

## PHYSICO-CHEMICAL PROPERTIES OF CHROMIUM TRIOXIDE AND ITS SUBOXIDES

M.A. KHILLA, Z.M. HANAFI and A.K. MOHAMED

*National Research Centre, Dokki, Cairo (Egypt)*

(Received 31 March 1982; revised 18 May 1982)

### ABSTRACT

Seven samples of chromium suboxides of composition  $\text{CrO}_{3-x}$  are prepared from the thermal decomposition of  $\text{CrO}_3$ . The O/Cr ratio of each is determined by chemical analysis and ignition loss. X-Ray analysis reveals that they are more or less of the correct structure contaminated with the nearest suboxide. The specific gravity is determined pycnometrically and varies linearly with the O/Cr ratio.

TGA indicates weight losses which agree with the calculated O/Cr ratio. DTA and DTG give endothermic peaks corresponding to the temperature of preparation of the successive samples.

### INTRODUCTION

Oxide systems of metals which exhibit variable valency are often complicated by the occurrence of non-stoichiometric compounds and the existence of more or less extensive regions of solid solution. One of the most complex of such systems is that formed between oxygen and chromium as  $3d$ .

From the band structure standpoint, the  $3d$  transition metals and their compounds have attracted considerable interest due to their wide variety of magnetic, electrical, thermal and mechanical properties. These materials are widely applied in magnetic recording tabs and inorganic pigments.

Although the structure and physical properties of  $\text{CrO}_3$  and  $\text{Cr}_2\text{O}_3$  have already attracted a good deal of attention, the Cr–O<sub>2</sub> system is so complex that certain fundamental problems remain unsolved. It has yet to be established which oxidation states, other than  $\text{Cr}^{3+}$  and  $\text{Cr}^{6+}$ , are formed during calcination. This was achieved by studying the IR absorption [1] of this system. The electrical conductivity was also studied [2] to establish the variation of resistivity with variation of the O/Cr ratio.

The present work deals mainly with the chemistry of the calcination products of  $\text{CrO}_3$ . The prepared oxides between  $\text{CrO}_3$  and  $\text{Cr}_2\text{O}_3$  are chemically analyzed and studied using the following experimental techniques:

density, X-ray diffraction, thermogravimetric analysis (TGA), and differential thermal analyses (DTA and DTG).

## EXPERIMENTAL

### *Preparation of samples*

Chromium oxides of varying O/Cr ratio had been previously prepared by the thermal decomposition of chromium trioxide [3–12]. The thermal decomposition was found to be a slow process and showed the existence of non-stoichiometric compounds. Thus Ryss and Selyanskaya [3] found  $\text{Cr}_5\text{O}_{13}$ ,  $\text{Cr}_7\text{O}_{18}$ ,  $\text{Cr}_8\text{O}_{21}$  and  $\text{Cr}_5\text{O}_{12}$ . Cameron et al. [4] observed two non-stoichiometric oxides,  $\text{CrO}_{(2.6-2.2)}$  and  $\text{CrO}_{(1.7-1.9)}$ , with average compositions  $\text{Cr}_5\text{O}_{12}$  and  $\text{Cr}_5\text{O}_9$ . The non-stoichiometric oxides of chromium having O/Cr ratios between 3:1.5 could be obtained from the thermal decomposition of chromium trioxide. Thus the determination of the effect of temperature on  $\text{CrO}_3$  was undertaken as a prerequisite to the preparation of the samples. From TGA, it was clear that there were consecutive weight losses, ending with the green  $\text{Cr}_2\text{O}_3$  at  $\sim 450^\circ\text{C}$ . At  $198^\circ\text{C}$  melting occurred, followed by successive small changes in composition. The changes in  $\Delta T$  ( $\text{mV cm}^{-1}$ ) were also

