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A THERMOANALYTICAL STUDY OF THE SOLID STATE REACTIONS IN THE Cr_2O_3–Na_2CO_3–O_2 SYSTEM

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ABSTRACT

The solid state reactions in the Cr_2O_3–Na_2CO_3 system under an oxygen atmosphere were investigated by means of thermoanalytical techniques. CrO_3 is formed during the initial stages of the reaction. The oxide is then converted to an intermediate species which is characterized by an exothermic reaction on the DSC between 310 and 420 °C and by two reversible endothermic changes at 495 °C and 570 °C respectively. The conversion of Cr_2O_3 to Na_2CrO_4 was incomplete even at 950 °C. The method of sample preparation influences the processes which take place.

INTRODUCTION

Although the preparation of sodium chromate by roasting chromite ore under oxidizing conditions with sodium carbonate is a long-established commercial process, very little is known of, or published on, the intermediate reactions and products which form in the chromite furnace.

More, however, is known of the various non-stoichiometric chromium suboxides which can be prepared from the thermal decomposition of CrO_3 [1–3], of how Na_2CO_3 reacts at elevated temperatures [4] and of the preparation of compounds with varying sodium–chromium–oxygen contents in vacuum and inert atmospheres [5,6].

In the present work, thermal studies were carried out in oxygen and inert atmospheres, and X-ray powder diffraction analysis, IR spectroscopy and ESCA measurements were used to describe the processes which take place in the Cr_2O_3–Na_2CO_3–O_2 system.

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EXPERIMENTAL

Sample preparation

Two different techniques were used. In method A, mixtures of Cr_2O_3 and Na_2CO_3 were prepared in 1 : 2, 1 : 4 and 1 : 8 molar ratios by stirring the required amounts in petroleum ether for 18 h. The mixtures were then vacuum dried and sieved to fall in the particle size range 125–250 μm. In method B, the Cr_2O_3 and Na_2CO_3 powders were separately sieved, then weighed and mixed to give 1 : 4 and 1 : 8 molar ratios and finally agitated on a shaker for 18 h. The Cr_2O_3 particle size range was kept constant between 125 and 250 μm while that of the Na_2CO_3 was varied. Particle sizes which are smaller than 125 μm, which fall in the range 125–250 μm and which are greater than 250 μm were used.

Thermal analysis

TG and DTA experiments were carried out on a Stanton Redcroft STA 780 simultaneous thermal analyser, while a Du Pont 910 DSC controlled by a 1090 thermal analyser was used for the DSC experiments.

A heating rate of 10 °C min^{-1} was employed in all experiments using dynamic oxygen and argon atmospheres (40 cm^3 min^{-1}). Sample sizes varied between 25 and 65 mg. Platinum sample and reference containers were used.

Isothermal experiments were carried out in the 450–515 °C temperature range in a dynamic oxygen atmosphere.

Surface area measurements

A Flowsorbed II 2300 instrument was used for surface area determinations using the B.E.T. method. For the X-ray powder diffraction analysis, samples of the different reaction products were analysed at room temperature on a Seifert MZ IV diffractometer using Cu $K\alpha$ radiation.

IR absorption analysis

IR spectra of samples were measured at room temperature on a Bruker IFS 113 V spectrophotometer from 500 to 4000 cm^{-1}, using the KBr technique.

ESCA measurements

Samples were analysed on a Physical Electronics spectrophotometer over the binding energy range 570–590 eV.

RESULTS AND DISCUSSION

The formation of Na_2CrO_4 from Cr_2O_3 in the presence of Na_2CO_3 and in an oxidizing atmosphere was found to be incomplete, even at 950 °C.

Dynamic studies

The method of sample preparation seems to influence the processes which take place in the system as can be seen from Figs. 1–3.

The TG curve of samples prepared according to method A, shows a continuous mass loss over the temperature range 300–950 °C. It seems as if a stable intermediate exists over the approximate temperature range 500–700 °C. The mass loss is accompanied by the evolution of CO_2 as indicated by the precipitation of $BaCO_3$ when the volatile gases were passed through a concentrated solution of $Ba(OH)_2$.

The DSC curves are characterized by an endotherm at about 100 °C owing to the dehydration of Na_2CO_3, an exotherm in the temperature range 320–420 °C and three endotherms at temperatures above 450 °C.

