

EFFECTS OF VARIOUS ATMOSPHERES AND SOME METAL OXIDE ADDITIVES ON THE THERMAL DECOMPOSITION ON AMMONIUM CHROMATE

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(Received March 22, 1993; in revised form December 14, 1993)

Abstract

The thermal decomposition of ammonium chromate (AC) in dynamic air, CO₂ and N₂ and in static atmospheres and in the presence of MoO₃, V₂O₅, Fe₂O₃, CuO, MnO₂ and Nd₂O₃ additives was studied by means of TG, DTA, IR spectroscopy and electrical conductivity measurements. It was found that AC decomposes in four stages, forming unstable intermediates which produce Cr₂O₃ as a final product. The presence of the different atmospheres and the oxide additives affected the decompositions of these intermediates and the oxidation state of the chromium ions. Finally, the mechanisms associated with the different decomposition stages are discussed.

Keywords: ammonium chromate

Introduction

It is well known that ammonium chromate, (NH₄)₂CrO₄, (AC) decomposes to ammonium dichromate (ADC) (NH₄)₂Cr₂O₇, and eventually to Cr₂O₃, the most stable oxide of chromium at higher temperatures, through a series of intermediates. Extensive studies [1–7] have been carried out on the thermal decomposition of ADC to Cr₂O₃ and a few of these studies [3–5] also included the decomposition of AC as a precursor to the decomposition of ADC. On the other hand, chromium oxide is known as a powerful redox catalyst [8, 9]. Many investigations [10–12] have shown that the adsorptive and catalytic properties of chromium oxide are controlled primarily by both the nature and concentration of surface Cr–O species. Since catalysts were obtained via the thermal decomposition of relevant inactive precursors in most of these investigations, various correlations were plausibly set up between the surface properties of the products, the thermal pretreatment conditions imposed and the nature of the precursors. Thus, the presence of the atmosphere in contact with the solid during the thermal decomposition should exert a decisive influence on the redox species on

the surface of the catalyst produced. However, a literature survey indicates that little work has been done on the thermal decomposition of AC in different atmospheres and in the presence of metal oxide additives. Thus, the present work was devoted to a study of the influence of dynamic air, N₂ and CO₂ and static atmospheres and some metal oxide additives on the steps of thermal decomposition of AC. The techniques employed were TG, DTA, electrical conductivity measurements and IR spectroscopy.

Experimental

All the starting materials used in this study were Analar grade chemicals. The metal oxides were ground with AC (10% w/w) in an agate mortar for thermal decomposition experiments.

TG and DTA were carried out with a Shimadzu DT-40 computerized thermal analysis system. The rate of heating of the samples was kept at 10 deg·min⁻¹ and a sample of about 6 mg of each solid specimen was analysed in each case, using dried air, N₂ or CO₂ flowing at 40 ml min⁻¹ or static atmospheres. α -Alumina powder as standard material for DTA was applied as a reference. Peak integration and subsequent activation energy calculations were performed by using the Shimadzu partial area integration program.

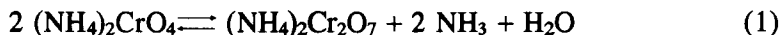
The electrical conductivity measurements were carried out by using a method discussed previously [13].

The IR spectra of the thermal products of pure AC in static atmospheres were recorded on KBr discs with a Pye Unicam SP 3–300 spectrophotometer.

Results and discussion

The TG–DTA curves of AC in static and dynamic air, N₂ and CO₂ atmospheres are shown in Fig. 1 (curves a, b, c and d, respectively). Table 1 lists the maximum temperature (T_m), activation energy (E) and weight loss (W) corresponding to each decomposition step. These curves show that AC decomposed in four stages in the various atmospheres. These results permitted the following conclusions:

(i) The maximum decomposition temperature for the first endothermic peak is little affected by the presence of different gases in contact with the solid. This step involves the decomposition of AC into ADC according to the following equation [5]:



This step was accompanied by mass losses of 16.9, 16.4, 15.6 and 14.9% in the presence of dynamic air, dynamic CO₂, static and dynamic N₂ atmospheres, respectively (Table 1). These values indicated the evolution of 2 molecules of ammonia and 1 molecule of water. In air and CO₂, the loss is in good agreement with the theoretical value (17%) while it is lower for the static and N₂ atmospheres. The IR spectra of AC and its decomposition products are shown in Fig. 2. The sample heated at 150°C for 3 h gave curve c, with a typical spectrum of ADC in curve b for comparison. On the other hand, the activation energies accompanying this step (Table 1) are lower in CO₂ and static atmospheres than in the other atmospheres.

