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A THERMOANALYTICAL STUDY OF THE SYNTHESIS AND OXIDATION OF $NaCrO_2$

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ABSTRACT

The formation of $NaCrO_2$ from Na_2O and Cr_2O_3 as well as the oxidation of the chromite by O_2 were studied by thermal analysis. TG, DTA and DSC were used to obtain quantitative results. The enthalpy of the formation reaction in the temperature range 240 °C to 490 °C was found to be -142.0 ± 3.8 kJ, in agreement with the calculated values. X-ray powder diffraction and ESCA analysis were used to identify and characterise materials.

INTRODUCTION

The chemical reaction for the production of Na_2CrO_4 by roasting chromite ore with Na_2CO_3 is considered to be

$$2Cr_2O_3 + 4Na_2CO_3 + 3O_2 \rightarrow 4Na_2CrO_4 + 4CO_2 \qquad (1)$$

It was pointed out that although this reaction seems to be thermodynamically favourable, $\Delta G^0_{298} = -369.53$ kJ mol^{-1}, the reaction was found to be incomplete in a thermobalance at 950 °C [1], Cr_2O_3 being present in the product mixture. It was also pointed out that various oxides, such as $NaCrO_2$, Na_3CrO_4 and Na_4CrO_4 were formed as intermediates during the oxidation reaction. These intermediates determine the reaction mechanism and it was therefore important to obtain more information regarding their physical and chemical properties.

Our previous work indicated that $NaCrO_2$ was an important intermediate in the reaction and since the preparation of the oxide is well documented [2], it was decided to continue the work by studying the thermal oxidation of $NaCrO_2$.

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EXPERIMENTAL

Materials

Mixtures with a 1 : 1 molar ratio of Na_2O and Cr_2O_3, used for the preparation of $NaCrO_2$ and for other thermal experiments, were prepared by stirring the required amounts in petroleum ether for 24 h. The mixture was then vacuum-dried and kept in a glove box under dry nitrogen. Only the amount necessary for a particular experiment was removed from the glove box, prior to the experiment.

$NaCrO_2$ was prepared according to the method described by Barker and Hooper [2]. The Na_2O/Cr_2O_3 mixture was heated in an argon atmosphere at 450 °C for 8 h. The X-ray powder diffraction pattern of the dull green compound corresponded with that already reported [3] for $NaCrO_2$ and is given in Table 1.

Thermal analysis

A DuPont 951 thermogravimetric analyser was used to collect TG data. A DuPont 910 differential scanning calorimeter controlled by a 1090 thermal analyser was used for the DSC studies. Peak integration and subsequent enthalpy calculations were performed using the DuPont partial area integration program. The melting endotherms of pure indium metal ($\Delta H_f = 28.4$ J g^{-1}) and pure zinc metal ($\Delta H_f = 102.0$ J g^{-1}) were used for calibration.

Oxygen and argon were used as carrier gases at a flow rate of approximately 50 ml min^{-1}. Platinum sample holders were used and sample sizes varied between 20 mg and 30 mg.

X-ray powder diffraction

X-ray powder diffraction data of the different reaction products were obtained at room temperature using a Seifert MZ IV diffractometer with Cu Kα radiation.

TABLE 1

X-ray powder diffraction data for $NaCrO_2$

Relative intensity	D (obs.) (Å)	D (lit. [3]) (Å)
90	5.316	5.311
60	2.655	2.658
50	2.540	2.531
40	2.442	2.440
100	2.157	2.156
60	1.574	1.574
60	1.480	1.480

ESCA analysis

Samples were analysed on a Physical Electronics spectrophotometer over the binding energy range 0–1000 eV.