The 25–300 °C temperature range

It was found that the DSC curves of a mixture of CrO_3 and Na_2CO_3 (CrO_3: Na_2CO_3 molar ratio of 1 : 2) heated in oxygen or argon and that heated in oxygen are similar up to 600 °C (Figs. 4 and 5). It thus seems as if

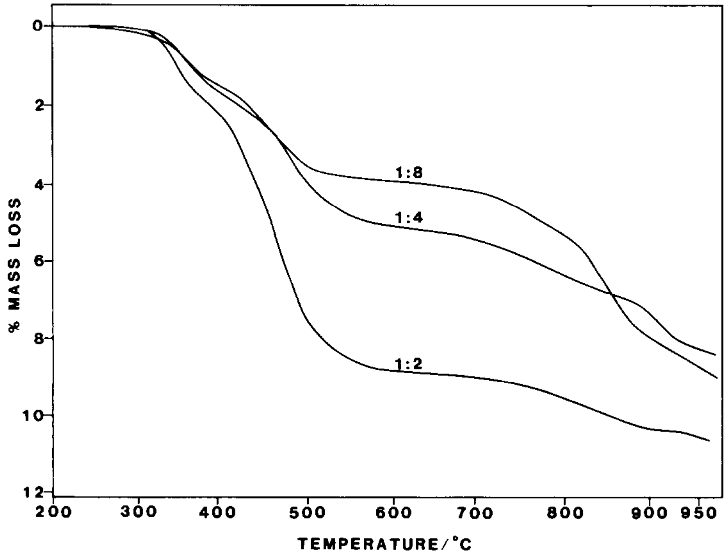

Fig. 1. TG curves for mixtures with different molar ratios of Cr_2O_3 to Na_2CO_3 (method A) in an oxygen atmosphere.

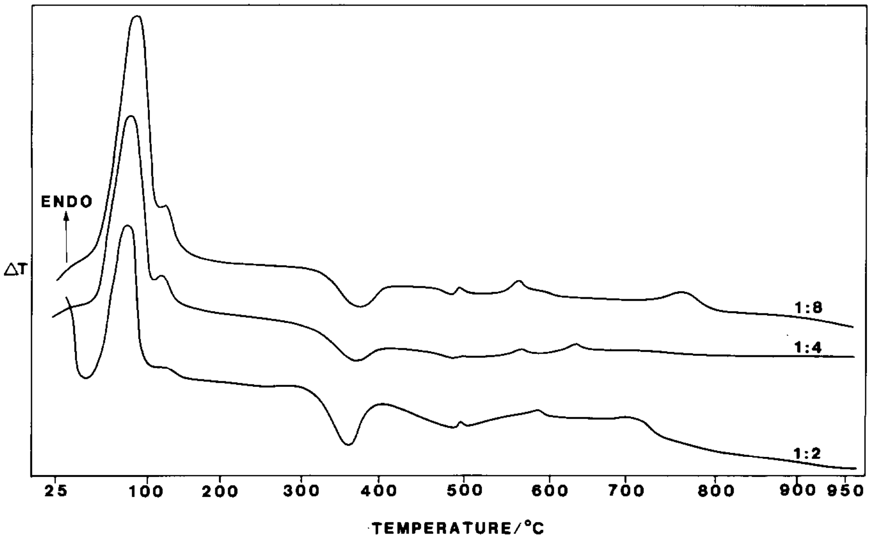

Fig. 2. DTA curves for mixtures with different molar ratios of Cr_2O_3 to Na_2CO_3 (method A) in an oxygen atmosphere.

CrO_3 forms during the initial stages of the reaction, i.e. between 25 and 300 ° C. This result was confirmed by an ESCA analysis of a sample taken at 310 ° C which showed a band with a peak maximum at a binding energy of 578.0 eV (c.f. 578.1 eV for pure CrO_3). Since neither the X-ray powder

