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Effect of thermal treatment on physicochemical properties of pure and mixed manganese carbonate and basic copper carbonate

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Abstract

A series of pure and mixed Mn and Cu oxides were prepared by calcination of $MnCO_3$ and $CuCO_3{\cdot}Cu(OH)_2$ at different temperatures, (250, 500, 750 and 1000°C) for 4 h in air. Pyrolyses of pure and mixed solid salts were investigated using the thermal analysis (DTA and TG) technique in a flow of air. Also, the calcined samples were analyzed for different species using X-ray diffraction (XRD). A solid-state reaction model accounting for the Mn oxide–Cu oxide interaction in mixed systems is discussed. The catalytic activity of the thermal products of pure and mixed solids was tested in H_2O_2 decomposition as a model reaction. © 1998 Elsevier Science B.V.

Keywords: Thermal decomposition; Mn carbonate; Copper carbonate mixed oxides; H_2O_2 decomposition

1. Introduction

A great deal of fundamental research has been done on mixed oxides in the field of heterogenous catalysis [1–3]. The results illustrated that the combination of two oxides leads to new systems with new physical and chemical properties [4]. The catalytic activities of mixed catalysts were often found to be many times higher than those of mechanical mixtures of separate components [5,6]. It is well known that the thermal decomposition of solids depends largely on sample and reaction conditions [7–9]. The morphology and physicochemical properties of the solid product are thus affected by both the applied conditions and the mode of thermal decomposition.

The present investigation is devoted to studying the effect of thermal treatment on pure and mixed Mn–Cu carbonates and the solid–solid interaction at different temperatures as well as the activity of the products in a model reaction.

2. Experimental

2.1. Materials

The starting materials used in this investigation were manganese carbonate ($MnCO_3$) provided by May and Baker, Dagenham, England, and basic copper carbonate ($CuCO_3{\cdot}Cu(OH)_2$) provided by Aldrich, Dorset, England.

Three mixtures of molar ratios 3:1, 1:1, and 1:3 with respect to the starting materials were prepared by mixing the solids, and homogenizing and grinding them. The pure manganese carbonate, pure basic copper carbonate and their mixtures were heated at 250, 500, 750, and 1000°C.

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The decomposition of hydrogen peroxide was used as a model reaction for determining the catalytic activity of the solids produced from the thermal treatment of pure and mixed manganese carbonate and basic copper carbonate at different conditions.

2.2. Procedure and physical measurement

Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out on a Shimadzu DT-40 thermal analyzer. Pure and mixed samples were studied under air atmosphere at a flow rate of 30 ml min^{-1}, α-Al_2O_3 was used as a reference material, chart speed was 5 mm min^{-1} and rate of heating was 15°C min^{-1}.

X-ray diffraction patters were obtained at room temperature using a Philips X-ray diffractometer (Goniometer PW 1050/50), employing cobalt radiation as the X-ray source. The X-ray tube was operated at 36 kV and 16 mA. Samples were finely ground and packed in a plastic holder. The diffraction angle of 2° was scanned at a rate of 2° min^{-1}.

The reaction was followed up through a gasometric measurement of evolved oxygen using the apparatus shown in Fig. 1 [10]. The apparatus made of Pyrex glass consists of: (a) a graduated gas burette, 50 cc, filled with 5% sodium chloride solution by drops of methyl orange; (b) a moving vessel mounted on a holder to equate the inside pressure with the atmospheric pressure; (c) a magnetic stirrer and a Pyrex reactor of 100 cc capacity with a glass spoon charged with a definite weight of catalyst (d) and the outer jacket of which is connected to an ultrathermostat.

The kinetic experiments were carried out at different conditions. Twenty milliliters of bi-distilled water and 0.5 ml of hydrogen peroxide (30% by volume) were first introduced into the reactor. The temperature of the solution was adjusted by ultra-thermostat at 30, 40 and 50°C. Ten or 100 mg of the catalyst sample was placed on the glass spoon depending on the activity of the catalyst. The zero level in the burette (a) was adjusted and the position of the tap (e) was adjusted to permit the evolved gas to pass directly to the burette. After attaining the required temperature, the time was recorded as the glass spoon was turned upside down.

The volume of collected oxygen (*V*) at STP was obtained at different intervals until complete decomposition was attained.

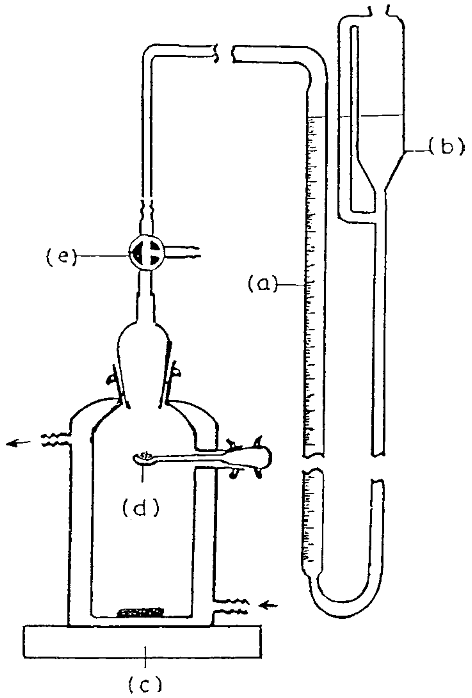

Fig. 1. The apparatus used for catalytic activity measurements.

