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THE ROLE OF COPPER-CHROMIUM OXIDE CATALYSTS IN THE THERMAL DECOMPOSITION OF AMMONIUM PERCHLORATE

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The catalytic effects of doped or mixed $CuO-Cr_2O_3$ oxides on the thermal decomposition of ammonium perchlorate (AP) were investigated by using DTA, electrical conductivity and X-ray diffraction techniques. The results obtained revealed that the decrease in the defect electron of CuO catalyst doped with 1 at.% Cr^{3+} inhibited its activity, while the opposite effect was observed when Cr_2O_3 was doped with 1 at.% Cu^{2+}. On increase of the concentrations of both oxides, the catalyst containing 70 at.% Cr^{3+} was found to be the most active during the decomposition of AP. The existence of $CuCr_2O_4$ at this ratio was demonstrated by X-ray diffraction. The activity of this spinel was explained on the basis of a hopping mechanism between Cr^{3+}/Cr^{4+} active sites. Finally, the activation energies of different decomposition stages of AP alone and mixed with catalysts were calculated.

The thermal decomposition of ammonium perchlorate (AP) in the presence of metal oxide additives has been intensively investigated [1–8]. Rudloff and Freeman [9] stated that *p*–type semiconducting oxides exerted a marked effect on the decomposition of perchlorates. Freeman and Anderson [10] proposed that the rate-controlling mechanism is the transfer of an electron from the perchlorate ion to a positive hole in *p*–type oxides. The results have indicated that CuO and Cr_2O_3 are the most active catalysts in the thermolysis of perchlorates [5, 11–15]. Moreover, it was elucidated that copper chromite catalyst decreases the decomposition temperature of AP [1, 16–19]. For this spinel, the additive efficiency was found to depend on

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the distribution of the ions between the tetrahedral and octahedral positions in the spinel lattice. However, the influence of the CuO–Cr_2O_3 system in the whole range of compositions has received less attention.

The present paper reports a study of the role of the CuO–Cr_2O_3 system as a ctalyst of the thermolysis of AP. The techniques employed were DTA, electrical conductivity and X–ray diffraction patterns.

Experimental

1. Materials

Reagent grade chemicals of basic copper carbonate [$2CuCO_3 \cdot Cu(OH)_2$] and chromium nitrate [$Cr(NO_3)_3 \cdot 9H_2O$] were used. Pure CuO and Cr_2O_3 were prepared by the thermal decomposition of the corresponding salts in a muffle furnace at 773 K in air atmosphere for 4 h. The doped and mixed samples were prepared by the impregnation method. Calculated amounts of basic copper carbonate and chromium nitrate in the desired ratio were mixed carefully by continuous stirring in doubly distilled water at room temperature till the formation of homogeneous pastes. The products were evaporated to dryness over a water bath and were then dried in an oven at 373 K for 24 h. The catalysts were calcined at 773 K to the pure oxides. The atomic ratios of the mixed CuO-Cr_2O_3 system used in this study ranged from 0 to 99%. The anhydrous AP was ground in an agate mortar with the prepared catalysts in a 10% w/w ratio and stored.

2. Techniques

Differential thermal analysis (DTA) of pure AP and AP admixed with CuO, Cr_2O_3 or their mixtures was carried out with a Shimadzu computerized thermal analysis system (DT–40). This system includes the programs which process the data from the Shimadzu thermal analyser with the Chromatopac (C–R3A). The rate of heating was kept at 10 deg·min^{-1} under a static air atmosphere. An 8 mg sample of each solid mixture was employed in each experiment. Al_2O_3 calcined at 1473 K was applied as a reference material.

The electrical conductivity measurements on the solid catalysts calcined at 773 K for 4 h were carried out in an air atmosphere, using the method described previously [21].

X-ray investigation of the thermal products of basic copper carbonate, chromium nitrate and their mixtures calcined at 773 K for 4 h was performed with a Philips diffractometer (model PW 2103/00). The patterns were run by applying CuK radiation and a nickel filter at a scanning speed of 2° in 20 min^{-1} The results were matched with ASTM cards [22].

