

PREPARATION OF MIXED Co AND Cu OXIDES VIA THERMAL DECOMPOSITION OF THEIR OXALATES, AND STUDY OF THEIR CATALYTIC PROPERTIES

A. M. Donia¹, N. R. E. Radwan² and A. A. Atia¹

¹Department of Chemistry, Faculty of Science, Menoufia University, Shebin El-Kom

²Department of Chemistry, Faculty of Education, Suez Canal University, Suez, Egypt

(Received May 2, 1999; in revised form August 30, 1999)

Abstract

Mixed oxides were prepared by the thermal decomposition of the oxalates of cobalt(II) and copper(II) coprecipitated from aqueous solution or made by mechanical mixing. The compositions and structures of the oxides were confirmed by means of TG and X-ray powder diffraction spectroscopy. The catalytic behaviour of the oxides obtained was studied by using the decomposition of H₂O₂ as a model reaction. The results were compared with those on the oxides produced from the thermal decomposition of mechanically mixed oxalates. The catalytic activities of the mixed oxides were found to be lower than that of pure cobalt oxide, but higher than that of copper oxide. This result was interpreted in terms of the relative standard reduction potential of the catalyst as compared with that of H₂O₂. The catalytic activity of the mixed oxides obtained from the coprecipitate was found to be lower than that of the oxides obtained from the mechanical mixture at the same temperature. As the temperature of preparation was increased, the catalytic activities of the oxides obtained decreased. This was attributed to the solid-solid interactions, which gave a new phase with lower catalytic activity than those of the interacting phases.

Keywords: catalytic properties, coprecipitated oxalates, mixed oxides

Introduction

Catalysts have many important applications in the field of fuels, the manufacture of foods, pharmaceuticals, semiconductors, paints and chemicals [1–4]. Binary oxides are widely used in catalysis [5–8]. A great deal of fundamental research has been carried out on mixed oxides [9, 10]. These mixed oxide systems may be more or less active than their individual oxide components [11, 12]. In generally, the catalytic activity of an oxide depends on many factors; these include the method of preparation, the sintering conditions and the interactions between the different components of the catalyst [13].

The decomposition of H₂O₂ has been adopted as a model reaction to measure the catalytic activities of different metal oxides. Oxides involved in redox systems are

good catalysts in the decomposition of H_2O_2 [14]. Cobalt oxide is a good catalyst, whereas copper oxide appears to be a poor one in the same reaction [15, 16].

Binary oxides are usually prepared through the mechanical mixing of salts of the desired metals at specific molar ratios. When the mixture is heated, different phases are produced and can be detected. The phase $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ was obtained through heating of a mechanical mixture of copper and cobalt carbonates [17]. However, no work has been done on the mixed oxides obtained from the thermal decomposition of their coprecipitated and mechanically mixed oxalates. In the present work, the textural and catalytic properties of copper and cobalt oxides and of their mixed oxides obtained via thermal decomposition of their mechanical and coprecipitated oxalates are investigated.

Experimental

Materials

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ were from Fisher Scientific. Oxalic acid was from J. T. Baker Chemical Co. All these compounds were chemically pure and were used without further purification.

Method

Cobalt oxalate (1), copper oxalate (2) and their coprecipitate (3) were prepared by the methods reported earlier [18]. The elemental analyses, IR and TG data confirmed the following formulae:



The individual oxalates (1) and (2), their coprecipitate (3), and mechanical mixture with the same mole ratio were subjected to different temperatures (350, 600 and 900°C) in order to produce and identify the studied oxides.

Measurements

The oxides obtained were investigated by means of X-ray diffraction (XRD), using a Shimadzu XD-3 diffractometer with CuK_α radiation. The thermal analysis (TG/DTA) was carried out on an SDT 2960 simultaneous DTA-TG-TA instrument. The analysis was performed at a heating rate of $10^\circ\text{C min}^{-1}$ in a dynamic air flow of $50 \text{ cm}^3 \text{ min}^{-1}$. Table 1 details the thermal products obtained from the investigated oxalates, as indicated by TG. The surface area measurements (BET) were performed by using the low-temperature adsorption of nitrogen at -196°C .

