ELSEVIER

Thermochimica Acta 275 (1996) 83–91

thermochimica acta

The role of copper cobaltite spinel, $Cu_xCo_{3-x}O_4$ during the thermal decomposition of ammonium perchlorate

A.A. Said [a,*], R. Al-Qasmi [b]

[a] *Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt*
[b] *Chemistry Department, UAE University, P.O. Box 1771, United Arab Emirates*

Received 21 February 1995; accepted 12 August 1995

Abstract

The catalytic effect of copper cobaltite, $Cu_xCo_{3-x}O_4$ spinel in the range ($0 \leq x \leq 3$) on the thermal decomposition of ammonium perchlorate (AP) has been studied using thermogravimetry (TG) and differential thermal analysis (DTA). The results revealed that the addition of CuO ($x = 0.1$ or 0.3) led to an observable increase in the catalytic activity of Co_3O_4 towards the decomposition of AP, while the activity of CuO decreases at $x = 2.9$ and 2.7. The creation of more holes within the p-type semiconducting catalyst is responsible for enhancing the decomposition of AP. In contrast, the catalysts containing copper cobaltite spinels are less active than the doped catalysts. The active redox sites established in these spinels, Co^{3+}/Co^{2+}, Cu^{2+}/Cu^{+} and Co^{3+}/Cu^{+}, are not as efficient as holes in promoting electron exchange with the perchlorate ions.

Keywords: Ammonium perchlorate; Catalyst; Copper cobaltite spinel; $Cu_xCo_{3-x}O_4$; DTA; p-Type semiconductor; TG

1. Introduction

The catalyzed thermal decomposition of ammonium perchlorate (AP) is remarkably sensitive to metal oxide additives [1–7]. Several researchers have studied the surface structure of solid catalysts with particular reference to the identification of the active sites responsible for the catalytic activity [2, 7]. Moreover, the semiconducting properties of the simple oxides or their mixtures were found to play a major role in the decomposition of AP [7]. Also, the reaction mechanism for the decomposition of ammonium perchlorate was influenced by the presence of supported metal or metal

* Corresponding author.

0040-6031/96/$15.00 © 1996 – Elsevier Science B.V. All rights reserved
SSDI 0040-6031(95)02721-1

oxide catalysts [8, 9]. Recently, we reported [10] that the formation of copper cobaltite spinel showed activity towards the decomposition of H_2O_2. The presence of Co^{2+}/Co^{3+}, Cu^{+}/Cu^{2+} and Cu^{+}/Co^{3+} were characterized as active "redox" sites for promoting the reaction.

The catalytic decomposition of ammonium perchlorate by Cu–Co spinel has not been studied. The present study was devoted to the decomposition of ammonium perchlorate in the presence of $Cu_xCo_{3-x}O_4$ spinel catalysts in the range ($0 \leq x \leq 3$) and to the identification of the active sites responsible for the enhancement of the decomposition of ammonium perchlorate.

2. Experimental

2.1. Materials

All reagents used in this study were analytical grade chemicals. Pure cobalt and copper oxides and their mixtures over the composition range of the system, $Cu_xCo_{3-x}O_4$, ($0 \leq x \leq 3$) were prepared from their corresponding basic metal carbonates according to the previous method [10]. The basic carbonate precursors were calcined in air at 250°C for 4 h.

The resultant oxide catalysts were ground with NH_4ClO_4 (10 wt%) in an agate mortar to prepare the samples for the thermal decomposition experiments.

2.2. Techniques

Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out using a Shimadzu DT-40 computerized thermal analyzer. The system includes programs which process data from the thermal analyzer with the chromatopac CR3A integrator. The rate of heating was 10°C min^{-1} in a static air atmosphere. α-Alumina powder was used as the DTA reference material.

The kinetic activity of spinel oxide catalysts in the decomposition of H_2O_2 was evaluated by the rate of production of oxygen gas in the liquid phase. A constant weight of catalyst (100 mg) was injected into the reaction vessel thermostatted at 30°C containing 50 cm^3 of 0.13 N H_2O_2 for each catalyst specimen. The H_2O_2 solution was standardized against $KMnO_4$ immediately before use. The rate of oxygen liberated at atmospheric pressure was measured using the gasometric technique [11]. The time-dependent volume, V_t, of evolved oxygen was monitored at different times and values of V_∞ (the initial volume of O_2 gas present in 50 cm^3).