Results and discussion

DTA curves of the decomposition of AP and of AP catalyzed by the CuO–Cr_2O_3 system are presented in Fig. 1, and the maximum decomposition temperatures of the different stages are shown in Table 1.

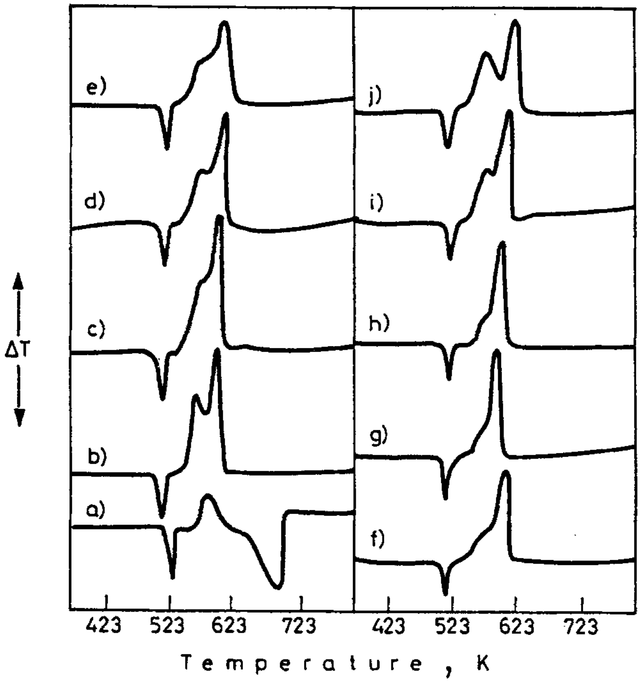

Fig. 1 DTA curves of NH_4ClO_4 (*a*) and of NH_4ClO_4 catalysed with CuO–Cr_2O_3 mixed oxide systems, pure CuO (*b*), 1 at.% Cr^{3+} (*c*), 10 at.% Cr^{3+} (*g*), 90 at.% Cr^{3+} (*h*), 99 at.% Cr^{3+} (*i*) and pure Cr_2O_3 (*j*)

Curve (*a*) for pure AP is characterized by two endothermic peaks and one exothermic peak. The first, endothermic peak, maximized at 517 K, denotes a reversible crystallographic transition from the orthorhombic to the cubic form. The second, exothermic peak, located at 580 K, corresponds to the step-like weight loss region in which perchlorate ion (ClO_4^-) dissociates to chlorate ion (ClO_3^-) and oxygen. The third, main, endothermic peak, maximized at 687 K, corresponds to the complete decomposition [5]. Curve (*b*) shows a remarkable enhancement in the thermal decomposition of AP in the presence of CuO catalyst. On the other hand, curves (*c*) and (*d*) indicate that the enhancement effect decreases when the CuO contains 1 and 10 at.% Cr^{3+}, respectively. On increase of the content of Cr^{3+} ions in the CuO lattice, a further increase in its activity is noted, reaching a maximum at 70 at.% (curves (*e*), (*f*) and (*g*).

Table 1 The maximum decomposition temperatures T_{max} and the corresponding activation energy of each stage for the decomposition of pure AP and AP catalyzed by the CuO–Cr_2O_3 system.

Catalyst	First stage		Second stage		Third stage	
	T_{max}, K	ΔE kJ·mol^{-1}	T_{max}, K	ΔE kJ·mol^{-1}	T_{max} K	ΔE kJ·mol^{-1}
NH_3ClO_4	517	–9.6	580	19.01	687	–75.01
CuO	518	–8.0	578	14.45	618	31.40
CuO + 1% Cr^{3+}	517	–8.1	588	11.22	627	38.1
CuO + 10% Cr^{3+}	517	–8.5	584	9.89	532	25.6
CuO + 30% Cr^{3+}	517	–8.6	582	7.64	616	32.24
CuO + 50% Cr^{3+}	520	–7.8	–	–	614	64.7
CuO + 70% Cr^{3+}	519	–8.70	–	–	609	57.9
CuO + 90% Cr^{3+}	520	–8.1	–	–	615	55.2
CuO + 99% Cr^{3+}	516	–8.8	301	9.4	620	44.2
Cr_2O_3	520	–8.3	311	18.2	638	27.6