Table 1 Thermal products of the investigated oxalates

Compound	Temperature range/°C	Mass loss/% calcd (found)	Reaction	Product
Co(ox)·2H ₂ O	120–180	19.7(19.6)	a	Co(ox)
	250–277	56.2(56.7)	b	Co ₃ O ₄
Cu(ox)·1/3H ₂ O	40–215	3.8(3.8)	a	Cu(ox)
	215–320	52.4(52.4)	b	CuO _{0.75}
Co _{0.7} Cu _{0.3} (ox)·2H ₂ O	100–160	14.6(14.0)	a	Cu _{0.3} Co _{0.7} (ox)·0.5H ₂ O
	160–260	4.9(5.0)	a	Cu _{0.3} Co _{0.7} (ox)
	260–310	54.1(54.1)	b	Cu _x Co _{3-x} O _{4.45} (x=0.9)

a=dehydration, b=decomposition, ox=C₂O₄²⁻

The catalytic behaviour of the oxides was investigated by studying their effects on the decomposition of H₂O₂ [19]. 20 ml of distilled water and 0.5 ml of H₂O₂ (30%) were introduced into the glass reactor, and the temperature of the reaction was adjusted to the desired temperature by using an ultrathermostat. 50 mg of the oxide sample was introduced into the reaction cell and the reaction was followed by measuring the volume of gas released in different time intervals.

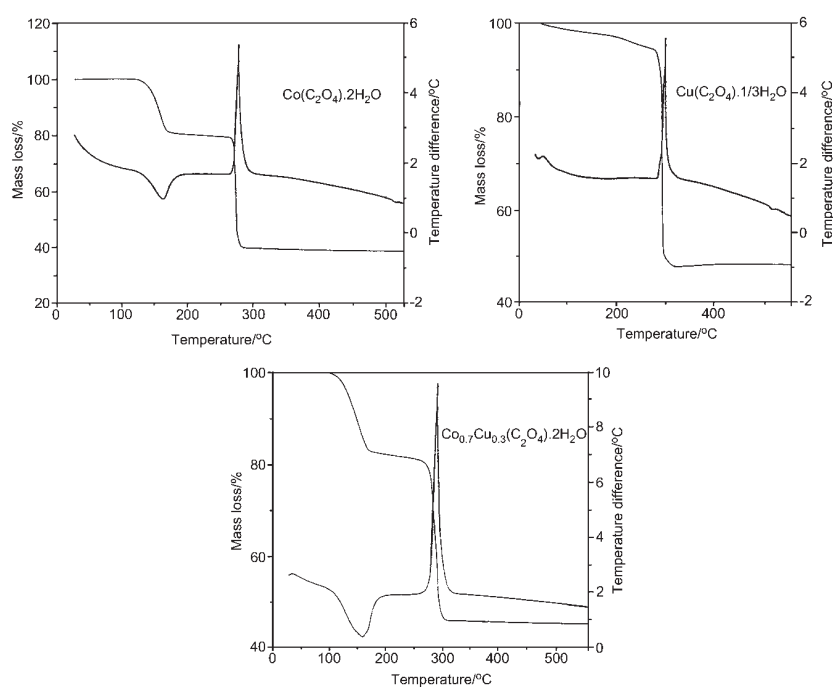


Fig. 1 TG-DTA curves of Co(C₂O₄)·2H₂O, Cu(C₂O₄)·1/3H₂O and their coprecipitate, Co_{0.7}Cu_{0.3}(C₂O₄)·2H₂O, in air