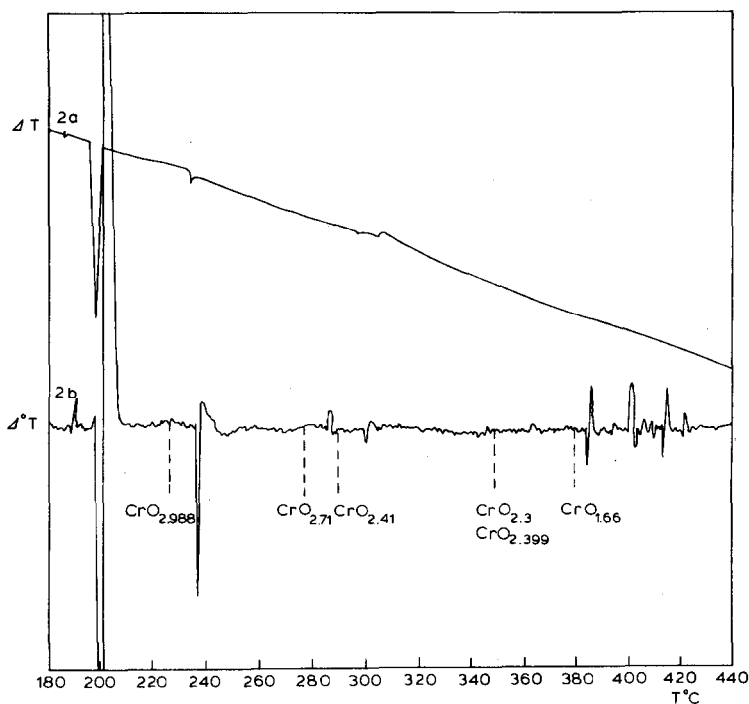


Fig. 1. DTA of  $\text{CrO}_3$ .

observed at almost the same temperatures where losses occurred. Thus the following temperatures of preparation were chosen in temperature regions before every change, whatever the change (Fig. 1). The method of Costea [11] was applied using a silica crucible and the temperature was controlled to  $\pm 3^\circ\text{C}$  by using a temperature regulator (Diamond H Control Ltd., Norwich, England).

### *Chemical analysis*

The determination of the O/Cr ratio was done following two principles. The first was through the oxidation of chromium ions to  $\text{Cr}^{6+}$ , then the consumption of this formed  $\text{Cr}^{6+}$  in the oxidation of  $n/10$   $\text{FeSO}_4$ . The excess ferrous sulphate was back titrated with standard 0.1 N  $\text{KMnO}_4$ . Two oxidizing media were used; the first was 70%  $\text{HClO}_4$  after Schwartz et al. [5]; the second was after Glemser et al. [6] by dissolving the sample in 80%  $\text{H}_2\text{SO}_4$ , then oxidizing it with ammonium bisulphate.

The second principle depends on the weight loss which occurs on the ignition of each sample to the final product  $\text{Cr}_2\text{O}_3$ . This method was after Kubota and Hirota [13].

The O/Cr ratios calculated from the two methods were in reasonable agreement. The composition reported in Table 1 represents the mean values of both.

### *Density*

The density of the different samples was measured pycnometrically using freshly distilled  $\text{CCl}_4$ .

### *X-Ray analysis*

X-Ray diffraction patterns were obtained by using Siemens diffractometer D 500/501 with  $\text{CuK}_\alpha$  radiation.

### *Thermal analyses*

Thermal analyses, including TGA, DTA and DTG, were done by means of a "MOM" derivatograph (Budapest; system: F. Paulik–J. Paulik–L. Erdey). About 1 g of each prepared sample was heated gradually ( $10^\circ\text{C min}^{-1}$ ) up to  $1000^\circ\text{C}$ , with  $\text{Al}_2\text{O}_3$  as reference material. The following sensitivities were used: DTA 1/5, TGA 500 and DTG 1/10. All samples were analyzed under the above constant instrumental conditions.