RESULTS AND DISCUSSION

Formation of NaCrO$_2$

The DSC curve for the reaction of Na_2O with Cr_2O_3 in an inert atmosphere is shown in Fig. 1. The X-ray powder diffraction pattern of the dull green product corresponded with that of $NaCrO_2$ (see Table 1) as reported by Barker and Hooper [2]. The enthalpy of the reaction

$$Cr_2O_3 + Na_2O \rightarrow 2NaCrO_2 \qquad (2)$$

was calculated as -142.0 ± 3.8 kJ from the DSC curve. The value is in agreement with the calculated value of -139.79 kJ at 427 °C and -150.46 kJ at 527 °C.

An interesting feature of the DSC curve was the endotherm which appeared between 270 °C and 310 °C (Fig. 2). The reaction which is characterised by this endotherm seems to be a reversible process. Curve A represents the endotherm obtained when the sample was heated to 330 °C in an inert atmosphere, while curve B was obtained by re-heating the same sample, after it was cooled to room temperature in an inert atmosphere.

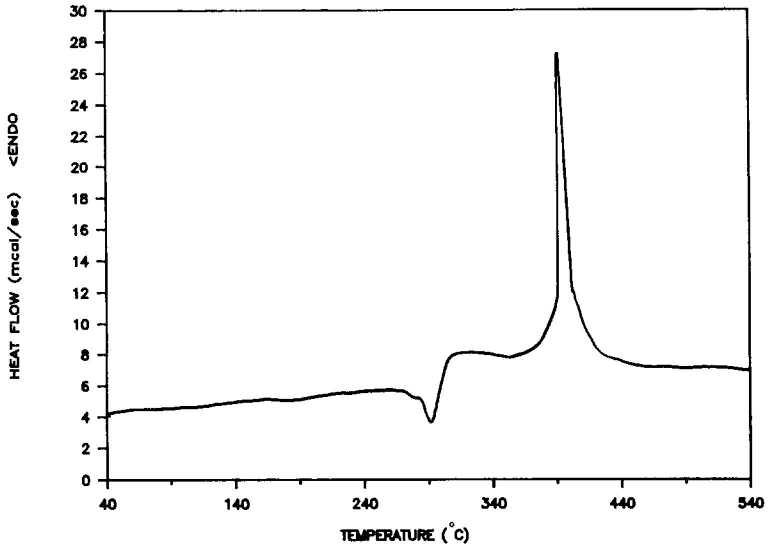

Fig. 1. DSC curve for the formation of $NaCrO_2$ from Na_2O and Cr_2O_3.

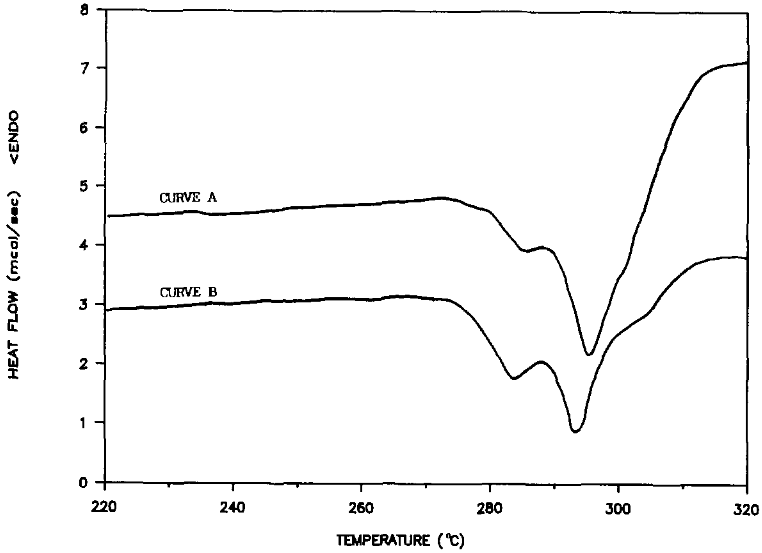

Fig. 2. DSC curve for the reversible transition which occurs during the formation of $NaCrO_2$: curve A, heating curve for Na_2O and Cr_2O_3 in argon; curve B, heating curve for the same mixture after cooling to room temperature in argon.