Results and discussion

Thermal studies

Figure 1 depicts the TG and DTA curves of the individual oxalates (1) and (2) and their coprecipitate (3). The DTA curves reveal an endothermic dehydration peak in the ranges 120–180 (max. 160), 40–215 (broad) and 100–260 (max. 160°C) for (1), (2) and (3), respectively. This dehydration process was confirmed by the TG mass losses (Table 1), which correspond to $2\text{H}_2\text{O}$, $1/3\text{H}_2\text{O}$ and $2\text{H}_2\text{O}$ (in two steps, Table 1), respectively. The dehydration process was followed by an exothermic peak, with maxima at 283, 300 and 290°C for (1), (2) and (3), respectively. The TG data (Table 1) indicate that the exothermic event may be assigned to decomposition to give the oxygen-deficient $\text{CuO}_{0.75}$, stoichiometric Co_3O_4 and oxygen-rich non-stoichiometric $\text{Cu}_x\text{Co}_{3-x}\text{O}_{4.45}$ ($x=0.9$) phases as final products. The IR spectra exhibit no peaks corresponding to the oxalate moiety, confirming the formation of oxides. The spectra display bands in the region $665\text{--}495\text{ cm}^{-1}$, which are assigned to $\nu\text{M--O}$. The formation of these oxides was confirmed by XRD studies, as indicated below.

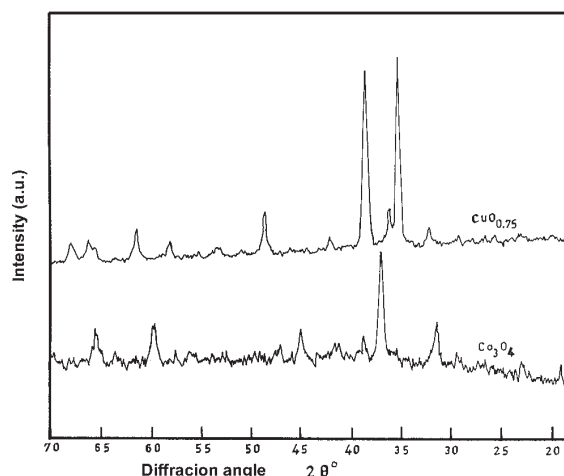


Fig. 2a X-ray diffraction patterns of cobalt oxide and copper oxide

X-ray studies

Figure 2a gives X-ray diffraction patterns of the oxides obtained from the thermal decomposition of copper and cobalt oxalates at 350°C in air. The pattern of copper oxide is characterized by two strong lines with d -spacings of 2.5265 Å (most intense line) and 2.3305 Å. These lines are close to those given in the ASTM card for monoclinic CuO ($d=2.5230$ and 2.3230 Å). The line with $d=2.7526$ Å also coincides with that found in the ASTM (2.7510 Å). The pattern further demonstrates weak lines with $d=2.4727$, 2.1396 and 1.5065 Å. These lines are characteristic of the cubic phase

Cu_2O , as indicated by the ASTM card values for this phase ($d=2.4650, 2.1350$ and 1.5100 \AA). This indicates the presence of two phases, monoclinic CuO and cubic Cu_2O . These results are in conformity with the TG data, which indicate the formation of the oxygen-deficient phase $\text{CuO}_{0.75}$ ($\text{Cu}^{2+}/\text{Cu}^+$). As we shall discuss later, the presence of Cu^+ is responsible for the catalytic properties of this type of oxide. The pattern for cobalt oxide (Fig. 2a) obtained from the thermal decomposition of cobalt oxalate at 350°C indicates the formation of stoichiometric Co_3O_4 with a spinel-type structure.

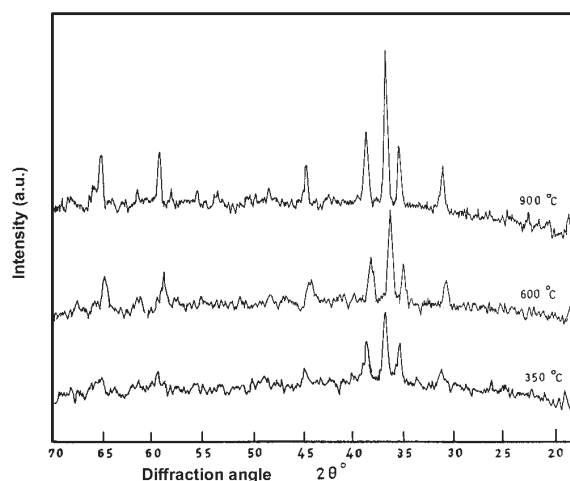


Fig. 2b X-ray diffraction patterns of mixed oxides obtained from thermal decomposition of coprecipitate of copper and cobalt oxalates at 350, 600 and 900°C