3. Results and discussion

3.1. Thermal decomposition of pure and mixed manganese carbonate and basic copper carbonate

The TG–DTA curves for the pyrolysis of $MnCO_3$ are shown in Fig. 2. The first weight loss starts at about 300°C; the decomposition curve being smooth and achieves constant weight loss of 24.30% due to the decomposition of manganese carbonate to manganese dioxide. The second weight loss starts at about 440°C reaching a constant weight loss of 31.22% due to the reduction of manganese dioxide to manganese trioxide [11,12]. The third weight loss step starts at >900°C with a percentage weight loss of 33.57% due to the formation of Mn_3O_4 [6,13]. The DTA curve also shows three endothermic peaks corresponding to the same weight losses in the same temperature ranges [14].

Fig. 3 represents the pyrolysis of $CuCO_3 \cdot Cu(OH)_2$. The TG curve indicates only one step for the process of thermal decomposition. The DTA curve also shows only one strong and sharp endothermic peak located

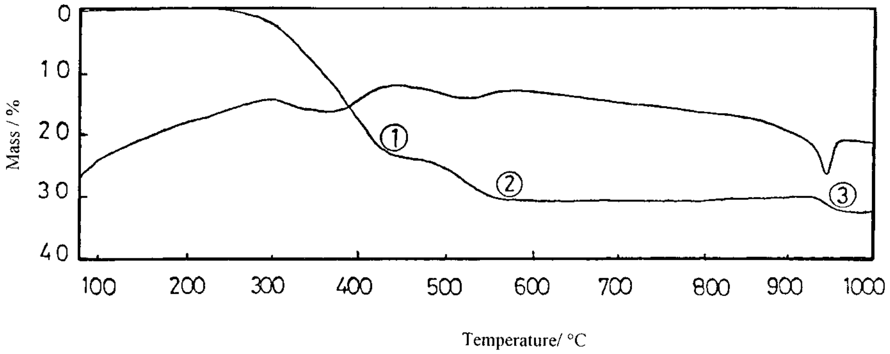

Fig. 2. Thermal analysis (DTA and TG) of pure $MnCO_3$.

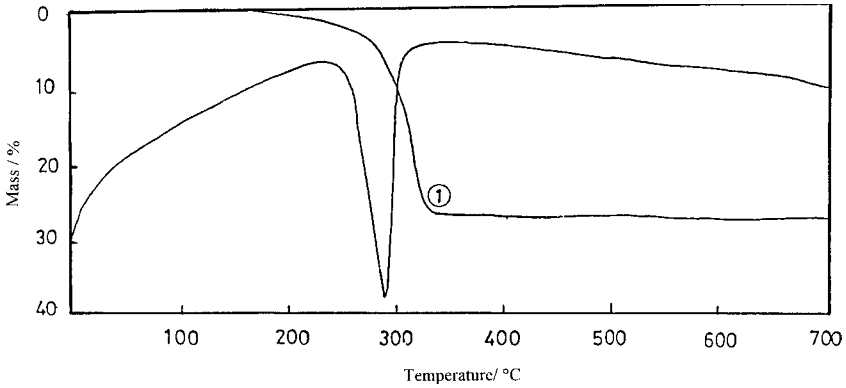

Fig. 3. Thermal analysis (DTA and TG) of pure $CuCO_3{\cdot}Cu(OH)_2$.

at a minimum of 291.5°C as mentioned before [15].

$$1/2CuCO_3.Cu(OH)_2 \xrightarrow{230-330^\circ C} CuO$$
$$+1/2CO_2 + 1/2H_2O$$

Fig. 4 represents the thermal decomposition of the mixture, 3Mn:1Cu. The DTA curve shows four endothermic peaks with their minima located at 305, 332, 390 and 540°C. The first and second peaks refer to the thermal decomposition of basic copper carbonate to copper oxide [16]. At the same time, a broad endothermic peak located at about 390°C points to the higher energy needed to decompose a large amount of manganese carbonate to manganese oxide. The last endothermic peak, located at 540°C, indicates the transformation of manganese dioxide into manganese trioxide [8].

The TG curve shows four steps for thermal decomposition of the mixture, 3Mn:1Cu. The first step starts at about 280°C and reaches a constant weight loss of 6.9%, corresponding to the decomposition of basic copper carbonate to copper oxide [15]. The second step starts at about 340°C and reaches a constant weight loss of 25.30% pointing to the decomposition of manganese carbonate to manganese dioxide. The third step starts at about 525°C reaching a constant weight loss of 25% which refers to the reduction of MnO_2 to Mn_2O_3. At temperature higher than 700°C, no noticeable weight change is observed. This may be attributed to a solid–solid interaction between copper oxide and manganese oxide to form $CuMn_2O_4$. The crystalline phase $CuMn_2O_4$ is detected in the XR diffractogram of the mixture, 3Mn:1Cu preheated at 750°C.