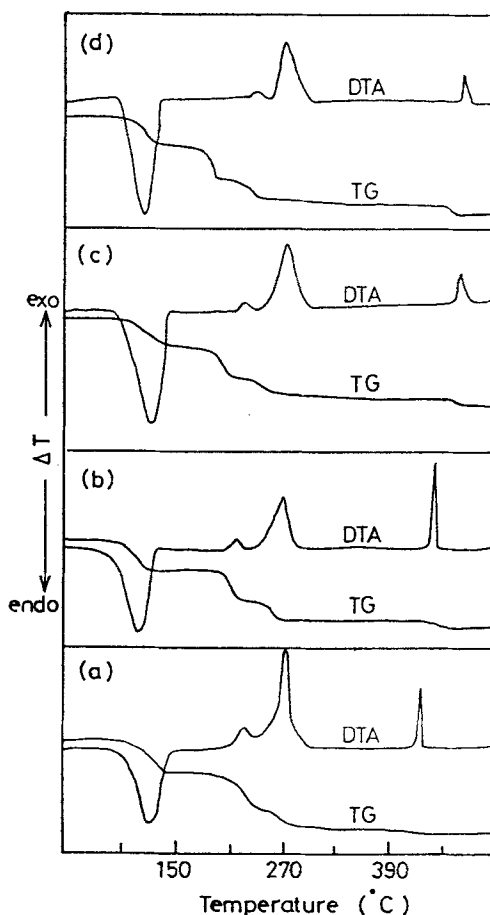
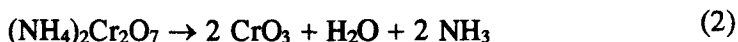


Fig. 1 TG-DTA curves of AC under different atmospheres, static (a), air (b), N₂ (c) and CO₂ (d)

Table 1 Thermal decomposition data of ammonium chromate (AC) in various atmospheres, the maximum decomposition temperature T_m , the activation energy E /kJ·mol⁻¹ and the weight loss at different decomposition stages W

Atmosphere	1st step			2nd step			3rd step			4th step			E_{total}
	T_m	E	W	T_m	E	W	T_m	E	W	T_m	E	W	
Static	124	94.3	15.6	228	7.1	18.6	273	57.9	8.7	429	8.3	2.3	167.6
Air	122	99.6	16.9	222	4.3	15.7	269	36.4	10.9	434	5.6	4.8	145.9
N ₂	121	100.1	14.9	217	2.1	14.6	268	36.1	9.0	472	9.3	2.2	147.6
CO ₂	123	92.9	16.4	219	2.5	18.0	265	30.0	12.3	477	11.3	2.7	136.7

(ii) The second, small exothermic peak that maximized at 217–228°C in the different gases corresponded to the decomposition of ADC into CrO₃ [14, 15]:



It may be noted in Table 1 that the mass loss accompanying this stage is lower in N₂ and air, whereas in CO₂ and the static atmosphere it is slightly lower than that anticipated theoretically (20.6%), as repeatedly reported for this step [14–16]. The IR spectrum of AC calcined at 240°C for 3 h (Fig. 2, curve d) indicates the major existence of a highly distorted Cr₂O₃-like structure, together with CrO₃ and surface species of NH₄⁺ absorption at 1400 cm⁻¹ and water [7] absorption at 1640 cm⁻¹. The energy of activation accompanying this step in the static air atmosphere is 7.1 kJ·mol⁻¹, but much lower in the other gases.