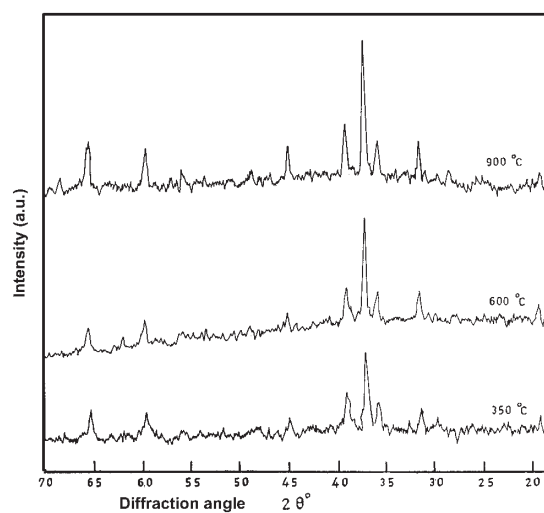


Fig. 2c X-ray diffraction patterns of mixed oxides obtained from thermal decomposition of mechanical mixture of copper and cobalt oxalates at 350, 600 and 900°C

The observed lines with $d=4.6668$, 2.8553 , 2.4275 (most intense line) and 1.4296 Å are close to those in the ASTM card ($d=4.6690$, 2.8600 , 2.4380 and 1.4293 Å) for the spinel Co_3O_4 . The TG data (Table 1) confirm this composition.

On comparison of the patterns for copper oxide, cobalt oxide and the oxide obtained from the thermal decomposition of coprecipitate (3) at 350, 600 and 900°C (Fig. 2b), it is seen that all the lines of the phase Co_3O_4 are shifted to lower 2θ (higher d values), but they are still largely close to the values in the ASTM card for the spinel phase Co_3O_4 . The observed shift is attributed to the modification (or distortion) of the spinel Co_3O_4 lattice due to the introduction of copper ions into the lattice, to give the oxygen-rich phase $\text{Cu}_x\text{Co}_{3-x}\text{O}_{4.45}$ ($x=0.9$). The formation of this phase may be accompanied by the redox reaction $\text{Cu}^+ + \text{Co}^{3+} \rightarrow \text{Cu}^{2+} + \text{Co}^{2+}$, as reported in similar systems [20].

The patterns (Figs 2b and 2c) of the mixed oxide phases obtained from the coprecipitate and the mechanical mixture are typically the same at different calcinations temperatures. This indicates that the two phases have the same structure. Moreover, as the calcinations temperature is increased, the degree of crystallinity increases. This can be inferred from the increased peak intensities with elevation of temperature.

BET measurements

The BET surface areas of the oxides prepared by heating at 350°C were measured and are reported in Table 2. The values obtained were used to normalize the rates of the catalytic reactions of the systems studied.

Table 2 Surface areas of the oxides obtained from the preheated oxalates at 350°C

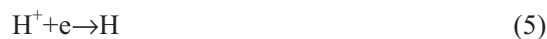
Sample	Surface area (BET)/m ² g ⁻¹
Co_3O_4	62.14
$\text{CuO}_{0.75}$	60.70
$\text{Cu}_x\text{Co}_{3-x}\text{O}_{4.45}$ ($x=0.9$), coprecipitate	50.2
$\text{Cu}_x\text{Co}_{3-x}\text{O}_{4.45}$ ($x=0.9$), mechanical mixture	46.5

Catalytic properties

The kinetics of H_2O_2 decomposition may be explained in terms of bivalent catalytic centers. The following mechanisms have been reported by other authors [16]:

For Co_2O_3 (Scheme I)

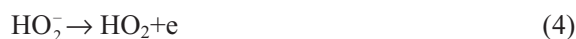
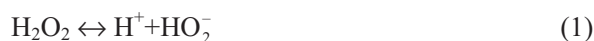




For CoO (Scheme II) [16]:



For Cu₂O (Scheme III) [21]:



It is assumed that the reaction proceeds on acceptor and donor centers. For the cobalt system, the sites $\text{Co}^{3+}/\text{Co}^{2+}$ have been proposed to be responsible for the catalytic activity in the case of Scheme I, and the sites Co^{2+}/Co in the case of Scheme II [16]. The types of the donor and acceptor sites depend on the system involved. For example, while the Co^{2+} centers act as donor sites in systems in which the reaction mechanism follows Scheme I, they behave as acceptor sites in reactions following Scheme II. For the copper oxide system, the sites $\text{Cu}^+/\text{Cu}^{2+}$ are presumed to be responsible for the catalytic activity [21]. While Cu^+ behaves as a donor site, Cu^{2+} behaves as an acceptor.

The catalytic properties of cobalt oxide, copper oxide and their mixed oxides were evaluated by studying the rate of decomposition of H_2O_2 at 30°C. The results are illustrated in Fig. 3. The specific rate constant (k) and the activation energy values were calculated from studies of the catalytic decomposition at different reaction temperatures. The results are shown in Figs 4–6 and in Tables 3 and 4. These data allow the following conclusions:

Table 3 Specific rate constants (k , min^{-1}) for the decomposition of H_2O_2 at different temperatures on different calcined oxides

System	Temperature of calcination								
	350°C			600°C			900°C		
	Reaction temperature								
	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C
Co_3O_4	0.350	0.450	0.600	–	–	–	–	–	–
$\text{CuO}_{0.75}$	0.013	0.024	0.047	–	–	–	–	–	–
$\text{Cu}_x\text{Co}_{3-x}\text{O}_{4.45}$, mechanical	0.060	0.090	0.125	0.028	0.050	0.074	0.015	0.027	0.050
$\text{Cu}_x\text{Co}_{3-x}\text{O}_{4.45}$, coprecipitate	0.050	0.070	0.100	0.020	0.035	0.06	0.010	0.020	0.040

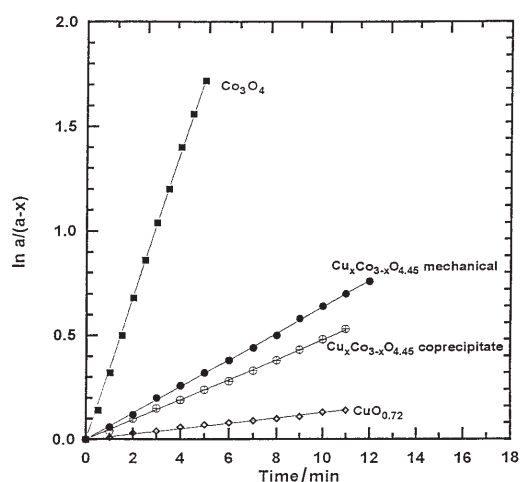


Fig. 3 Decomposition of H_2O_2 at 30°C on cobalt and copper oxides and their mixtures preheated at 350°C

1. Over all the oxides used, the decomposition follows first-order kinetics.
2. The catalytic activities of the oxides decrease in the sequence $\text{Co}_3\text{O}_4 > \text{Cu}_x\text{Co}_{3-x}\text{O}_{4.45}$ (mechanical) $> \text{Cu}_x\text{Co}_{3-x}\text{O}_{4.45}$ (coprecipitated) $> \text{CuO}_{0.72}$ (Table 3). The activation energies given in Table 4 are in accordance with the catalytic activities of the corresponding oxides.