On the other hand, curve (*j*) indicates that the presence of Cr_2O_3 catalyst enhances the decomposition of AP, but less markedly as compared with CuO. The incorporation of Cu^{2+} ions into the Cr_2O_3 lattice enhances its activity, as shown in curves (*f*)–(*i*). Moreover, it is observed that the third, endothermic peak accompanying the thermal decomposition of AP without (curve (*a*)) changes to an exothermic peak in the presence of all catalysts, while the second, exothermic peak becomes less pronounced in the presence of the catalysts at 50-90 at.% Cr^{3+}.

In order to interpret these findings, two factors must be considered. The first is the mechanism by which AP decomposes, and the second is the role of the active sites of the added catalyst. A series of consecutive reactions has been proposed to explain the thermal decomposition of perchlorates [9, 10, 14]. In the presence of *p*–type semiconductors, the following mechanism has been suggested [10] for both the electron transfer between oxides and perchlorate ion and the abstraction of atomic oxygen from perchlorate ion by oxides:

$$\underset{\text{I}}{|\dot{e}|_{\text{oxide}} + ClO_4^-} \rightarrow \underset{\text{II}}{O_{\text{oxide}} + ClO_3^-} \rightarrow \frac{1}{2}O_2 + \underset{\text{III}}{ClO_3^-} + e \tag{1}$$

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

It can be seen from Fig. 1, curve (*b*) and Table 1 that CuO decreases the main decomposition stage of AP by 69 deg. This result could be attributed to the presence of Cu^+/Cu^{2+} active sites [23]. It was observed [24] that almost all good catalysts have sites available at the surface, associated with single valence changes of the cation, often considered highly active both as adsorption sites and in electron exchange. Hence, the establishment of the Cu^+/Cu^{2+} redox cycle will work in the direction of promoting the decomposition of AP. On doping of the CuO with 1 at.% Cr^{3+} ions, curve (*c*) and Table 1 show a decrease in its activity. This behaviour may be attributed to the decrease in the acceptor sites via the consumption of holes during the annealing of the doped sample. The following doping mechanism may explain this point:

$$Cr_2O_3 + |\dot{e}| \rightarrow 2Cr|Cu^{\cdot}| + 2CuO + \frac{1}{2}O_2 \tag{2}$$

where $Cr|Cu^{\cdot}|$ represents a Cr^{3+} ion replacing the Cu^{2+} ion in its normal site position and $|\dot{e}|$ is a defect electron. It has been found that the electrical conductivity of CuO is increased when Cr_2O_3 is incorporated [25]. These results were attributed to the increase in the electron concentration. In the present study, a noticeable decrease in the conductivity of CuO doped with 1 at.% Cr^{3+} was observed. The electrical conductance values of catalysts calcined at 773 K are shown in Table 2.

The decrease in the electrical conductivity can be attributed to a decrease in the charge carriers, as mentioned above.

The enhancement role of pure Cr_2O_3 catalyst was detected from the lowering of the decomposition temperature of AP (third stage) by 49 deg (curve (*j*)) as a result of its non-stoichiometry [26]. Cr_2O_3 calcined at 773 K can chemisorb oxygen, producing a defect structure, such as cationic vacancies and holes [27], according to the following mechanism:

$$\frac{3}{4}O_2 \rightarrow V|Cr^{'''}| + \frac{1}{2}Cr_2O_3 + 3|\dot{e}| \qquad (3)$$