3. Results and discussion

3.1. Thermal analysis

The TG and DTA curves of uncatalyzed AP and catalyzed with $Cu_xCo_{3-x}O_4$ spinel are shown in Fig. 1. Table 1 gives the maximum temperatures of the two stages of catalyzed decomposition.

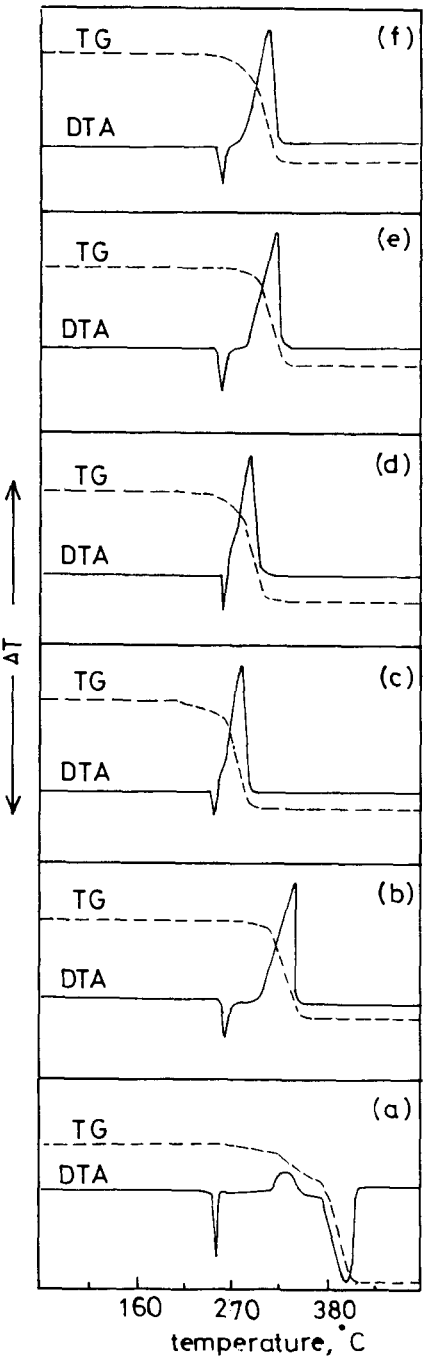

Fig. 1. TG–DTA curves for decomposition of pure AP (a) and as catalyzed by $Cu_xCo_{3-x}O_4$ oxides, $x = 0$ (b), $x = 0.1$ (c), $x = 0.3$ (d), $x = 0.5$ (e), $x = 1$ (f), $x = 1.5$ (g), $x = 2.0$ (h), $x = 2.5$ (i), $x = 2.7$ (j), $x = 2.9$ (k) and $x = 3$ (l).