Table 4 Activation energies (E_a) of decomposition of H_2O_2 on different oxides obtained at 350°C

System	$E_a/\text{kJ mol}^{-1}$
Co_3O_4	23.50
$\text{CuO}_{0.75}$	52.46
$\text{Cu}_x\text{Co}_{3-x}\text{O}_{4.45}$, mechanical	26.20
$\text{Cu}_x\text{Co}_{3-x}\text{O}_{4.45}$, coprecipitate	30.37

3. The rate of decomposition on pure cobalt oxide is considerably higher than that on pure copper oxide at the same temperature. This could be interpreted on the basis of the X-ray patterns of the corresponding phases. The higher catalytic activity of cobalt oxide was attributed to the presence of the spinel phase Co_3O_4 . This phase contains both Co^{2+} and Co^{3+} species. It has been reported that in such systems the Co^{3+} determines the rate of decomposition of H_2O_2 [16]. Change in the Co^{3+} content in the phase leads to variations in its catalytic activity. In the case of copper oxide, the monoclinic phase CuO and the cubic phase Cu_2O were identified as the main constituents. The presence of the phase Cu_2O (Cu^+) has been reported to be responsible for the catalytic activity towards H_2O_2 [21]. The relative catalytic activities of the cobalt and copper oxides could be interpreted in terms of the standard reduction potentials of these systems as compared with that of H_2O_2 . The standard reduction potentials for $\text{Co}^{3+}/\text{Co}^{2+}$, $\text{Cu}^{2+}/\text{Cu}^+$ and $2\text{H}^+/\text{O}_2/\text{H}_2\text{O}_2$ are 1.842, 0.167 and 0.682 V, respectively [22].

Since the potential of $\text{Co}^{3+}/\text{Co}^{2+}$ is higher than that of $2\text{H}^+/\text{H}_2\text{O}_2$, H_2O_2 will be oxidized in such systems and consequently Co^{3+} will be reduced to Co^{2+} . Higher concentrations of Co^{3+} give higher rates of decomposition of H_2O_2 and vice versa. An opposite mechanism is proposed in the case of $\text{Cu}^{2+}/\text{Cu}^+$, where H_2O_2 is reduced by accepting electrons from Cu^+ , which is transformed into Cu^{2+} . Thus, the rate of decomposition of H_2O_2 will be related to the concentration of Cu^+ as donor sites. The differences in the catalytic activities is confirmed by the activation energy values reported in Table 4, where E_a for Co_3O_4 is lower than that for $\text{CuO}_{0.75}$. A high concentration of active sites lowers the activation energy of the catalytic reaction, and consequently the rate increases.

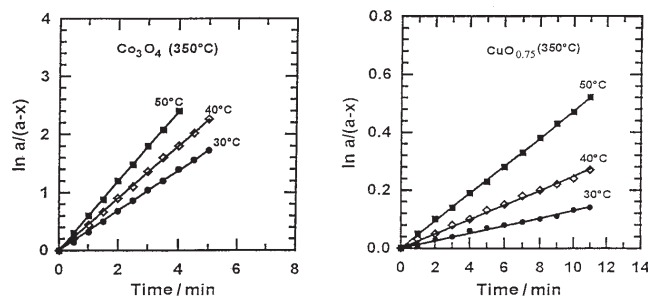


Fig. 4 Decomposition of H_2O_2 on pure cobalt and copper oxides at different reaction temperatures

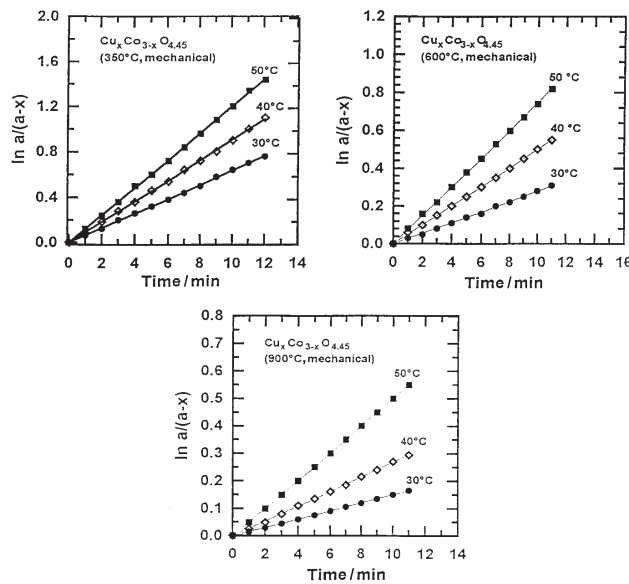


Fig. 5 Decomposition of H_2O_2 on $\text{Cu}_x\text{Co}_{3-x}\text{O}_{4.45}$ ($x=0.9$) (mechanically mixed) at different reaction temperatures