where $V|Cr^{'''}|$ is a cationic vacancy and $|\dot{e}|$ is a hole. On the creation of holes [26], i.e. Cr^{6+} ions, the catalyst surface undergoes an oxidation-reduction cycle $Cr^{3+} \rightarrow Cr^{6+} \rightarrow Cr^{3+}$. Therefore, these sites should accept the electrons released from perchlorate ions and consequently enhance the decomposition process. The doping of Cr_2O_3 with 1 at.% Cu^{2+} ions results in an improvement in its activity, as illustrated in curve (*i*). The influence of doping on the surface electronic state of the host Cr_2O_3 catalyst (*p*–type) semiconductor is controlled primarily by the mode and mechanism of incorporation of foreign ions [28]. This influence should affect the concentration of positive holes in the valence band. Therefore, in the presence of CuO as a dopant, the holes can be created according to the following mechanism:

$$O_2 + CuO \rightarrow Cu|Cr^{'}| + Cr_2O_3 + 2|\dot{e}| \qquad (4)$$

where $Cu|Cr^{'}|$ represents a Cu^{2+} ion replacing the Cr^{3+} ion in its normal lattice position and $|\dot{e}|$ is a hole. The defect electron produced in Eq. (4) should push the thermolysis of AP forward. It is worthy of mention that the doping of Cr_2O_3 with 1 at.% Cu^{2+} increases the concentration of charge carriers, which is associated with a noticeable increase in its electrical conductance, as shown in Table 2.

Table 2 Variation of σ values with the catalyst composition (the values of σ were measured in the steady state at 573 K in the presence of air atmosphere)

Catalyst	CuO	1 at.% Cr^{3+}	50 at.% Cr^{3+}	70 at.% Cr^{3+}	99 at.% Cr^{3+}	Cr_2O_3
σ, $ohm^{-1}\cdot cm^{-1}\cdot 10^{-3}$	15.8	3.3	1.5	2.6	12.9	3.1

The effects of mixed oxide catalysts on the decomposition of AP are presented in Fig. 1. The data relating to curves (*d*), (*e*), (*f*), (*g*)) and (*h*) and T_{max} for the different stages are given in Table 1. It appears that the most active catalysts are the samples in the range 50–70 at.% Cu^{3+}. These results can be explained on the basis of the formation of a new phase, i.e. copper chromite spinel. The existence of this spinel was demonstrated via the X-ray diffraction patterns.

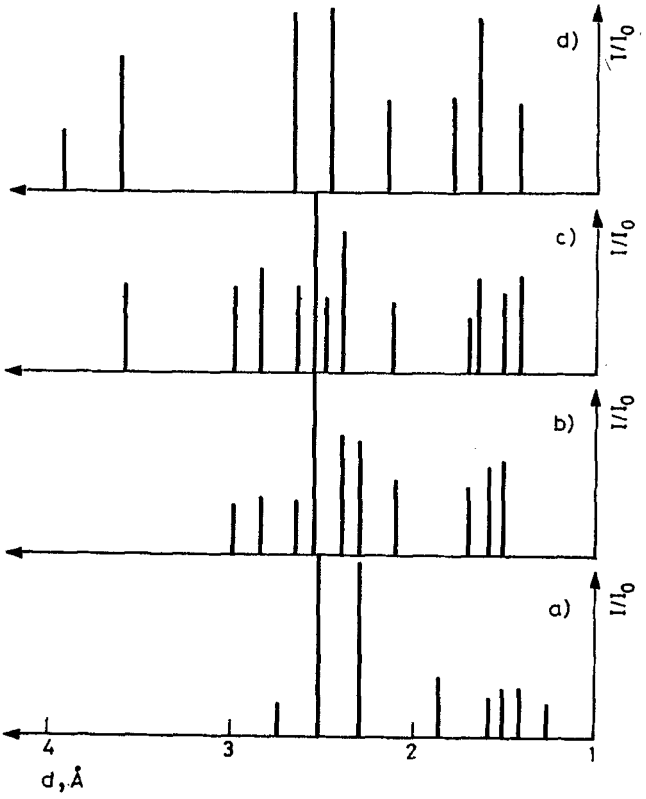

Fig. 2 X-ray diffraction patterns of pure CuO and mixed with Cr_2O_3 calcinated at 773 for 4 h, (*a*) pure CuO, (*b*) 30 at.% Cr^{3+}, (*c*) 50 at.% Cr^{3+} and (*d*) pure Cr_2O_3