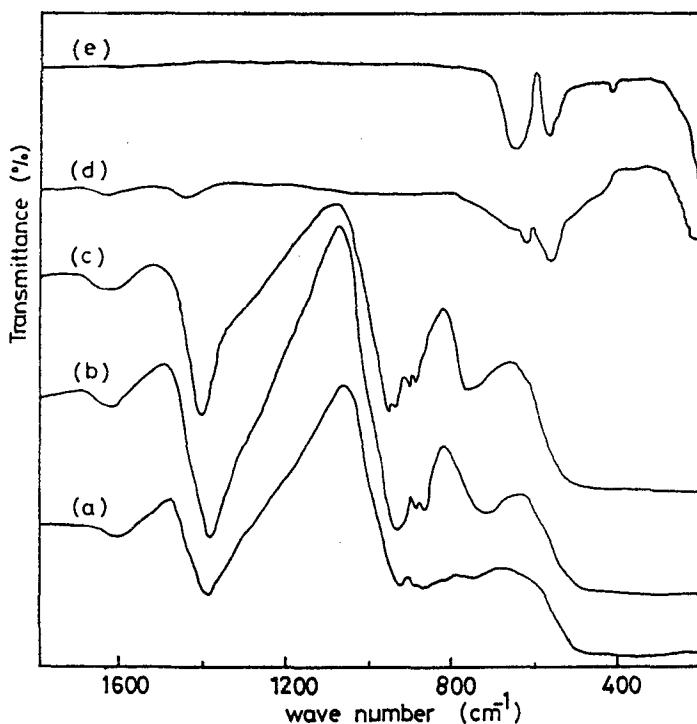


Fig. 2 IR spectra of AC (a), ADC (b) and AC calcined at 150°C (c), 240°C (d) and 500°C (e) for 3 h in static atmosphere

(iii) The third, strong and sharp exothermic peak that maximized at 273, 269, 268 and 265°C in the static and dynamic air, N₂ and CO₂ atmospheres, respectively, is attributed to the evolution of oxygen from the relatively unstable

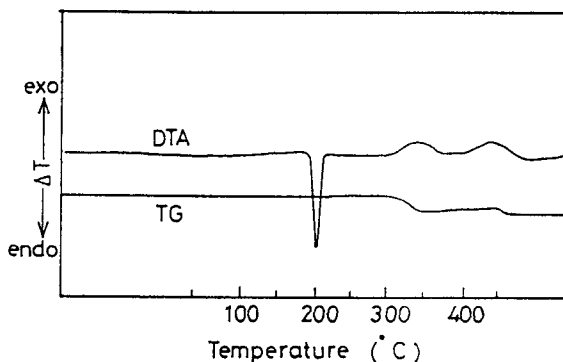


Fig. 3 TG-DTA curves of CrO_3 in static air atmosphere

CrO_3 [4]. The mass losses in Table 1 indicate that the amount of oxygen evolved may be dependent on the gas in contact with the solid surface. The thermal decomposition of CrO_3 in the static air atmosphere is presented in Fig. 3. The DTA curve shows that the decomposition proceeds in three peaks, maximized at 200, 340 and 434°C. The first sharp endothermic peak corresponds to the melting point of CrO_3 [7]. The second exothermic peak is due to the formation of chromium dichromate [17], $\text{Cr}_2(\text{Cr}_2\text{O}_7)_3$, i.e. the formation of a trace of CrO_2 with dominating CrO_3 . However, Park [14] has claimed the formation of a double compound of Cr^{3+} and Cr^{6+} oxides with the composition $\text{Cr}_5\text{O}_9 \sim \text{Cr}_2\text{O}_3 \cdot \text{CrO}_3$. In the present study, the mass loss accompanying this stage was 13.5%, as determined by TG, which suggests the formation of a compound of composition $\text{CrO}_{2.2}$, i.e. $[\text{Cr}_2(\text{CrO}_4)_3]$, and excludes the formation of Cr_5O_9 . The third exothermic peak accompanying a significant mass loss has been considered to correspond to the formation of Cr_2O_3 [17]. The mass losses associated with the third stage of the decomposition of AC in the different atmospheres (Table 1) demonstrate that the amount of CrO_2 formed from CrO_3 depends on the gas phase in contact with the solid. This stage can be suggested as the following equation,



The large difference between the mass loss accompanying this step and the theoretical value (18%) suggests that some of CrO_3 decomposed into CrO_2 , its amount depending on the type of the gas in contact with the decomposing solid. The notable thermal stability exhibited by this phase in the range above 300°C has been attributed to the establishment of strong electron spin interactions [19] between the Cr^{3+} , Cr^{4+} and Cr^{6+} involved through a mechanism similar to that described by Zener [19].