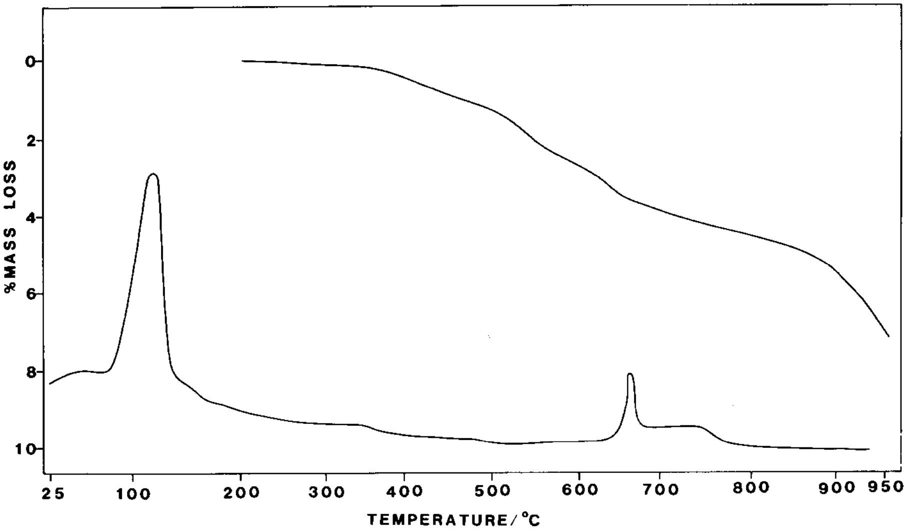

Fig. 3. TG and DTA curves for the mixture with a Cr_2O_3:Na_2CO_3 molar ratio of 1:4 (method B) in an oxygen atmosphere.

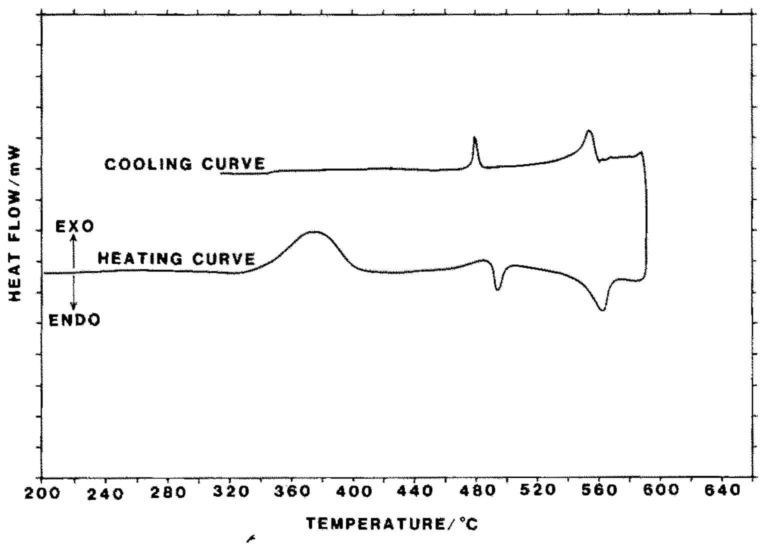

Fig. 4. DSC heating and cooling curves for the mixture with a $CrO_3:Na_2CO_3$ molar ratio of 1:2 (method A) in oxygen.

diffraction patterns nor the IR spectra revealed the presence of CrO_3 or any other high valence chromium oxide at temperatures in the 25–310 °C range, it is postulated that oxygen is adsorbed on the surface of the Cr_2O_3 which leads to the formation of islands of CrO_3 of poorly definable structure.

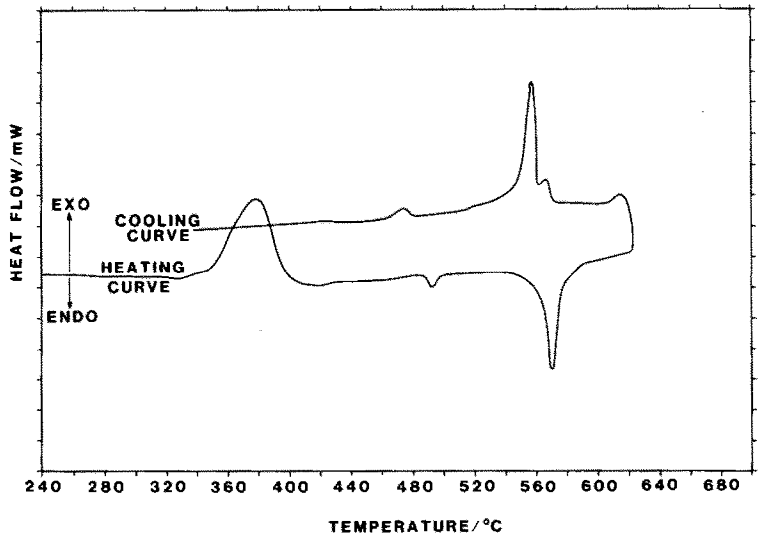

Fig. 5. DSC heating and cooling curves for the mixture with a $Cr_2O_3:Na_2CO_3$ molar ratio of 1:8 (method A) in oxygen.