Figure 2 presents the X-ray diffraction patterns of CuO–Cr_2O_3 mixed catalysts calcined at 773 K. Parts (*a*) and (*d*) depict the diffraction lines of CuO and Cr_2O_3 calcined at 773 K, respectively. A comparison of the diffraction lines of the pure and mixed oxides (parts (*b*) and (*c*)) showed that new lines were detected at 50 at.% Cr^{3+}, the crystallinity of which reaches a maximum at 70 at.% Cr^{3+}. The I/I_0 values and *d*-spacings of these lines were calculated and found to be I/I_0 = 47.1, 57.7, 46.2, 100 and 77.5 and d = 3.00, 2.86, 2.65, 2.56 and 2.40, respectively. These lines correspond to the copper chromite phase [29]. From the electrical conductivity measurements, the conductance values of the samples with 50–70 at.% Cr^{3+} were found to be lower than those of the pure and doped oxides as given in Table 2. This indicates that the formation of $CuCr_2O_4$ was accompanied by the reduction process [30] $Cr^{6+} \rightarrow Cr^{3+}$, i.e. the number of acceptor sites decreased. However, the role of copper chromite catalyst in the course of AP decomposition may depend on a new site responsible for such activity. Recently, an important study concluded that $CuCr_2O_4$ is a p-type semiconductor [31] and its conduction is due to charge hopping between the Cr^{3+} and Cr^{4+} ions. Thus, the catalytic activity [32] of the catalyst containing 70 at.% Cr^{3+} can be attributed to the presence of Jahn-Teller active sites Cr^{3+}/Cr^{4+}.

It is of interest to note here that the spinel, which behaves as a p–type semiconductor, can be considered a good catalyst in the course of the decomposition of AP.

The calculated activation energies of the different decomposition stages of AP and of AP catalysed by the $CuO–Cr_2O_3$ system are shown in Table 1. From such data, it can be concluded that: (i) All the decomposition stages of AP are influenced by the presence of the catalysts. This means that the role of the catalysts in the decomposition processes concerns both the lattice (first stage) and electronic (second and third stages) parameters of AP. (ii) Marked decreases in the activation energies were observed in the second and third stages. It was also observed that the third step was completely altered, from an endo- to an exothermic process, and the released energy was found to depend on the catalyst activity. This can be interpreted as being due to the promotion of breakdown of the Cl–O bond [33]. The decrease in the activation energy in the presence of additives via rupture of a Cl–O bond plays a decisive role in the decomposition of AP.

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Zusammenfassung — Mittels DTA, Röntgendiffraktion und elektrischer Leitfähigkeit wurden die katalytischen Wirkungen von versetzten oder gemischten CuO-Cr_2O_3 Oxiden auf die thermische Zersetzung von Ammoniumperchlorat (AP) untersucht. Die erhaltenen Ergebnisse zeigen, daß die Abnahme an Defektelektronen von CuO-Katalysator, versetzt mit 1 mol% Cr^{3+}, seine Aktivität vermindern, während ein entgegengesetzter Effekt bei Cr_2O_3 beobachtet wird, das mit 1 mol% Cu^{2+} versetzt ist.

Durch Erhöhung der Konzentrationen beider Oxide zeigt der Katalysator bei der Zersetzung von AP die größte Aktivität bei einem Cr^{3+}-Gehalt von 70 mol%. Mittels Röntgendiffraktion konnte bei dieser Zusammensetzung die Existenz von $CuCr_2O_4$ gezeigt werden. Die Aktivität dieser Spinellstruktur wurde durch einen Hüpfmechanismus zwischen Cr^{3+}/Cr^{4+}-aktiven Stellen erklärt. Weiterhin wurden die Aktivierungsenergien von verschiedenen Zersetzungsstufen von AP mit und ohne Katalysatoren berechnet.