These curves indicated that the same processes occur when the sample is taken through a heating/cooling/re-heating cycle. The shift in baseline before and after the reaction, which can be attributed to a significant change in the heat capacity of the sample during the transition, did not allow an accurate calculation of the enthalpy involved.

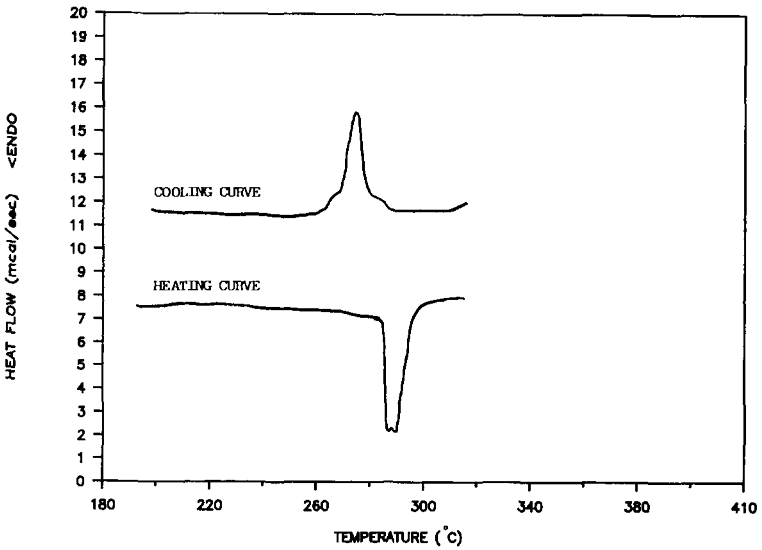

Fig. 3. DSC heating and cooling curve for Na_2O in argon.

This reversible process was linked to a reversible transition observed in Na_2O as illustrated in Fig. 3. On heating, Na_2O showed an endothermic change at 285 °C with $\Delta H = 2.95$ kJ mol^{-1}, while the cooling curve gave an exothermic peak, $\Delta H = -2.75$ kJ mol^{-1}, at 272 °C. By comparing Figs. 2 and 3, it is clear that the reversible transition detected in the mixture of Na_2O and Cr_2O_3 cannot be explained only by the transition detected in Na_2O. The peak at 282 °C (Fig. 2) can be assigned to this transition while the peak at 292 °C and the shoulder at 305 °C are possibly due to an intermediate which forms between Na_2O and Cr_2O_3. More experimental data are, however, necessary to clarify the exact nature of this process.

ESCA analysis of $NaCrO_2$

The X-ray photoelectron spectra of $NaCrO_2$ and Cr_2O_3 were recorded and ionisation from the core levels were compared. The results are summarised in Table 2. In general, ionisation from the inner core levels, $Cr(2p_{1/2})$ and $Cr(2p_{3/2})$ of the $NaCrO_2$, occurred at lower binding energies. This indicated that bonding in $NaCrO_2$ was more covalent than in Cr_2O_3. The observed O(1s) peak in $NaCrO_2$ was observed at 530.7 eV with a shoulder at 529.2 eV.

The reaction of $NaCrO_2$ with O_2

The TG curve for the reaction of $NaCrO_2$ with O_2 is given in Fig. 4. A total mass gain of 11.0% was observed, and Cr_2O_3 and Na_2CrO_4 were identified by X-ray powder diffraction as the only constituents in the final product. The reaction seems, therefore, to be

$$8NaCrO_2 + 3O_2 \rightarrow 4Na_2CrO_4 + 2Cr_2O_3 (\text{calculated mass gain} = 11.2\%) \quad (3)$$

The TG and DTA curves (Fig. 5) suggest that the oxidation process consists of various overlapping reactions. Isothermal TG measurements at 190 °C, 420 °C and 700 °C did not give a plateau which could be linked to a stable intermediate. Instead, the mass gain curve showed a continuous increase with time. Samples taken during various stages of the reaction in the DTA, at 220 °C, 470 °C and 700 °C, were very hygroscopic, making direct analysis of the intermediates extremely difficult. X-ray analysis showed the presence

TABLE 2

Experimental binding energies (eV)

Compound	$Cr(2p_{1/2})$	$Cr(2p_{3/2})$	O(1s)	Na(1s)
Cr_2O_3	586.8	576.7	530.5	
$NaCrO_2$	585.0	575.3	530.7 529.2 sh	1069.0

sh, Shoulder.