The 300–400° C temperature range

The exothermic process observed in this temperature range was found to be influenced by the Na_2CO_3 content of the mixture. The peak maximum was found to shift towards higher temperatures and the enthalpy of the process increased with an increase in Na_2CO_3 content (Tables 1 and 2). Although the presence of oxygen during the initial stages of the reaction was essential in order to observe this exotherm, an increase in pressure did not have any effect on the enthalpy of the reaction.

It seems as if this process involves a reaction between the CrO_3 (formed below 300° C) and Na_2CO_3 in which a ternary oxide, consisting of sodium, chromium and oxygen forms on decomposition of the Na_2CO_3. ESCA analysis pointed to the presence of $NaCrO_2$ (peak maximum at 576.8 eV) while the X-ray powder diffraction patterns suggested the presence of a mixture of $NaCrO_2$ and Na_4CrO_4 in a sample taken at 420° C. IR analysis of the same sample showed absorption bands at ± 850, 880 and 909 cm^{-1} which suggested the presence of chromium in an oxidation state greater than $+3$ and species of the type CrO_4^{x-}, where $x = 2$, 3 and 4, as well as polymeric species [7,8].

The 440–600° C temperature range

The endothermic reactions occurring at about 494 and 564° C were found to be reversible (Fig. 5) in oxygen and argon atmospheres, provided the

TABLE 1

DSC peak positions for mixtures with different molar ratios of Cr_2O_3 to Na_2CO_3

Molar ratio $Cr_2O_3:Na_2CO_3$	Exotherm (° C)	Reversible endotherms (° C)		Melting endotherm (° C)
		1st	2nd	
1:2	360	494	568	760
1:4	369	494	564	640
1:8	375	494	563	760

TABLE 2

Enthalpies associated with the various changes

Molar ratio $Cr_2O_3:Na_2CO_3$	Exotherm ($J g^{-1} Cr_2O_3$)	Reversible changes ($J g^{-1} Cr_2O_3$)	
		1st (494° C)	2nd (546° C)
1:2	−113.8	2.9	– [a]
1:4	−129.2	7.2	30.7
1:8	−252.4	21.6	67.4

[a] No accurate baseline could be obtained for integration.

mixture is heated in oxygen to 410 °C. The cooling curve showed peaks at about 480 °C and 554 °C respectively and was not accompanied by further mass losses or gains, once the mixture was heated to 600 °C. The enthalpies associated with these processes in a 1 : 8 molar mixture, are listed in Table 3. The enthalpies were found to be favoured by an increase in Na_2CO_3 content (Table 2). Similar observations were made for a mixture consisting of CrO_3 and Na_2CO_3 (Fig. 4).

It seems therefore as if these reversible reactions can be associated with the intermediates which form at about 400 °C. X-ray powder and ESCA (broad band with maximum at 580.6 eV) analysis of a sample taken at 580 °C indicated the presence of a mixture consisting of Na_2CrO_4 and other ternary oxides. The X-ray powder diffractograms of a mixture of Cr_2O_3 and Na_2CO_3 (Cr_2O_3 : Na_2CO_3 molar ratio of 1 : 8) taken at 495 and 565 °C indicated the presence of Na_4CrO_4. It therefore seems as if an excess of Na_2CO_3 in the starting mixture benefits the formation of ternary oxides with Na : Cr ratios larger than 1 : 2.

The 600–950 °C temperature range

The endothermic peak in this temperature range can be assigned to the melting of Na_2CrO_4. It was found that the amount of Na_2CO_3 present in the mixture influenced the peak maximum (Table 1) but no direct correlation could be obtained.

The TG and DTA curves of the samples prepared according to method B were found to be different. The TG curve showed a continuous mass loss over the temperature range 300–950 °C. The DTA curve is marked only by an endotherm at 100 °C owing to dehydration of the Na_2CO_3, two weak endothermic changes at about 352 and 480 °C which can be attributed to polymorphic changes in Na_2CO_3 [4] and a melting endotherm at about 665 °C. These samples also showed a much smaller degree of sintering as compared with those prepared according to method A.