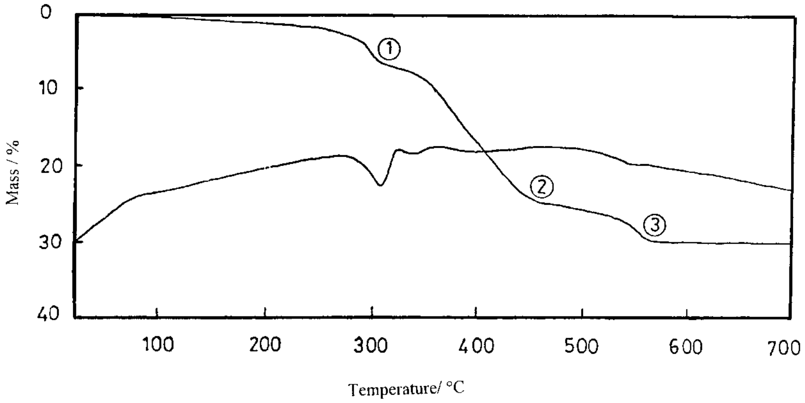

Fig. 4. Thermal analysis (DTA and TG) of mixed solids with molar formula ($3MnCO_3$:1/2$CuCO_3$·$Cu(OH)_2$).

The thermal decomposition of the mixture, 3Mn:1Cu, at different temperatures and the corresponding suggested formula are listed in Table 1.

Fig. 5 shows DTA and TG analysis of the mixture, 1Mn:3Cu. The DTA curve shows three endothermic peaks. Their minima are located at 290, 325 and 368°C corresponding to the thermal decomposition of this mixture. The TG curve shows three steps for the thermal decomposition of the mixture, 1Mn:3Cu. These steps and the corresponding weight loses as well as the suggested formulae are summarized in Table 2.

Table 1
Thermal analysis of the mixture (3Mn:1Cu)

Thermal step	Temp. ranges (°C)	% loss		Suggested formulae
		Calc.	Theor.	
1	(280–320)	6.90	6.80	$3MnCO_3 + CuO$
2	(340–440)	25.30	25.25	$3MnO_2 + CuO$
3	(525–700)	30.50	30.51	$3/2Mn_2O_3 + CuO$
4	($\geq$ 750)	30.50	30.51	$1/2\ Mn_2O_3 + CuMn_2O_4$

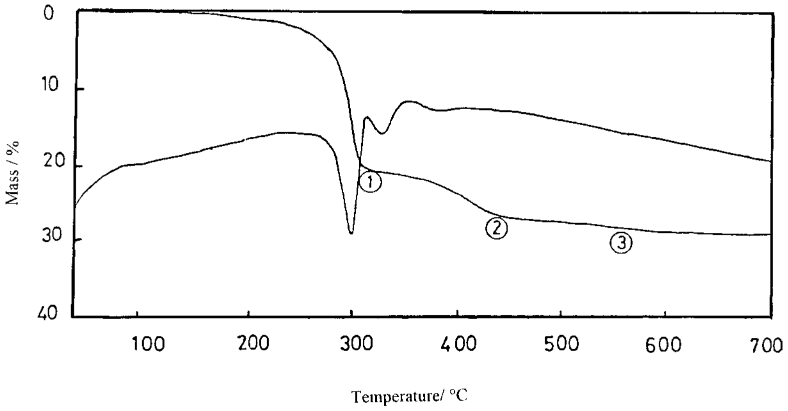

Fig. 5. Thermal analysis (DTA and TG) of mixed solids with molar formula ($1MnCO_3$:3/2 $CuCO_3$·$Cu(OH)_2$).

Table 2
Thermal analysis of mixture (1Mn: 3Cu)

Thermal step	Temp. ranges (°C)	% loss		Suggested formulae
		Calc.	Theor.	
1	(230–320)	20.80	20.80	$MnCO_3+3CuO$
2	(370–440)	27.00	27.09	MnO_2+3CuO
3	($\geq$ 540)	28.80	28.89	$1/2Mn_2O_3+3CuO$
4	($\geq$ 750)	28.85	28.89	$2.5\ CuO+1/2CuMn_2O_4$

Above 750°C, the TG curve shows negligible weight loss due to the formation of $CuMn_2O_4$ which is detected in the XR-diffractogram for the mixture, 1Mn:3Cu preheated at 750°C.

A comparison between the TG curves of individual and mixed $MnCO_3$ and $CuCO_3.Cu(OH)_2$, (Figs. 2–5) reveals that:

1. The presence of basic copper carbonate in combination with manganese carbonate retards the decomposition of manganese carbonate in the mixture.
2. The presence of $MnCO_3$ leads to the splitting of the endothermic peak characterizing the decomposition of $CuCO_3{\cdot}Cu(OH)_2$ into two endothermic peaks; the first (major) being at 303°C and the second (minor) being at 325°C.
3. The endothermic peak located at 395°C is detected in the case of pure manganese carbonate and the mixture, 3Mn:1Cu, but it disappears in case of the mixture, 1Mn:3Cu.
4. The presence of CuO retards to a certain extent the process of transformation of MnO_2 to Mn_2O_3.
5. Above 700°C, no noticeable weight change is observed for the mixtures, 3Mn:1Cu and 1Mn:3Cu. This may be attributed to the probability of the formation of $CuMn_2O_4$ as a result of solid–solid interaction between the thermal decomposition products.