TABLE I

Conditions of preparation, X-ray main lines and density data for chromium trioxide and its suboxides

Ser.	Oxide	Time (h)	Temp. (°C)	X-Ray main lines					
				<i>d</i>	<i>I/I<sub>0</sub></i>	<i>hkl</i>	<i>d</i>	<i>I/I<sub>0</sub></i>	<i>hkl</i>
1	CrO <sub>3</sub>			4.164	100		3.371	40	
				4.164	100	110	3.36	100	111
2	CrO <sub>2.988</sub>	3	227	4.129	100		3.38	70	
				4.164	100	110	3.36	100	111
3	CrO <sub>2.71</sub>	6	278	11.77	100		3.336	77	
				11.8	70		3.34	80	
				+					
				3.27	50		5.959	20	
				3.26	100		5.95	70	
4	CrO <sub>2.41</sub>	6	290	3.27	100		2.66	25	
				3.29	20	311	2.66	60	411
				+					
				6.25	33		5.90	50	
				6.24	70		5.95	70	
5	CrO <sub>2.399</sub>	3	350	8.415	100		5.94	45	
				8.45	80		5.95	70	
				+					
				3.687	14		3.462	32	
				3.665	40	021	3.50	20	112
6	CrO <sub>2.3</sub>	4	350	8.415	67		5.94	41	
				8.43	80		5.95	70	
				+					
				4.100	11		3.623	26	
				4.098	20	020	3.61	60	310
7	CrO <sub>1.66</sub>	6	380	2.478	33		1.669	31	
				2.48	96	110	1.672	90	116
				+					
				2.657	92		2.478	100	
				2.666	100	104	2.480	96	110
8	CrO <sub>1.516</sub>	6	450	8.41	41		3.264	25	
				8.44	5		3.26	5	
				+					
				2.664	100		2.481	97	
				2.666	100	104	2.480	96	110

<i>d</i>	<i>I/I</i> <sub>0</sub>	<i>hkl</i>	Ref.	Identification	Density	Density obtained by previous authors
3.416	30				2.76	2.78 [14], 2.7 [15]
3.42	100	021	30	CrO <sub>3</sub>		2.81 [14,16,17]
3.434	100				2.79	
3.42	100	021	30	CrO <sub>3</sub>		
3.85	70				3.24	3.34 [18] for Cr <sub>5</sub> O <sub>8</sub>
3.88	100		5	Mainly Cr <sub>3</sub> O <sub>8</sub>		
3.46	20					
3.48	50		5	Cr <sub>2</sub> O <sub>5</sub> (traces)		
3.67	42				3.69	3.68 [18] for Cr <sub>4</sub> O <sub>12</sub>
3.66	40	021	18		Mainly Cr <sub>5</sub> O <sub>12</sub>	
1.63	18					
1.63	m		5, 6	Cr <sub>2</sub> O <sub>5</sub> (traces)		
3.28	90				3.74	
3.26	100		5	Mainly Cr <sub>2</sub> O <sub>5</sub>		
2.798	40					
2.813	20	122	18	Cr <sub>5</sub> O <sub>12</sub> (traces)		
3.275	100				3.90	
3.26	100		5		Mainly Cr <sub>2</sub> O <sub>5</sub>	
2.668	33					
2.669	60			Cr <sub>5</sub> O <sub>12</sub>		
1.429	17					
1.431	40	300	31	Cr <sub>2</sub> O <sub>3</sub> (traces)		
1.670	83				4.98	4.93 [19], 4.86 [20] for Cr <sub>2</sub> O <sub>3</sub>
1.672	90	116	31	Cr <sub>2</sub> O <sub>3</sub>		
3.122	10					
3.114	100	221	34.32	CrO <sub>2</sub> (traces)		4.90 [21] for CrO <sub>2</sub> 4.955 [21] for CrO <sub>1.945</sub>
1.67	89				5.2	5.2 [15,16,22-29] for Cr <sub>2</sub> O <sub>3</sub>
1.672	90	116	31	Mainly Cr <sub>2</sub> O <sub>3</sub>		

## RESULTS AND DISCUSSION

*Density*

The density values are tabulated in Table 1, along with those obtained by different authors for the corresponding compositions. It is clear that the obtained densities agree well with those obtained by the various authors [14–29]. The slight variations of the samples in between may be due to the contamination of the specified sample with other phases which change the O/Cr ratio.