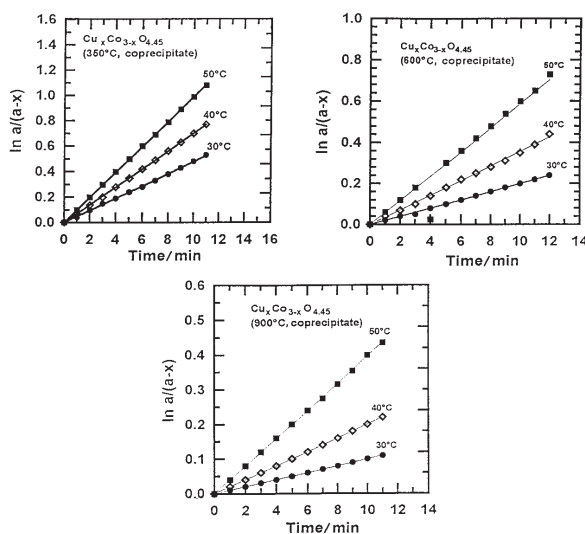


Fig. 6 Decomposition of H_2O_2 on $\text{Cu}_x\text{Co}_{3-x}\text{O}_{4.45}$ ($x=0.9$) (coprecipitated) at different reaction temperatures

4. The rate of decomposition over the oxide obtained from the mechanical mixture is lower than that over pure Co_3O_4 and higher than that over CuO . From the X-ray patterns (Figs 2b and 2c), the phases Co_3O_4 , $\text{CuO}_{0.75}$ and $\text{Cu}_x\text{Co}_{3-x}\text{O}_{4.45}$ were identified. The phase $\text{Cu}_x\text{Co}_{3-x}\text{O}_{4.45}$ is probably formed through interaction between the pure phases Co_3O_4 and $\text{CuO}_{0.75}$. This interaction leads to the insertion of copper into the lattice of Co_3O_4 . The phase $\text{Cu}_x\text{Co}_{3-x}\text{O}_{4.45}$ has lower catalytic activity than the initially reacted pure Co_3O_4 . The change in the catalytic activity may be correlated to the content of Co^{3+} available for the decomposition of H_2O_2 . Since the reaction rate decreases, the concentration of Co^{3+} sites must decrease. The decrease in the concentration of Co^{3+} could be interpreted on the basis of the solid-solid interaction between Co_3O_4 and $\text{CuO}_{0.75}$. The interaction may be accompanied by the following redox reaction: $\text{Cu}^+ + \text{Co}^{3+} \rightarrow \text{Cu}^{2+} + \text{Co}^{2+}$. Other investigators have reported the possibility of such an interaction for different systems [20]. Their conclusion was that ions in higher valence states could be reduced to lower valence states in the presence of other ions. However, the suggested mechanism mentioned above leads to a decrease in the Co^{3+} concentration. When this is taken into consideration, it may be concluded that the interaction will give a phase with lower Co^{3+} content and consequently the catalytic activity decreases.

5. The catalytic effect of the oxides obtained from the decomposition of the mechanical mixture revealed higher rates than that for the corresponding coprecipitate. Moreover, the activation energy of the mechanical mixture was lower than that of the coprecipitates. This may be attributed to the lower extent of the solid-solid interaction between Co_3O_4 and copper oxide in the case of the mechanical mixture. Thus, the per-

centage of Co_3O_4 and copper oxide are higher in the case of the mechanical mixture, indicating a higher catalytic activity.

6. For both the mechanical and coprecipitated mixtures, the catalytic activity decreases as the calcinations temperature is increased. This may be attributed to two reasons: First, as the calcinations temperature is increased, the interaction between Co_3O_4 and copper oxide increases. This increase in the interaction produces the phase $\text{Cu}_x\text{Co}_{3-x}\text{O}_{4.45}$ with a lower content of Co^{3+} . Second, the sintering effect leads to a dramatic decrease in the surface area of the final product. These two factors together lead to a decrease in the number of active sites, and consequently the catalytic activity decreases appreciably with increase of the calcination temperatures.