3.2. XRD investigation of the thermal products of pure and mixed manganese carbonate and basic copper carbonate

3.2.1. Pure solids

Figs. 6 and 7 show the XRD patterns of pure manganese carbonate and basic copper carbonate

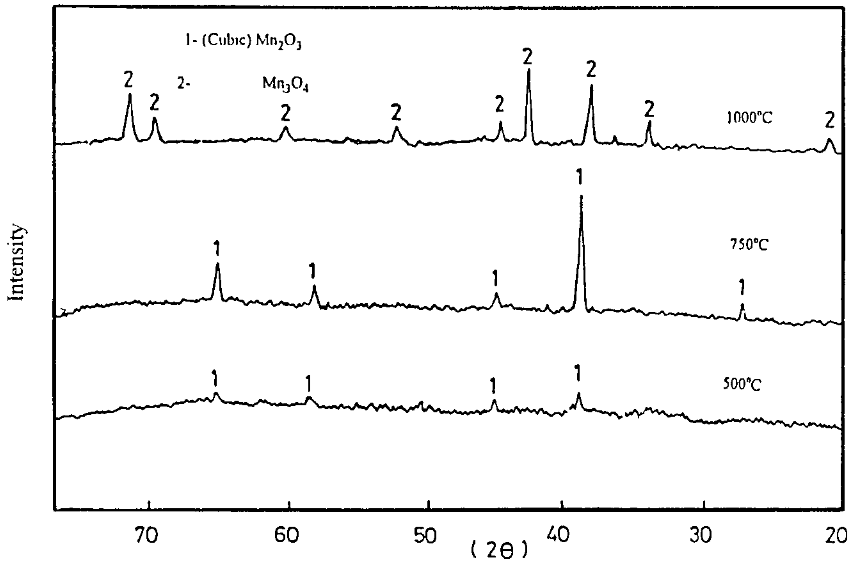

Fig. 6. XR diffractograms of pure $MnCO_3$ preheated in air at different temperatures – 500, 750 and 1000°C.

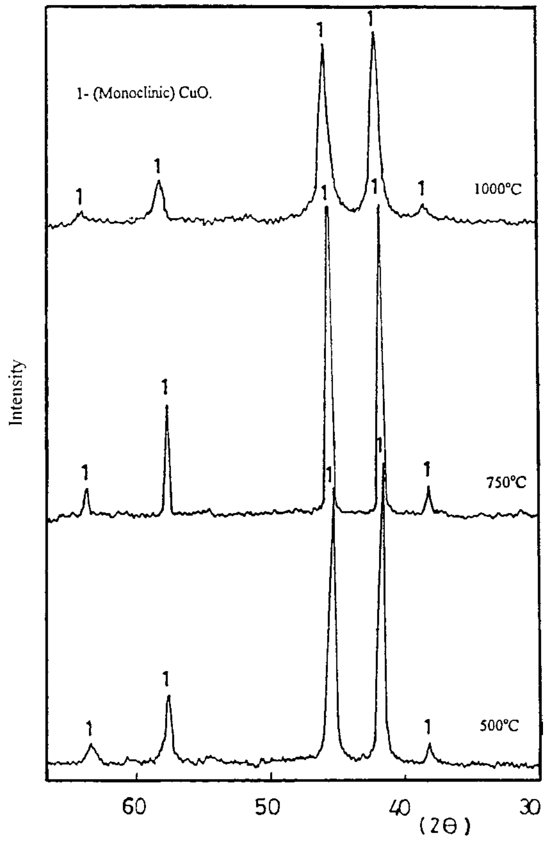

Fig. 7. XR diffractograms of pure $CuCO_3\cdot Cu(OH)_2$ preheated in air at different temperatures – 500, 750 and 1000°C.

preheated in air at different temperatures. The thermal treatment of $MnCO_3$ at 500°C produces a solid with a small degree of crystallinity of cubic Mn_2O_3 with *d*-spacing: 2.694, 2.339, 1.834 and 1.658 Å. By increasing the treatment temperature up to 750°C, the crystallinity of the manganese trioxide phase increases. Further increase in the calcination temperature up to 1000°C leads to the formation of a new crystalline phase Mn_3O_4 [17] as a result of the reduction of manganese trioxide according to:

$$3Mn_2O_3 \xrightarrow{\geq 940^{\circ}C} 2Mn_3O_4 + 1/2O_2$$

On the other hand, the thermal products of $CuCO_3$.-$Cu(OH)_2$ at 500°C yield a crystalline phase of monoclinic CuO. The degree of crystallinity increases by increasing the temperature of treatment up to 750°C. Further increase in the calcination temperature up to 1000°C leads to a decrease in the degree of crystallinity of the CuO phase. This may be attributed to the partial reduction of bivalent copper oxide into amorphous monovalent cuprous oxides [14] according to:

$$CuO \xrightarrow{\text{At high temperature}} Cu_2O$$

3.2.2. Mixed solids

Figs. 8–10 illustrate the results of the XRD analysis of the mixtures, 3Mn:1Cu, 1Mn:1Cu, and 1Mn:3Cu, preheated at 500, 750 and 1000°C. The thermal treatment of all mixtures of (Mn:Cu) preheated at 500°C produces Mn_2O_3 and CuO crystalline phases. By increasing the temperature of treatment up to 750°C it was detected that it forms a new crystalline phase $CuMn_2O_4$ as a result of solid–solid interaction [24] between manganese trioxide and copper oxide as follows:

$$CuO + Mn_2O_3 \xrightarrow{750^{\circ}C} CuMn_2O_4$$

For all the mixtures, Mn:Cu preheated at 750°C, crystalline $CuMn_2O_4$ phase is observed where its maximum formation is detected in the case of excess CuO. Moreover, excess CuO appears as a separate crystalline phase in the mixture, 1Mn:3Cu.