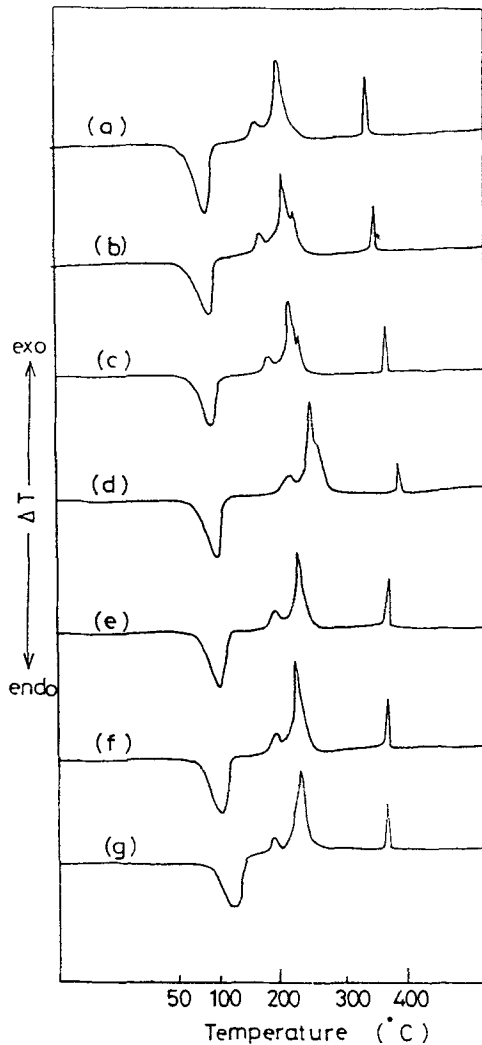
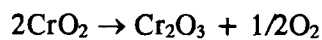


Fig. 4 DTA curves of thermal decomposition of pure AC (a) and mixed with 10% (w/w) MoO_3 (b), V_2O_5 (c), Fe_2O_3 (d), CuO (e), MnO_2 (f) and Nd_2O_3 (g) in static air atmosphere

(iv) The fourth exothermic peak, located at 429, 434, 472 and 477°C for AC in the static and dynamic air, N_2 and CO_2 atmospheres, respectively, corresponded to the reduction of CrO_2 formed from CrO_2 to Cr_2O_3 with the evolution of O_2 [3, 4]. This stage may proceed as follows:



The mass loss associated with this step in all the atmospheres is much lower than the theoretical value (9.5%). This indicates that the transformation of CrO_3 into CrO_2 is not stoichiometric, i.e. a trace of CrO_2 is formed, as discussed above. On the other hand, marked retardation of the fourth peak to higher temperature is observed in N_2 and CO_2 as compared with the static and air atmospheres. The IR spectrum of AC calcined at 500°C for 3 h is presented in Fig. 3, curve e. The bands at 630, 550 and 400 cm^{-1} provide clear evidence of the co-existence of a Cr_2O_3 -like structure [20].

Figure 4 shows the DTA curves of the thermal decomposition of AC mixed with 10% (w/w) MoO_3 , V_2O_5 , Fe_2O_3 , CuO , MnO_2 and Nd_2O_3 in the static atmosphere. These curves permit some trends and conclusions:

(i) These curves demonstrate the similar behaviour of the thermal decomposition of AC in the presence of Nd_2O_3 , MnO_2 and CuO (curves e-g) and of pure AC (curve a) except for slight effects on the maximum temperatures of the different steps.

(ii) The thermal decomposition of AC in the presence of MoO_3 , V_2O_5 and Fe_2O_3 (curves b-d) shows a new small peak associated with the third step, i.e. during the decomposition of CrO_3 . This new peak suggests that the presence of these oxides may enhance the reduction of some higher oxidation state of chromium into a lower one. It is known that Mo, V and Fe oxides exist in two oxidation states, i.e. $\text{Mo}^{5+}/\text{Mo}^{6+}$, $\text{V}^{4+}/\text{V}^{5+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$. The existence of the lower valency of these oxides should facilitate the electron exchange according to the following mechanism:



where M^{n+} is Mo^{5+} , V^{4+} or Fe^{2+} .

The significance of the new peak can be explained by using electrical conductivity measurements during the thermal decompositions in N_2 of pure AC and AC mixed with MoO_3 .

Figure 5a shows the variation of $\log \sigma$ with $1/T$ in the range $20\text{--}400^\circ\text{C}$ for pure AC in nitrogen. In the region AB, there is a continuous increase in the sample conductance with increasing temperature, reaching a maximum at about 192°C . This step corresponds to the decomposition of AC with the evolution of NH_3 and H_2O to give ADC, as obtained in the DTA. This maximum is followed by a decrease in the conductance, which falls to a minimum at 215°C (region BC). This process accompanies the decomposition of ADC and the formation of CrO_3 as intermediate, which has lower conductivity. On increase of the heating temperature, an increase in conductance is obtained in the region CD, reaching a maximum at 265°C . This process may explain the transformation of

some CrO_3 into CrO_2 , i.e. a mixed valence of chromium is obtained, which facilitates the electron hopping between Cr^{4+} and Cr^{6+} . In the region DE, in the range $265\text{--}282^\circ\text{C}$, a constant conductance is observed. Finally, in the region EF, at $> 282^\circ\text{C}$, there is a rapid increase in the conductance as the temperature increases. This stage is accompanied by the evolution of O_2 and the formation of Cr^{3+} . The formation of Cr^{3+} together with Cr^{4+} and Cr^{6+} may be responsible for such an increase.