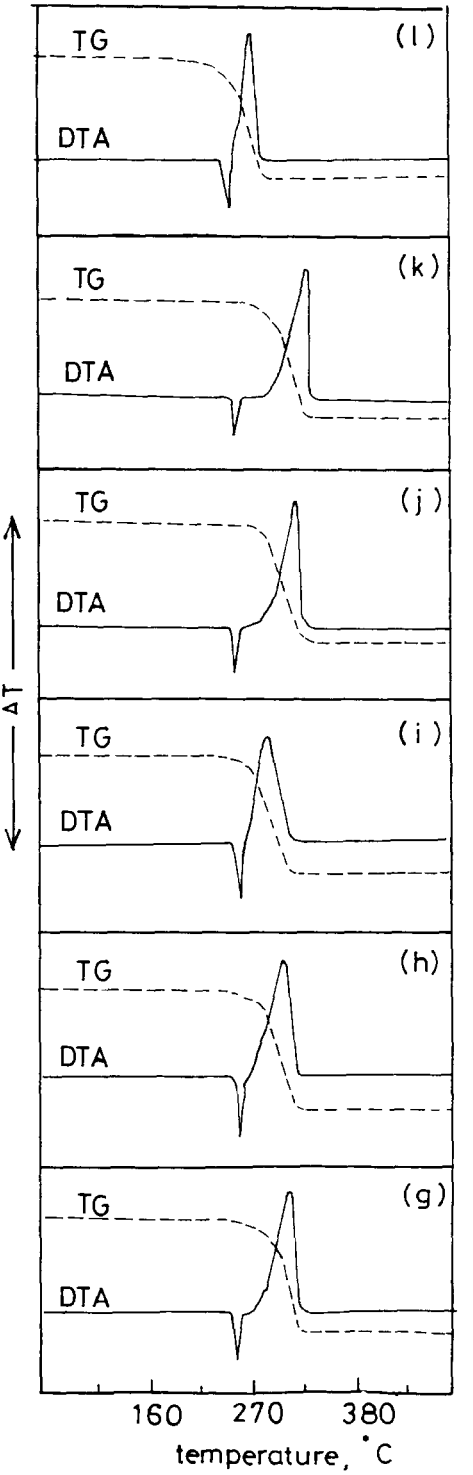

Fig.1. (*Continued*)

Table 1
The temperature ranges and the maximum temperatures (t_{max}/°C) of the different stages of decomposition of ammonium perchlorate in the presence of $Cu_xCo_{3-x}O_4$ oxides

Catalyzing reaction	1st Stage		2nd Stage	
	Temperature range	t_{max}/°C	Temperature range	t_{max}/°C
AP+Co_3O_4 (pure)	240–250	240	275–327	318
AP+Co_3O_4+0.1Cu^{2+}	235–241	237	241–280	264
AP+Co_3O_4+0.3Cu^{2+}	237–247	238	242–288	267
AP+Co_3O_4+0.5Cu^{2+}	237–247	239	261–313	300
AP+Co_3O_4+1.0Cu^{2+}	232–247	239	250–306	295
AP+Co_3O_4+1.5Cu^{2+}	236–247	239	251–307	295
AP+Co_3O_4+2.0Cu^{2+}	235–247	239	248–304	290
AP+Co_3O_4+2.5Cu^{2+}	235–246	239	244–300	280
AP+Co_3O_4+2.7Cu^{2+}	232–247	239	369–325	314
AP+Co_3O_4+2.9Cu^{2+}	236–246	239	271–323	316
AP+CuO (pure)	233–243	238	243–275	263

The DTA curve for uncatalyzed decomposition of AP (Fig. 1) shows three events, while the TG curve exhibits only two. The first endothermic DTA peak at 244°C, is accompanied by zero weight loss. This represents the transition from orthorhombic to cubic AP. The second exothermic peak at 307°C, accompanied by a weight loss of 29%, corresponds to the partial decomposition of AP and formation of an intermediate. The third, main endothermic peak at about 414°C is associated with a 70.5% weight loss. This corresponds to the complete decomposition of the intermediate to volatile products.

The TG and DTA curves for decomposition of AP in the presence of pure Co_3O_4, CuO and their mixtures showed a noticeable change in the decomposition pattern. These results can be summarized as follows.

(1) Similar TG and DTA curves are obtained for the decomposition of AP in the presence of all catalysts. The first peak (phase transition) showed only small changes in position while the second peak was absent. In contrast, the third endothermic peak changed into a sharp exothermic one. Its position depended strongly on the composition of the catalyst. The TG curves showed only a one-step weight loss corresponding to the main exothermic peak.

(2) The addition of pure Co_3O_4 lowers the thermal decomposition of AP by 96°C. On the other hand, the addition of pure CuO to AP lowers the main decomposition temperature by 151°C and decomposition starts just after the phase transition. CuO is obviously a more effective catalyst than Co_3O_4 for promotion of the decomposition of AP.

(3) The addition of CuO into Co_3O_4, with $x = 0.1$ and 0.3, increases the decomposition of AP at a lower temperature; decomposition occurs more quickly and with sharp exothermic peaks observed immediately after the phase transition at 264 and 267°C, respectively.

(4) Increasing the content of CuO up to $x = 2.5$ decreases the enhancement effect, with the maximum decomposition temperature in the range 280–300°C.

