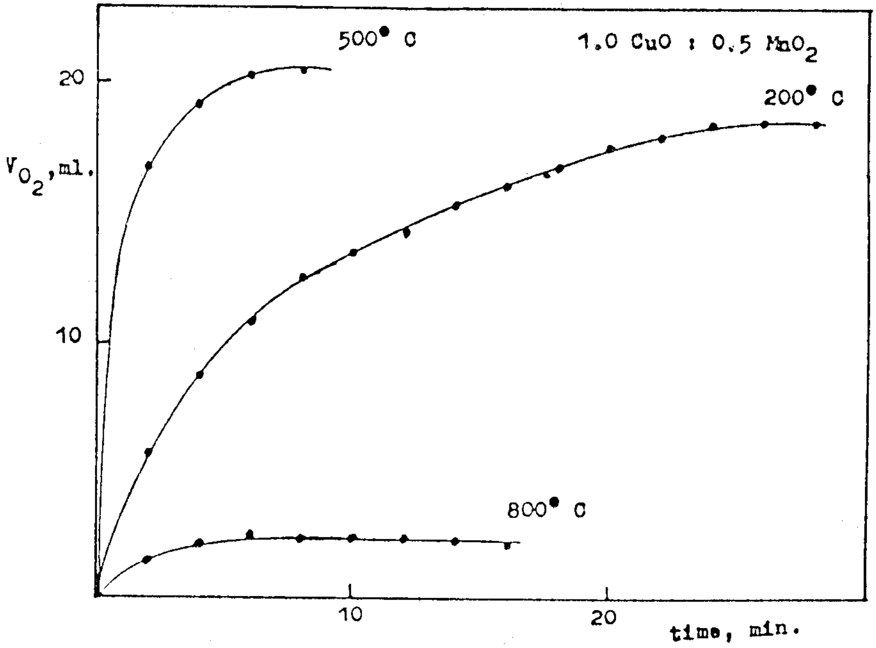

Fig. 6. The activity of catalyst 1.0 CuO: 0.5 MnO_2 proeheated at various temperatures.

is also a good catalyst. The oxides Cu_2O and CuO are poor catalysts in this reaction. It was shown that the oxide which may form a redox system with the oxide for the element at a lower valency state, and having a higher standard potential (reduction) of the system than the corresponding value of the O_2, $2H^+ / H_2O_2$ system, is a good catalyst in the decomposition of H_2O_2. This is in accordance with manganese oxides.

The standard potential(16) (reduction) of Cu–oxides system (Cu^+ / Cu or Cu^{2+} / Cu^+) are lower than the corresponding value of O_2, $2H^+ / H_2O_2$. So it is likely that H_2O_2 will be reduced primarily in the presence of such system as

$$H_2O_2 + e \longrightarrow OH + OH^-$$

leading to the formation of free radical OH which sets off the chain reaction(17,18). The electron can be obtained from Cu element as

$$Cu \longrightarrow Cu^+ + e$$

and / or

$$Cu^+ \longrightarrow Cu^{2+} + e$$

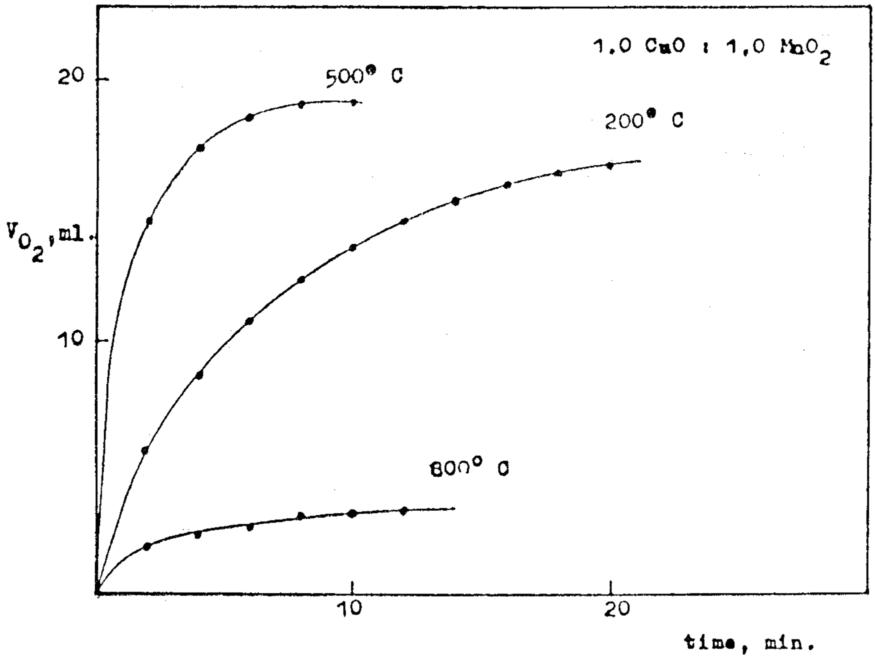

Fig. 7. The activity of catalyst 1.0 CuO: 0.25 MnO_2 preheated at various temperatures.

The chain reaction may be terminated(17), by the local excess of Cu–ions which will react with free radical OH as

$$Cu^{+} + OH \longrightarrow Cu^{2+} + OH^{-}$$

This reaction explains the poor catalytic activity of the copper oxide.

The combination of the active Mn–Oxide species with copper oxide of low activity, produced catalysts with higher activity due to a mutual effect and the homogeneous distribution of Mn–oxide over Cu–oxide surface.

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