The variation of the density values with the O/Cr ratio is represented in Fig. 2. It is clear that the specific gravity increases linearly with a decrease of the O/Cr ratio. This was interpreted by Kubota and Hirota [13] as being mainly due to an excess of chromium ions in the interstices of the lattice.

*X-Ray*

The main  $d$ -values of the strongest lines are tabulated in Table 1 along with those of the different authors. It seems that the prepared chromium oxide samples are more or less of the correct structure with respect to the position of the diffraction lines; they are identical with the corresponding phases given in the literature.

With respect to the intensities, the corresponding lines originating from the same crystal phase vary considerably. This may be due to the orientation

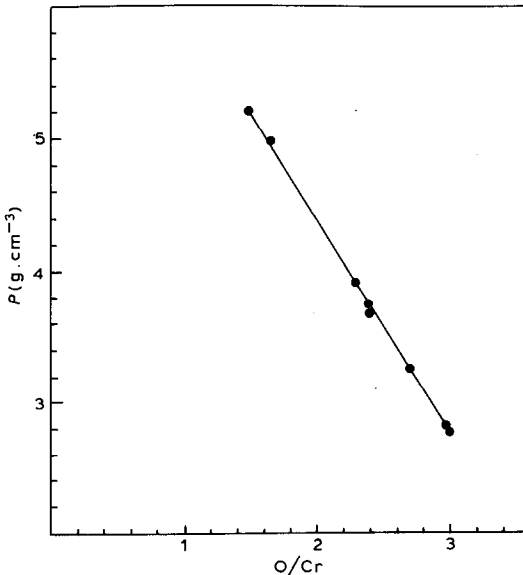


Fig. 2. Variation of the specific gravity of the chromium oxide samples with the O/Cr ratio.

of the scattering centres owing to the movement of the molecules, the formation of unstable small crystallites in which the molecules from certain crystal phases diffuse to other planes as the size of the crystallite grows, or to a temporary substitution of oxygen atoms for chromium atoms.

The presence of lines of more than one phase in the investigated samples suggests a contamination by other phases. Still some samples represent more than one phase but as a whole the contamination of the phases is of such a nature as to move the with O/Cr ratio, i.e., graduating as

1	$\text{CrO}_3$	
2	$\text{CrO}_3$	
3	mainly $\text{Cr}_3\text{O}_8 + \text{Cr}_2\text{O}_5$ (traces)	
4	$\text{Cr}_2\text{O}_5$ (traces) + mainly $\text{Cr}_5\text{O}_{12}$	
5	mainly $\text{Cr}_2\text{O}_5 + \text{Cr}_5\text{O}_{12}$ (traces)	
6	mainly $\text{Cr}_2\text{O}_5 + \text{Cr}_5\text{O}_{12}$ (traces)	+ $\text{Cr}_2\text{O}_3$ (traces)
7		$\text{CrO}_2$ (traces) + mainly $\text{Cr}_2\text{O}_3$
8		mainly $\text{Cr}_2\text{O}_3$

### *Thermal analyses*

The thermal properties of chromium oxides have been studied previously [9,16,33–44], from which it was possible to separate samples of one phase of composition intermediate between  $\text{CrO}_3$  and  $\text{Cr}_2\text{O}_3$ . For the sake of brevity, the TGA, DTA and DTG are tabulated in Table 2, together with plausible interpretations.