(5) When Co_3O_4 is added to CuO ($x = 2.7$ and 2.9), the enhancement effect observed for pure CuO is diminished.

It is convenient to classify the results obtained into three regions according to the behaviour, and to the content of both oxides. The first region in which the catalysts are more active is Co_3O_4 containing CuO, with $x = 0.1$ and 0.3. The catalysts in this region do not have the spinel structure as we previously reported [10]. The observed increase in catalytic activity results from the dissolution of Cu^{2+} ions in the cobaltic oxide lattice. This dissolution may occur in cationic vacancies in interstitial positions or by substitution for cobalt ions of the Co_3O_4 lattice. The location of Cu^{2+} in cationic vacancies or in interstitial positions in cobalt oxide should be accompanied by a decrease in the concentration of trivalent cobalt ions according to:

$$CuO + Co^{3+} \longrightarrow Cu|Co|' + Co^{2+} + \tfrac{1}{2}O_2$$

where Cu|Co|′ is copper ions located in cationic vacancies or in interstitial positions in non-stoichiometric Co_3O_4. Co^{3+} ions are the charge carriers in a non-stoichiometric p-type Co_3O_4 solid [12, 13]. The dissolution of Cu^{2+} is accompanied by loss of excess O_2 of Co_3O_4, followed by subsequent transformation of Co^{3+} into Co^{2+} ions. In other words, the creation of Co^{2+} ions by Cu^{2+} dopant ions should increase the p-type character of Co_3O_4.

However, it was also proposed [14] that the rate-controlling step in thermal decomposition of AP is the transfer of an electron from the perchlorate ion to the positive hole in p-type semiconducting additives [14–16]. Therefore, the annihilation of positive holes in the valence band of Co_3O_3, which are the effective sites for accepting the electrons released from the perchlorate ions, enhances the thermal decomposition of AP. Thus, the decomposition of AP can proceed via the following equation,

$$|e|^{\cdot} + ClO_4^- \longrightarrow O_{oxide} + ClO_3^{\cdot} \longrightarrow \tfrac{1}{2}O_2 + ClO_3^- + e$$

where $|e|^{\cdot}$ represents a positive hole in the valence band of Co_3O_4 and O_{oxide} is an oxygen abstracted by the oxide.

The second region of interest is copper oxide containing a low content of Co_3O_4, i.e., $x = 2.9$ or 2.7. The results show an observable decrease in the activity. The maximum decomposition temperature of AP (given in Table 1) increases from 263°C in case of pure CuO to 316–314°C in case of $x = 2.9$ or 2.7. It was reported [17] that the role of copper oxide catalyst could be interpreted in terms of establishing the Cu^{2+}/Cu^{+} redox cycle, which will work to promote the decomposition of AP. This behaviour may be attributed to the decrease of the acceptor sites via the consumption of holes within the p-type semiconductor [2] CuO according to the following equation.

$$Co_3O_4 + \tfrac{3}{2}|e|^{\cdot} \longrightarrow 3Co|Cu|^{\cdot} + 3CuO + \tfrac{3}{2}O_2$$

Where $Co|Cu|^{\cdot}$ represents a Co^{3+} ion replacing the Cu^{2+} ion in its normal lattice position and $|e|^{\cdot}$ is a positive hole. Consequently, the increase or decrease in the number

of holes in the solid catalysts parallels the order of their observed catalytic activities towards the decomposition of AP.

The third region consists of Co_3O_4 containing CuO in the range $0.5 \leq x \leq 2.5$, and which is accompanied by the formation of copper cobaltite spinel [10] $Cu_xCo_{3-x}O_4$. The activities of these catalysts are intermediate between the two other regions. The conclusion is that the formation of the spinel structure does not result in superior catalysts for the decomposition of AP.

To understand better the active sites established on the catalyst surfaces under investigation, the catalytic activities of these catalysts were also tested for the decomposition of H_2O_2. Fig. 2 shows that the relationship between $\log(V_x)/(V_x - V_t)$ and time, t, is first order for the decomposition of H_2O_2 in presence of all catalysts in the range $0 \leq x \leq 3$. The calculated rate constants are given in Table 2.