Conclusions

The phases Co_3O_4 , $\text{CuO}_{0.75}$ and $\text{Cu}_x\text{Co}_{3-x}\text{O}_{4.45}$ ($x=0.9$) were prepared from the thermal decompositions of the individual oxalates, their coprecipitate and their mechanical mixture in air. The compositions and structural characteristics of the oxides obtained were investigated by means of thermal analysis (DTA/TG), IR and X-ray powder diffraction. The catalytic activity of cobalt oxide was found to be higher than that of copper oxide. This was discussed on the basis of the relative standard reduction potentials of cobalt and copper oxides as compared with that of H_2O_2 . Co^{3+} and Cu^+ species were proposed to be responsible for the catalytic activity towards the decomposition of H_2O_2 . Further, the catalytic activities of the oxides prepared by the thermal decomposition of mechanically mixed oxalates were higher than those of the oxides prepared by coprecipitation at the same temperature. This was explained on the basis of solid-solid interactions, in which Co^{3+} was assumed to be transformed into Co^{2+} in the presence of Cu^+ . This leads to a decrease in the catalytic activity of the resulting phase. As the calcination temperature is increased, the catalytic activity of the oxides decreases. This was attributed to a decrease in the concentration of Co^{3+} and to a sintering effect.

References

- 1 B. C. Gates, *Catalysis Chemistry*, Wiley, New York 1992.
- 2 J. J. P. Biermann, M. Deor, A. J. Van Dillen, J. W. Geus and E. T. C. Vogt, *J. Mol. Catal.*, 60 (1990) 229.
- 3 L. D. Ahuja, D. Rajeshwer and K. C. Nagpal, *J. Colloid Interf. Sci.*, 119 (1987) 481.
- 4 V. Mucka and K. Lang, *Collect. Czech. Chem. Commun.*, 53 (1988) 1636.
- 5 M. F. R. Fouda, R. S. Amin and M. M. Selim, *Thermochim. Acta*, 141 (1989) 277.
- 6 V. Mucka, *Radiat. Phys. Chem.*, 48 (1996) 309.
- 7 S. A. Hassan, M. A. Mekewi, F. A. Shebl and S. A. Sadek, *J. Mater. Sci.*, 26 (1991) 3712.
- 8 V. Mucka, *Radiat. Phys. Chem.*, 41 (1993) 843.
- 9 Th. El-Nabarawy and G. A. El-Shobaky, *Surface Tech.*, 10 (1980) 401.
- 10 V. Mucka, *Can. J. Chem.*, 70 (1992) 1914.
- 11 V. Mucka and E. Zabranska, *Radiat. Phys. Chem.*, 45 (1995) 791.

- 12 M. A. Banares, H. W. Hu and E. Israel, *J. Catal.*, 150 (1994) 407.
- 13 L. Hui and K. Tsai, *J. Nat. Gas Chem.*, 3 (1994) 280.
- 14 N. A. Youssef, T. Farid and M. M. Selim, *AFINIDAD*, 443 (1993) 47.
- 15 E. A. Hassan, K. M. Abd-El-Salaam and A. A. Said, *Bull. Chem. Soc. Japan*, 61 (1988) 1331.
- 16 L. D. Ahuja and A. S. Brar, *J. Colloid Interf. Sci.*, 50 (1975) 197.
- 17 A. A. Said, *Bull. Fac. Sci., Assiut Univ., Egypt*, 25 (1996) 43.
- 18 A. M. Donia and D. Dollimore, *Thermochim. Acta*, 290 (1996) 139.
- 19 S. B. Kanungo, K. M. Parida and B. R. Sant, *Electrochim. Acta*, 26 (1981) 1157.
- 20 V. Mucka, *Collect. Czech. Chem. Commun.*, 51 (1986) 1874.
- 21 V. Mucka, *Collect. Czech. Chem. Commun.*, 42 (1977) 2074.
- 22 C. B. Roy, *J. Catal.*, 12 (1968) 129.