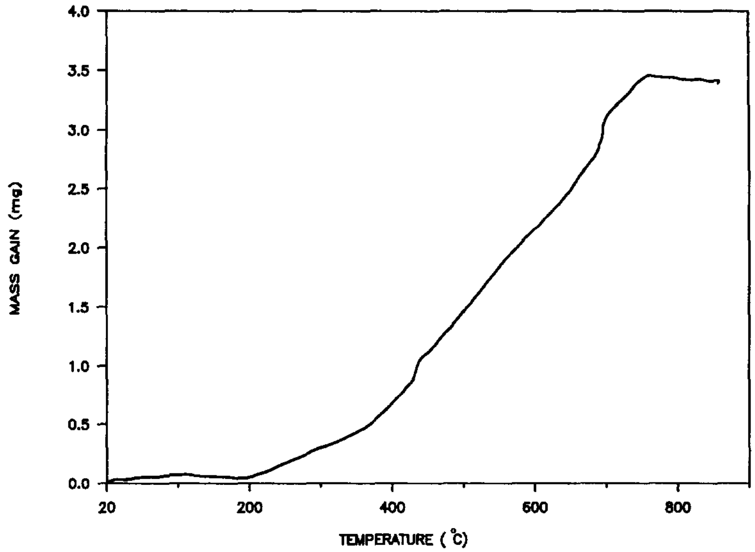

Fig. 4. TG curve for the oxidation of $NaCrO_2$.

of Na_2CrO_4 and Cr_2O_3, with traces of Na_4CrO_4 in the samples taken at 420 °C and 700 °C.

It seems, therefore, as if the mechanism of the reaction could be represented as an oxidation reaction to form an intermediate oxide which then

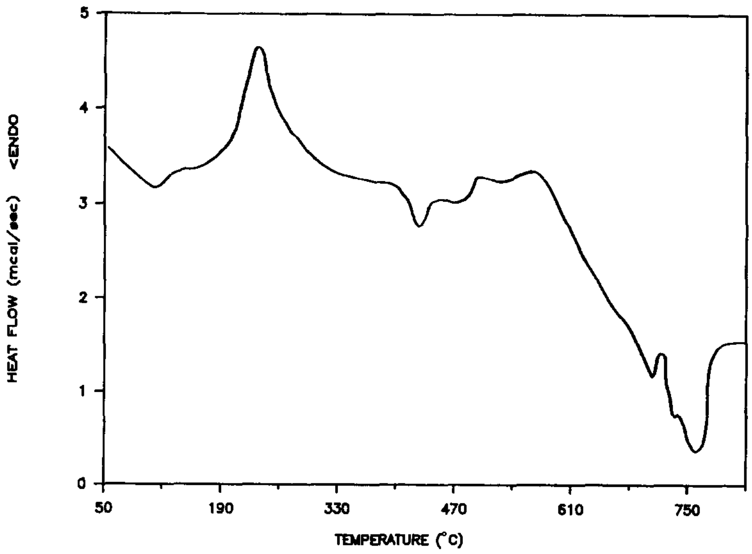

Fig. 5. DSC curve for the oxidation of $NaCrO_2$.

disproportionates to form Na_2CrO_4 and Cr_2O_3

$$NaCrO_2 + O_2 \rightarrow Na_xCrO_y \rightarrow Na_2CrO_4 + Cr_2O_3 \qquad (4)$$

This would explain the incomplete reaction observed during the oxidation of Cr_2O_3 in carbonate medium in the thermobalance [1].

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