Further increase of the calcination temperature up to 1000°C for the mixture, 3Mn:1Cu, leads to a transformation of Mn_2O_3 (detected at 750°C) to a new crystalline phase of calcinite Mn_3O_4, and the CuO phase disappears. This may be attributed to the formation of $CuMn_2O_4$ as detected [17] in the XR diffractogram. On the other hand, for mixtures, 1Mn:1Cu and 1Mn:3Cu preheated at 1000°C, only CuO and $CuMn_2O_4$ crystalline phases are observed. This means that $CuMn_2O_4$ is formed at a temperature higher than 500°C and is stable even up to 1000°C. Also, the crystallinity of the CuO phase decreases for all mixtures at 1000°C.

3.3. Catalytic decomposition of H_2O_2 over pure and mixed manganese and copper oxides

3.3.1. On pure oxides

Fig. 11 represents the plots of ln(*a*/*a*−*x*) vs. time (where: *a* is the initial concentration of H_2O_2 and *x*, the quantity of decomposed H_2O_2) for pure manganese

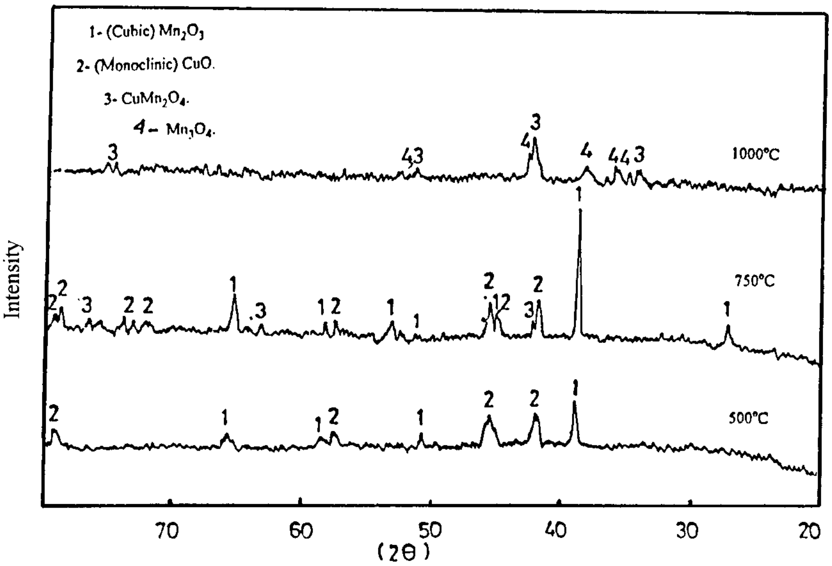

Fig. 8. XRD diffractograms of mixed solids with molar formula ($3MnCO_3$:1/$2CuCO_3$·$Cu(OH)_2$) preheated in air at different temperatures, 500, 750 and 1000°C.

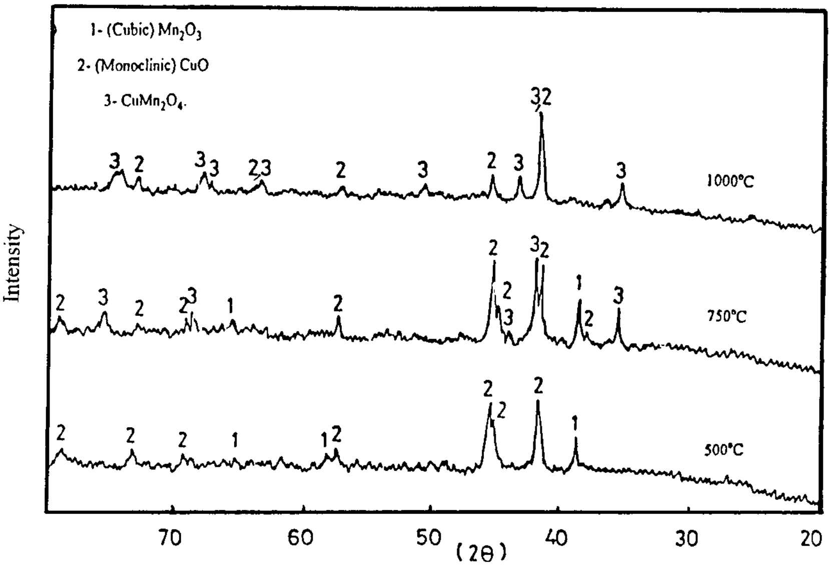

Fig. 9. XRD diffractograms of mixed solids with molar formula ($MnCO_3$:1/$2CuCO_3$·$Cu(OH)_2$) preheated in air at different temperatures, 500, 750 and 1000°C.

carbonate thermally treated at 250, 500 and 750°C. It can be observed that the salt preheated at 250°C is more active than that preheated at 500 and 750°C. It is known that the colour of manganese carbonate is buff, but treatment at 250°C converts its colour into black. This may be due to the fact that some of the carbonate is transformed into black amorphous manganese dioxide phase. The presence of manganese tetravalent with the carbonate [18,19] leads to high catalytic activity for the sample preheated at 250°C, while the salt