The data in Table 2 shows that the catalytic decomposition of H_2O_2 increases on addition of CuO into Co_3O_4, and reaches a maximum at $x = 1.5$. It then decreases up to $x = 3$. Moreover, the cobalt-rich region has higher activity than that of the CuO-rich region. Furthermore, the catalytic activity of pure CuO ($x = 3$) has a minimum value compared with the other prepared catalysts.

It is of interest to note that the order of activity of these catalysts towards the decomposition of H_2O_2 is not the same as observed for the decomposition of AP. However, as we reported recently [10], the decomposition reaction of H_2O_2 in the presence of CuO–Co_3O_4 mixtures depends on the establishment of active redox sites such as Co^{3+}/Co^{2+}, Cu^{2+}/Cu^{+} and Co^{3+}/Cu^{+}, of which Co^{3+}/Co^{2+} is the most active. Thus, the high activity of the samples associated with the formation of $Cu_xCo_{3-x}O_4$ spinel for the decomposition of H_2O_2 is the result of electron exchange between the octahedral and tetrahedral sites. The decrease in the activity of the samples containing $x > 1.5$ is explained on the basis of the hindrance of electron exchange within the octahedral sites [18, 19]. Therefore, our results on the decomposition of H_2O_2 are consistent with the decomposition reaction depending on electron exchange between donor and acceptor centres in the solid catalyst.

The catalytic activity of the mixed oxide system. MnO_2–CuO, in the thermal decomposition of $KClO_4$ and the decomposition of H_2O_2 has been reported [17]. The results obtained indicated that the activity–composition relationships were the same for both reactions. However, our results show that the presence of holes in pure oxides or the creation of more holes within CuO–Co_3O_4 oxide catalysts as a result of doping plays a main role in determining the decompositions pattern of AP. In contrast, for copper cobaltite spinel, $Cu_xCo_{3-x}O_4$, catalysts the electron exchange between active redox sites such as Co^{3+}/Co^{2+}, Cu^{2+}/Cu^{+} and Co^{3+}/Cu^{+}, and the perchlorate ion is

Table 2
Variation of the reaction rate constants (K/s^{-1}) for the catalytic decomposition of H_2O_2 as a function of catalyst composition

Catalyst x value	0	0.1	0.3	0.5	1	1.5	2	2.5	2.7	2.9	3.0
$K \times 10^3/s^{-1}$	10.1	11.2	11.9	12.3	13.6	19.0	16.5	8.2	3.3	1.8	3.3