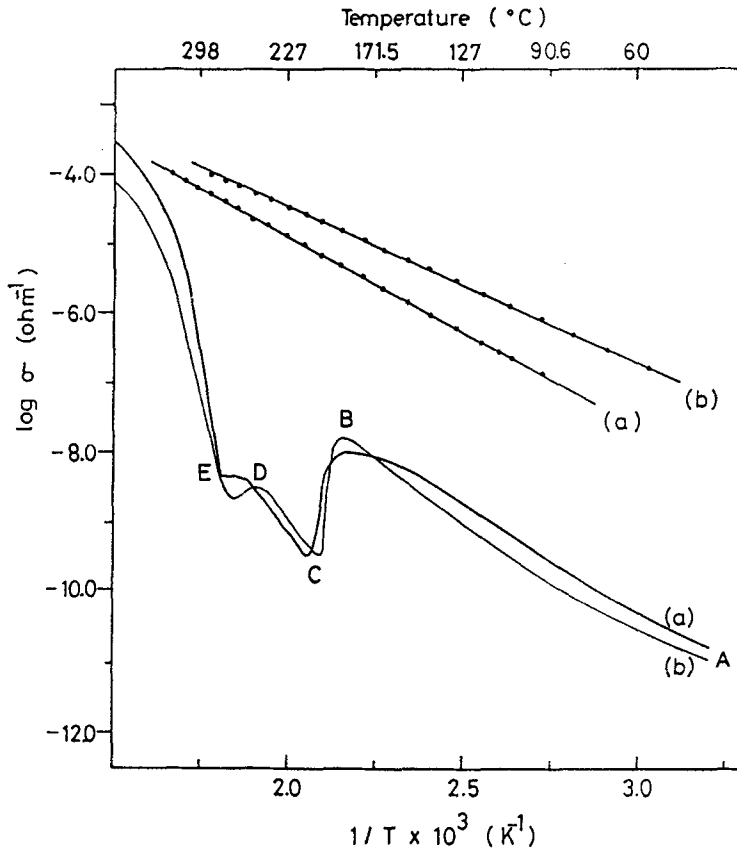


Fig. 5 Variation of $\log \sigma$ with $1/T$ of pure AC (a) and mixed with MoO_3 (b) under nitrogen gas

Figure 5b shows the variation of $\log \sigma$ with $1/T$ for the thermal decomposition of AC mixed with MoO_3 . This reveals the same behaviour of the decomposition steps but in the range $265\text{--}282^\circ\text{C}$ a small minimum is observed at 270°C . This latter may be attributed to the effect of Mo^{6+} on the valency of chromium oxides, which decreases the electrical conductivity of the solid by decreasing

the charge carrier, as suggested in Eq. (4). This result confirms the appearance of the small peak in the DTA curves of AC mixed with MoO_3 , V_2O_5 and Fe_2O_3 .

The activation energies of pure AC and that mixed with MoO_3 are obtained from the slope of the σ vs. T cooling curves (a and b), using the following relation:

$$\sigma = \sigma_0 \exp(-\Delta E/KT)$$

where σ is the conductance, σ_0 is a constant, ΔE is the activation energy of charge carriers, K is the Boltzmann constant and T is the absolute temperature. The results of these calculations are 2.31 and 1.88 eV for pure AC and AC mixed with MoO_3 , respectively.

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Zusammenfassung — Mittels TG, DTA, IR Spektroskopie und elektrischen Leitfähigkeitsmessungen wurde die thermische Zersetzung von Ammoniumchromat (AC) in Luft, CO_2 , N_2 und statischer Atmosphäre in Gegenwart von MoO_3 -, V_2O_5 -, Fe_2O_3 -, CuO -, MnO_2 - und Nd_2O_3 -Zusätzen untersucht. Daraus ergab sich eine AC-Zersetzung in vier Schritten, wobei instabile Zwischenprodukte gebildet werden, die letztlich zum Endprodukt Cr_2O_3 führen. Die Zersetzung und die Oxidationsstufe des Chromions werden durch die Art der Atmosphäre und die Oxidzusätze beeinflusst. Letztlich wurde der Mechanismus für die verschiedenen Zersetzungsstufen diskutiert.