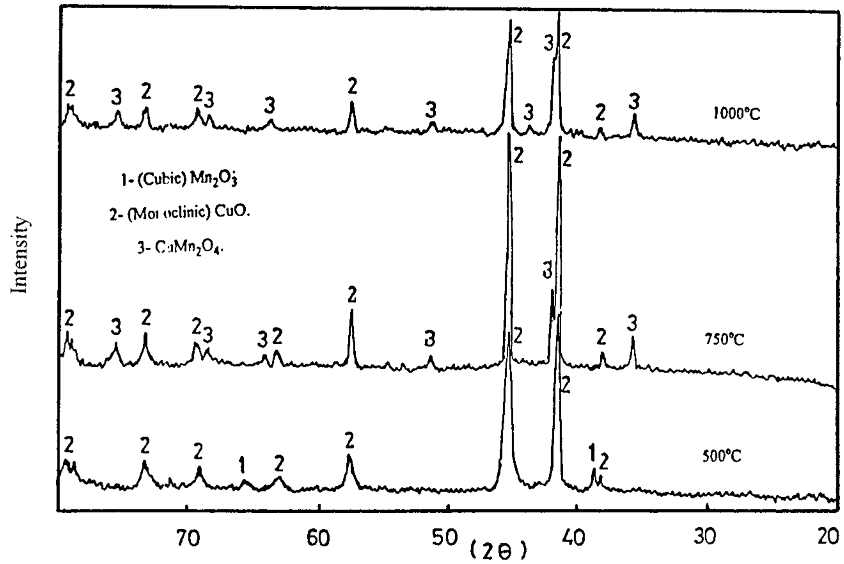

Fig. 10. XRD diffractograms of mixed solids with molar formula ($MnCO_3$:3/2 $CuCO_3 \cdot Cu(OH)_2$) preheated in air at different temperatures, 500, 750 and 1000°C.

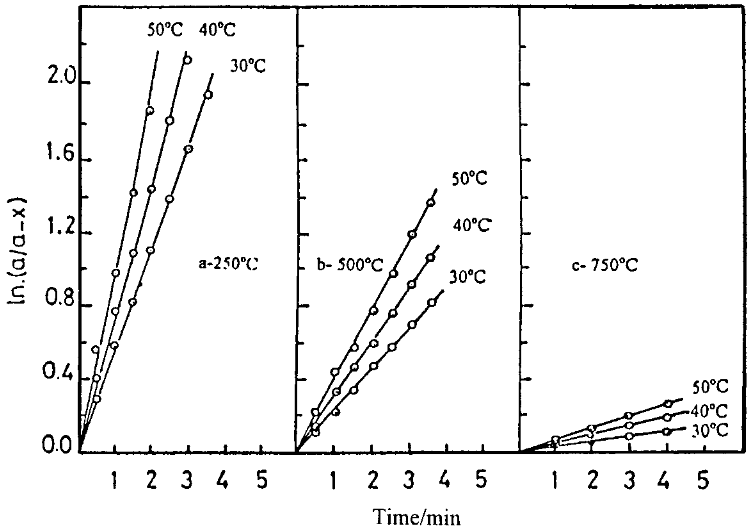

Fig. 11. Dependence of ln (*a*/*a*–*x*) vs. time for catalyst ($MnCO_3$) preheated at different temperatures: (a) 250°C, (b) 500°C and (c) 750°C.

preheated at 500°C produces less active manganese trioxide.

By increasing the calcination temperature up to 750°C, the degree of crystallinity of Mn_2O_3 increases leading to a pronounced decrease in catalytic activity. By further increase of the treatment up to 1000°C, no catalytic activity is observed. This can be attributed to the formation of less active species of Mn_3O_4 and/or sintering [20,21], which means that change in the catalytic activity can be attributed to change in the oxidation state [22], and the degree of crystallinity.

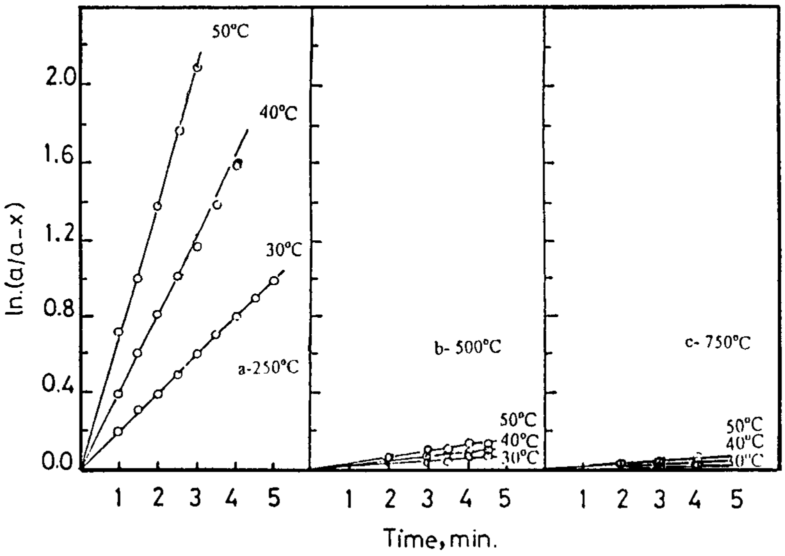

Fig. 12. Dependence of ln $(a/a{-}x)$ vs. time for catalyst ($CuCO_3{\cdot}Cu(OH)_2$) preheated at different temperatures, (a) 250°C, (b) 500°C and (c) 750°C.

From Fig. 12, it can be seen that, pure basic copper carbonate preheated at 250°C is somewhat active for H_2O_2 decomposition. Catalytic activity decreases by increasing the temperature of treatment up to 500 and 750°C, seemingly, due to the presence of the crystalline phase CuO. Further increase in the calcination temperature up to 1000°C produces inactive solid. This may be due to the formation of the amorphous phase of Cu_2O and/or sintering.