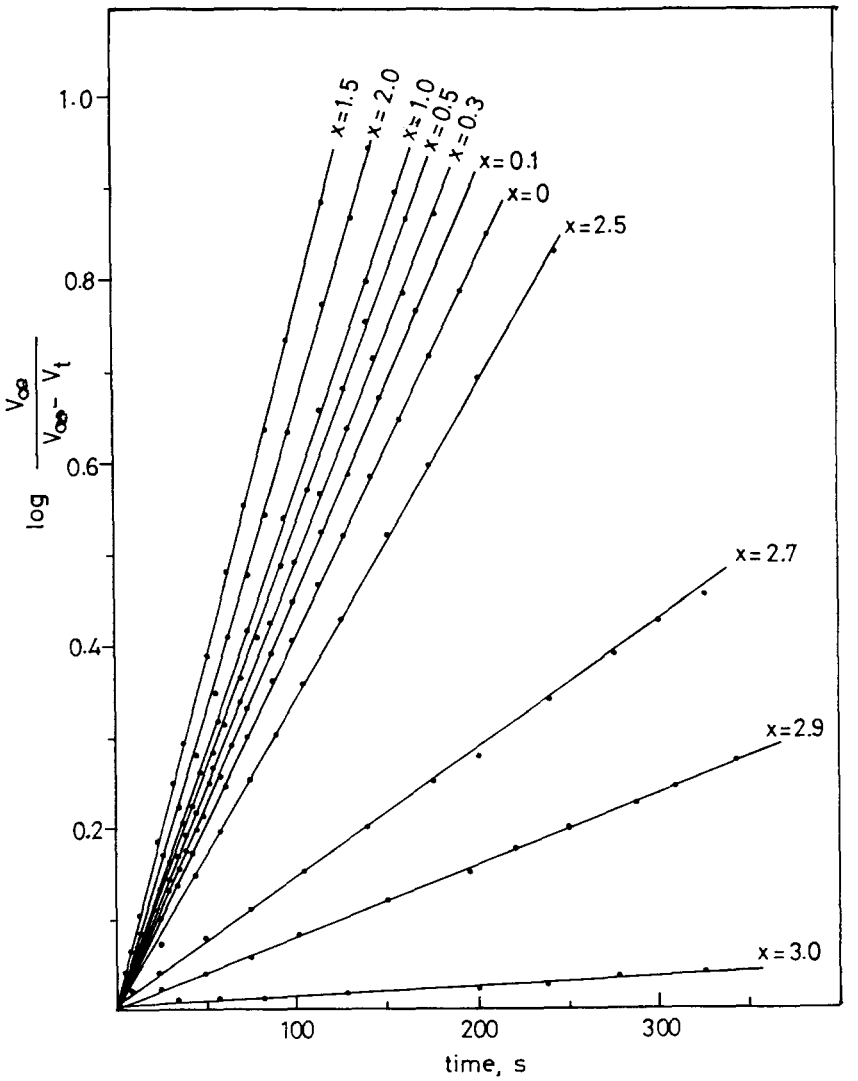

Fig. 2. Variation of log $(V_x)/(V_x - V_t)$ versus time for the decomposition of H_2O_2 by $Cu_xCo_{3-x}O_4$.

not as effective as holes in accelerating the decomposition of AP. The situation is reversed for the decomposition of H_2O_2. The creation of holes inside the solid catalysts is less effective than the establishment of Co^{3+}/Co^{2+}, Cu^{2+}/Cu^{+} and Co^{3+}/Cu^{+} redox couples.

References

[1] P.W.M. Jacobs and H.M. Whitehead, Chem. Rev., 69 (1969) 55.
[2] F. Solymosi and E. Krix, J. Catal., 1 (1962) 468.

[3] E.S. Freeman, D.A. Anderson and J.J. Campisi, J. Phys. Chem. Ithaca, 64 (1960) 1727.
[4] A.K. Galwey, M.A. Mohamed and D.S. Cromie, React. Solids, 1 (1986) 235.
[5] A.K. Galwey, P.J. Herley and M.A. Mohamed, Thermochim. Acta, 132 (1982) 105.
[6] R.P. Rastogi, G. Singh, B.L. Dubey and C.S. Shukla, J. Catal., 65 (1980) 25.
[7] A.A. Said, J. Therm. Anal., 37 (1991) 959.
[8] A.A. Said, J. Mater. Sci. Lett., 11 (1992) 1093.
[9] A.A. Said, Fuel, 73 (1993) 143.
[10] A.A. Said and R. Al-Qasmi, Submitted for publication, 1995.
[11] J. Deren, J. Haber, A. Pogorecka and J. Burzyk, J. Catal., 2 (1963) 161.
[12] G.A. El-Shobaky, I.F. Hewaidy and M.M. Ghoneim, Thermochim. Acta, 53 (1982) 105.
[13] P. Kostad, Non-Stoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides, Wiley-Interscience, New York, 1972, p. 426.
[14] E.S. Freeman and D.A. Anderson, Nature, (London) 206 (1965) 378.
[15] A.A. Said, E.A. Hassan and K.M. Abd El-Salaam, Surf. Technol., 20 (1983) 131.
[16] E.A. Hassan, A.A. Said and K.M. Abd El-Salaam, Surf. Technol., 21 (1984) 117.
[17] A.M. El-Awad, A.A. Said and K.M. Abd-El-Salaam, Thermochim. Acta, 126 (1988) 17.
[18] A.I. Onuchukwa, J. Chem. Soc. Faraday Trans. 1., 80 (1984) 1447.
[19] J.R. Goldstein and A.C.C. Tseung, J. Mater. Sci., 7 (1982) 1382; 76 (1992) 3646.