These observed differences in thermal behaviour of the differently prepared samples could perhaps be explained in terms of the greater specific area observed for the samples of method A. Although difficult to reproduce,

TABLE 3

Enthalpies for the reversible changes observed in a 1 : 8 molar ratio mixture

	Temperature (°C)	Enthalpy ($J g^{-1}$)
Heating curve	494	3.3
	563	10.3
Cooling curve	480	−4.3
	554	−12.2

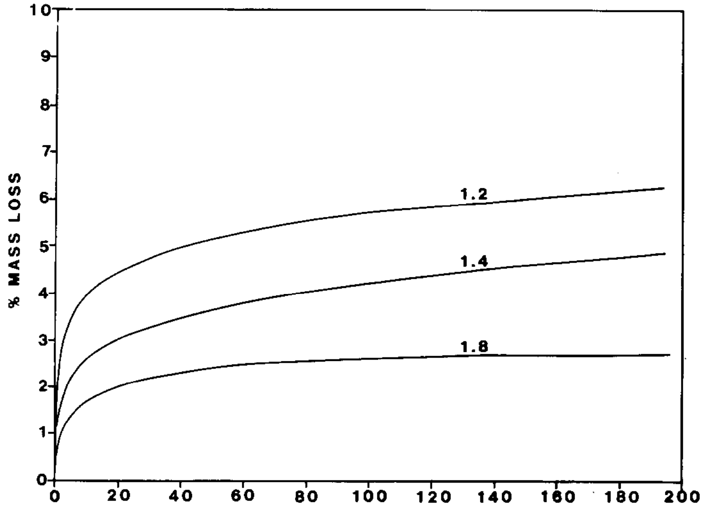

Fig. 6. Isothermal mass loss curves for the mixtures with different molar ratios of Cr_2O_3 to Na_2CO_3 in oxygen at 515 °C.

the specific area of these samples was throughout about 10 times greater than that of the samples of method B.

Isothermal studies

The isothermal decomposition of three different samples prepared according to method A is given in Fig. 6. It was found that the total mass loss

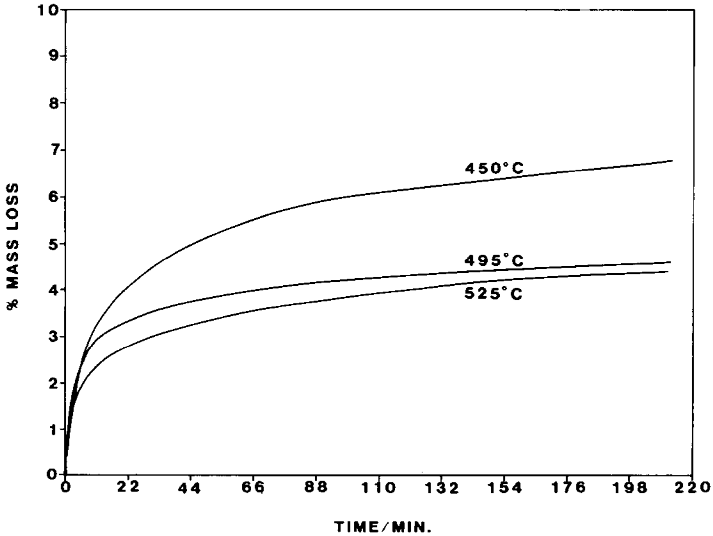

Fig. 7. Isothermal mass loss curves for the mixture with a $Cr_2O_3:Na_2CO_3$ molar ratio of 1:4 in oxygen.

observed was determined by the Na_2CO_3 content and the experimental temperature (Fig. 7). The fact that a greater mass loss was observed at lower temperature seems to suggest that the intermediates, which form during the course of the reaction, are unstable at higher temperatures, decompose at these temperatures and thus inhibit the reaction. This seems to be in agreement with the observation that conversion of the Cr_2O_3 is incomplete, even at 950 ° C.

These observations complicated a kinetic analysis of the reaction. However, it was found that the reaction of a specific sample at a specific temperature can be described in terms of a three-dimensional diffusion process. The Jander equation, $[1-(1-\alpha)^{1/3}]^2 = kt$, seems to describe the reaction in the temperature range 420–495 ° C, while the Ginstling–Brounshtein equation, $(1-2\alpha/3)-(1-\alpha)^{2/3} = kt$, described the reaction at temperatures above 505 ° C. It was noted that the linear plot did not pass through the origin. This is due to a rapid chemical reaction, promoted by oxygen during the initial stages of the reaction, after which the reaction is controlled by diffusion through a product layer [9].

CONCLUSIONS

The thermal oxidation of Cr_2O_3 in the presence of Na_2CO_3 to give Na_2CrO_4 passes through a number of intermediate species. Some of these species seem to be unstable at higher temperatures and decompose. This decomposition appears to inhibit the reaction with the result that the conversion of Cr_2O_3 is incomplete.

The method of sample preparation influences the thermal characteristics of the reaction.

The reaction seems to be diffusion controlled from a mechanistic viewpoint.

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