3.3.2. On (Mn:Cu) mixed oxides

Figs. 13–15 indicate that first-order kinetics holds for the mixtures 3Mn:1Cu, 1Mn:1Cu and 1Mn:3Cu, preheated at 250, 500 and 750°C as linear plots for the

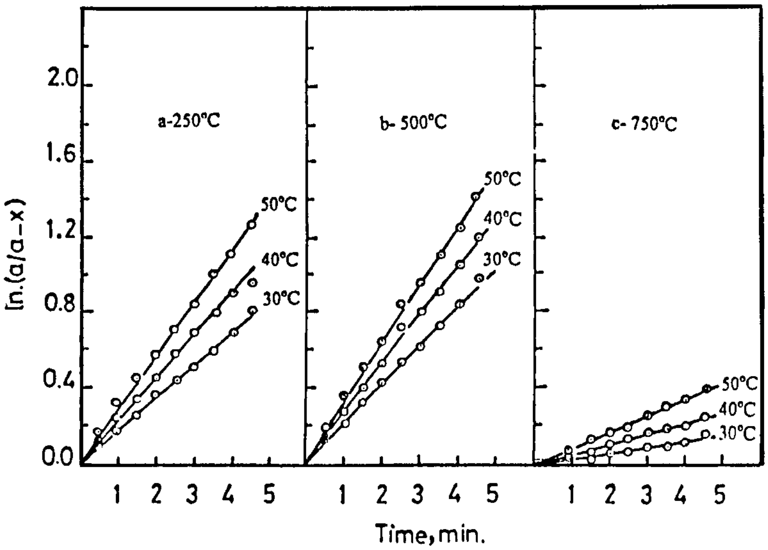

Fig. 13. Dependence of ln $(a/a{-}x)$ vs. time for catalyst (3Mn:1Cu) preheated at different temperatures: (a) 250°C, (b) 500°C and (c) 750°C.

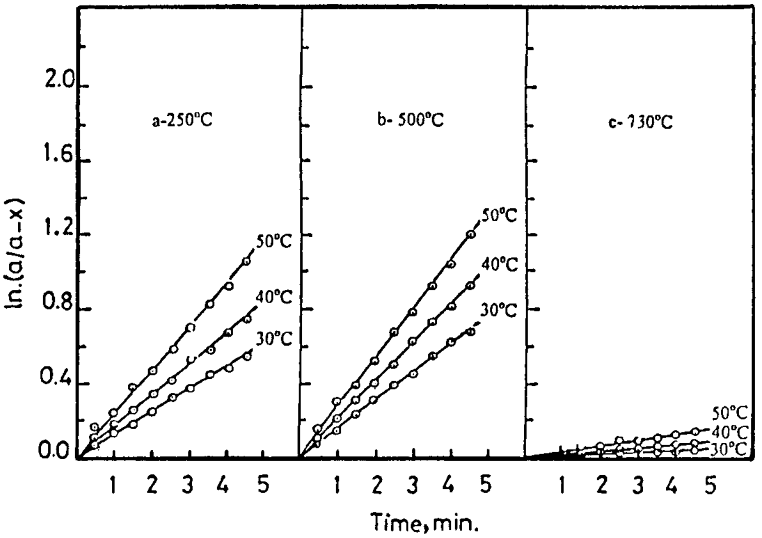

Fig. 14. Dependence of ln (*a*/*a*–*x*) vs. time for catalyst (1Mn:1Cu) preheated at different temperatures: (a) 250°C, (b) 500°C and (c) 750°C.

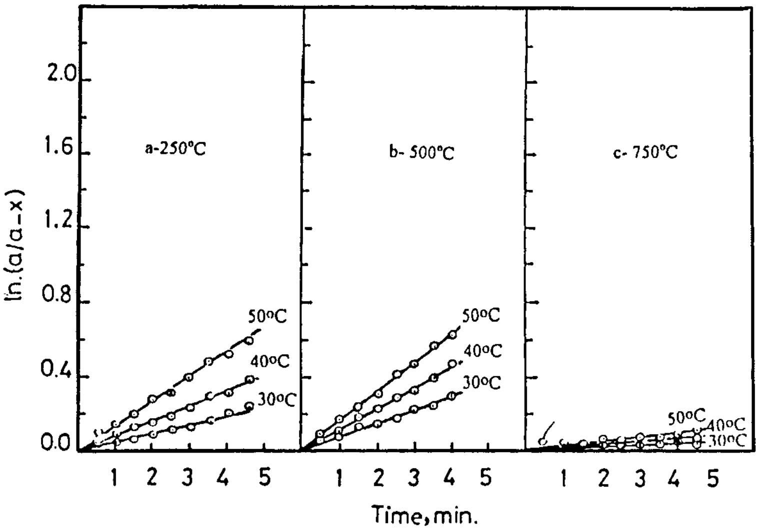

Fig. 15. Dependence of ln (*a*/*a*–*x*) vs. time for catalyst (1Mn:3Cu) preheated at different temperatures: (a) 250°C, (b) 500°C and (c) 750°C.

catalytic decomposition of H_2O_2. It can be seen that the catalytic activity of these solids in hydrogen peroxide decomposition increases as the activation temperature increases passing through a maximum at a pretreatment temperature of 500°C. This can be explained as follows:

1. Solid preheated at 250°C possesses active species of manganese carbonate and manganese tetravalent in amorphous phase. In this case, according to Kanungo et al. [23], the decomposition may take place by donating an electron from the substrate to the solution or vice versa. Then, if the catalyst accepts an electron, the possible active site is Mn^{4+} to yield a $HO_2^{\bullet}$ radical according to:

$$Mn^{4+} + H_2O_2 \rightarrow H^+ + HO_2^{\bullet} + Mn^{3+}$$

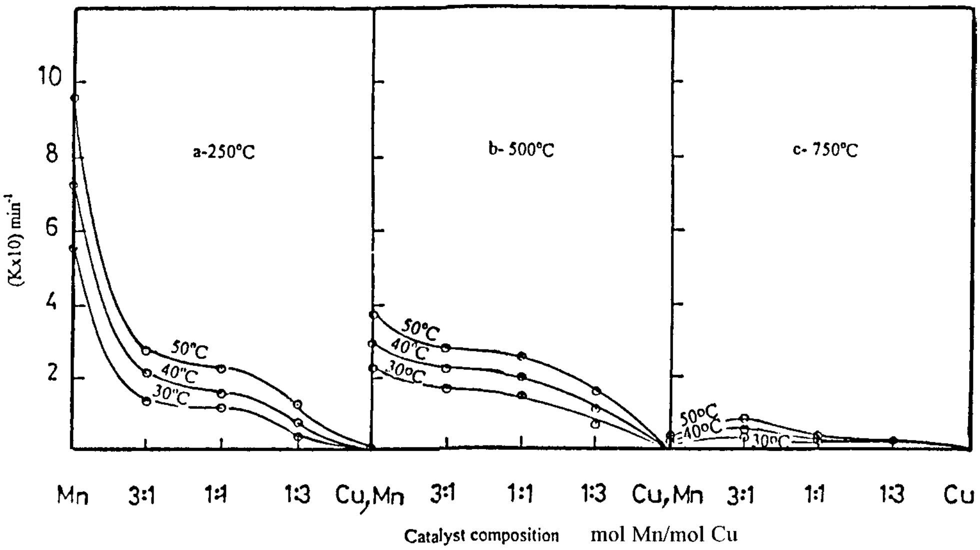

Fig. 16. Dependence of rate constant (k min^{-1}) on the catalyst composition (Mn:Cu). Catalyst thermally treated at different temperatures: (a) 250°C, (b) 500°C and (c) 750°C.

The presence of CuO in the mixture seems to be the reason for the less catalytic activity as compared with pure manganese carbonate preheated at the same temperature, i.e., copper has an inhibiting effect. Also, the presence of CuO may delay the decomposition of manganese carbonate to manganese dioxide (the highly active phase) and consequently less activity is observed at 250°C.

2. For samples preheated at 500°C, the XR diffractograms show crystalline phases of Mn_2O_3 and CuO. These samples possess high catalytic activity. These conditions [24] favour the increase of the active site concentration of manganese trivalent (Mn^{3+}) which yield an $OH^{\bullet}$ radical as follows:

$$Mn^{3+} + H_2O_2 \rightarrow OH^- + HO^{\bullet} + Mn^{4+}$$

3. Increasing the amount of CuO in the mixture leads to the decrease of the number of active species and consequently decrease in the catalytic activity.

By increasing the treatment temperature up to 750°C, catalytic activity decreases reaching a minimum for the mixture, 1Mn:3Cu. This is due to the formation of the inactive species, $CuMn_2O_4$ [17] spinal form. This form restricts the active species of Mn^{3+} in a strongly bounded octahedral site where the maximum formation is achieved at 750°C in the region of excess of CuO, i.e., 1Mn:3Cu. Upon increasing the treatment temperature to 1000°C, all samples show a marked inactivity in hydrogen peroxide decomposition which may be attributed to the formation of inactive sites, viz., Mn_3O_4, $CuMn_2O_4$ and/or sintering.

The relationship between the rate constants (k) for hydrogen peroxide decomposition and the composition of the mixtures, Mn:Cu, preheated at different temperatures is represented in Fig. 16. The observed changes of the catalytic activity are probably due to changes of the valence state of the catalytically active components of the catalyst.

Table 3 illustrates the activation energies for hydrogen peroxide decomposition by the mixtures Mn:Cu, preheated at 250, 500, and 750°C. It can be observed that the mixtures preheated at 250 and 500°C show almost the same activation energy as that for pure manganese carbonate preheated at the same temperatures. Increase of the Cu content increases the values of activation energy for all samples. Manganese carbonate preheated at 750°C shows an energy of activation of 33 kJ mol^{-1}. The introduction of copper shows energies of activation of the values 38–41 kJ mol^{-1}. The constancy of the values of activation energy points

Table 3

Catalyst from	Calcination temperature (°C)	Activation energy E (kJ mol^{-1})
$MnCO_3$ weight used=0.01 gm	250	22.5
	500	21.6
	750	33
$CuCO_3Cu(OH)_2$ weight used=0.01 gm	250	52.8
	500	42.2
	750	50
(3Mn:1CU) weight used=0.01 gm	250	20.8
	500	17.5
	750	38.5
(1Mn:1Cu) weight used=0.01 gm	250	27
	500	33
	750	42
(1 Mn:3 Cu) weight used=0.01 gm	250	44.3
	500	32
	750	39

to the same nature of active centers in all mixtures preheated at 750°C being different from that on pure manganese carbonate or basic copper carbonate preheated at 750°C, individually.

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