The TGA showed total weight losses which ended for all samples at  $1000^\circ\text{C}$  with the green  $\text{Cr}_2\text{O}_3$ . Back calculation of the corresponding oxide before loss of oxygen indicated that the starting oxide might have the same O/Cr ratio as that found by chemical analysis and ignition loss measurements. The weight loss of  $\text{CrO}_{2.988}$  is more than the calculated value due to the contamination of water in the starting weight.

The DTA data match the corresponding data obtained by previous authors. Thus, for example, the sample of  $\text{CrO}_{2.988}$  gave a broad peak covering the range  $270\text{--}370^\circ\text{C}$ , i.e., covering the range corresponding to the formation of  $\text{CrO}_{2.71}$  at  $278^\circ\text{C}$  and  $\text{CrO}_{2.41}$ ,  $\text{CrO}_{2.399}$  at  $350^\circ\text{C}$ . Lorthioir and Michel [34] observed stable peaks at  $280^\circ\text{C}$  for  $\text{Cr}_2\text{O}_{5.23}$  and another peak at  $370^\circ\text{C}$  corresponding to the composition  $\text{Cr}_2\text{O}_{4.87}$ . However, this peak is still present in all samples and increases in intensity as we pass to lower O/Cr ratios. This may be related to the presence of  $\text{Cr}_2\text{O}_3$ , as is clear from X-ray and IR absorption data [1].

The broad exothermic peak at  $880^\circ\text{C}$  begins at  $800^\circ\text{C}$  and is observed in all samples, and may correspond to the complete transformation to  $\text{CrO}_{1.5}$ . Rode [42] interpreted this as due to the transformation of  $\text{CrO}_{1.56}$  to  $\text{CrO}_{1.5}$ . Torokin et al. [40] observed a peak at  $765\text{--}790^\circ\text{C}$  and interpreted it as the phase transformation of the cubic  $\text{Cr}_2\text{O}_3$  to the rhombohedral form.

TABLE 2

TGA, DTA and DTG data obtained for the prepared samples and their interpretations

Sample	TGA (% total wt. loss)	DTA	DTG	Interpretation
CrO <sub>2.988</sub>	24.5	200°C (endo) 270-370 (exo) 420 (exo) 470 (endo) 860 (exo)	330, 370°C 420 470	CrO <sub>2.988</sub> CrO <sub>2.71</sub> , CrO <sub>2.41</sub> and CrO <sub>2.399</sub> CrO <sub>1.66</sub> CrO <sub>1.516</sub> Cr <sub>2</sub> O <sub>3</sub>
CrO <sub>2.71</sub>	20	100 (endo) 270 (exo) 380 (exo) 470 (endo) 880 (exo)	380 470	Due to water CrO <sub>2.71</sub> CrO <sub>2.41</sub> and CrO <sub>2.399</sub> CrO <sub>1.516</sub> Cr <sub>2</sub> O <sub>3</sub>
CrO <sub>2.41</sub>	16.5	100 (endo) 270 (exo) 470 (endo) 880 (exo)	470	Due to water CrO <sub>1.516</sub> Cr <sub>2</sub> O <sub>3</sub>
CrO <sub>2.399</sub>	16	270 (exo) 470 (endo) 880 (exo)	470	CrO <sub>1.516</sub> Cr <sub>2</sub> O <sub>3</sub>
CrO <sub>2.3</sub>	14.5	275 (exo) 470 (endo) 880 (exo)	470	CrO <sub>1.516</sub> Cr <sub>2</sub> O <sub>3</sub>
CrO <sub>1.516</sub>		275 (exo) 880 (endo)		Cr <sub>2</sub> O <sub>3</sub>

The DTG gave derivatives at temperatures corresponding to the temperature of preparation of the lower O/Cr ratio. So the preceding peaks in the DTA taking place at temperatures before the temperature of preparation of the sample may correspond either to adsorbed water and/or to the decomposition of a higher chromium oxide liable to be present.

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