Evolution of α-Cr_2O_3 from Hydrous Chromium Oxides: Magnetic Susceptibility and Extended *X*-Ray Absorption Fine Structure Studies †

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The evolution of α-Cr_2O_3 from hydrous chromium oxides heated in a hydrogen atmosphere has been examined by magnetic susceptibility and extended *X*-ray absorption fine structure studies for the first time. Infrared, differential scanning calorimetry, *X*-ray diffraction, and thermogravimetric studies were also used for characterization. The results show the absence of any CrO(OH) phase as an intermediate in the evolution of Cr_2O_3.

The structural evolution of chromia, Cr_2O_3, from chromium hydroxide gels or precipitates has been examined by several authors.[1–3] These studies are complicated by the fact that in most cases the products are amorphous and indirect methods have to be relied upon. Thus, Ratnasamy and Leonard[2] used *X*-ray radial distribution studies to characterise the materials and on the basis of a distance of 2.40 Å observed in their radial distribution pattern they proposed the presence of β-CrO(OH).[4] However, their samples were heated in air and it is likely that they were contaminated with CrO_2 or other higher oxidation states of chromium. Fenerty and Sing[1] proposed the presence of β-CrO(OH)[5,6] when the hydroxides are heated between 200 and 250 °C. The β-CrO(OH) is then converted topotactically[6] to CrO_2 in an oxygen atmosphere. Giovanoli and Stadelmann[3] found from *X*-ray evidence that the amorphous phase just before nucleation of α-Cr_2O_3 has very little short-range order although in the presence of water vapour a short-range order may develop which may be attributed to a form of CrO(OH). We have investigated the structural evolution of chromia from hydrous chromium oxide gels as a prototype in the study of the evolution of oxides from hydroxides and also to understand the nature of magnetic interactions in the partially dehydrated, amorphous hydroxides as this information could be of relevance to amorphous antiferromagnetism. For this purpose, we have carried out an extended *X*-ray absorption fine structure (EXAFS) study of the hydrous oxides of chromia obtained at various temperatures in order to obtain information on the local environment of the chromium ion at each stage of dehydration. Such EXAFS studies have not been carried out hitherto. In order properly to understand the dehydration process, we have also examined the temperature dependence of the magnetic susceptibility. The chromium hydroxides were heated in a hydrogen atmosphere in order to avoid complications in the magnetic susceptibilities due to the presence of higher oxidation states or CrO_2. Thermogravimetric analysis (t.g.a.), differential scanning calorimetry (d.s.c.), i.r., and *X*-ray and electron diffraction studies have been used to characterise completely the specimens. This paper presents the results of our studies.

Experimental

Chromium hydroxide gel was prepared by the method of Turkevich *et al.*[7] An aqueous solution of $Cr(NO_3)_3 \cdot 9H_2O$ (0.40 mol dm^{-3}) containing 1 mol dm^{-3} ammonium acetate was heated to 80 °C and a 20% ammonia solution was added dropwise with continuous stirring till a gel was formed. The gel was allowed to stand overnight, washed several times with water, and then filtered off and dried at 110 °C for 24 h in air. This was the starting material for the preparation of other samples and is designated as 110A. Portions of the starting materials were then heated at 200, 350, 400, 600, and 800 °C in hydrogen for 12 h. The samples are thus termed 200H, 350H, 400H, 450H, 600H, and 800H respectively.

Thermogravimetric analysis was carried out in a nitrogen atmosphere as well as in vacuum. There was good agreement between the two methods. The differential scanning calorimetry studies were carried out on a Perkin-Elmer DSC-2 machine. A Perkin-Elmer 581 i.r. spectrometer was used for i.r. studies. The samples were prepared in the form of pellets using KBr prepared in a dry nitrogen atmosphere. The *X*-ray measurements were carried out on a Phillips PW1140 *X*-ray diffractometer and the electron diffraction and microscope studies using a Phillips EM301 machine. The magnetic susceptibility studies were carried out at fields of 1 500 kG using the Faraday technique and a recording Cahn-RG vacuum electrobalance.

A bent crystal *X*-ray spectrograph[8] was used for recording the *X*-ray absorption spectra; Cu radiation from a sealed *X*-ray tube was used as the source. The absorbers of the compounds were prepared by spreading their fine powders on Cellophane adhesive tape. A Carl Zeiss MD 100 microphotometer was used to record the traces of the absorption spectra with a reverse linear dispersion of 0.7 eV mm^{-1}.

Results and Discussion

Diffraction Studies.—The *X*-ray diffraction studies showed that all samples heated below 450 °C were amorphous. The samples 450H, 600H, and 800H showed diffraction lines of only α-Cr_2O_3. Electron diffraction studies showed a diffuse ring pattern for the samples 110A and 200H, typical of amorphous materials. Electron diffraction patterns of 350H and 400H showed rings with distinct spots typical of microcrystalline materials. The distance measured corresponded to that of α-Cr_2O_3. Transmission electron micrographs of the materials showed that 110A and 200H had a layer like texture while 350H showed a very porous structure. The electron diffraction patterns of the other samples were similar to that of α-Cr_2O_3.

T.G.A. Studies.—These studies revealed three broad regions: (*a*) region A which is below 150 °C and attributed to the loss of loosely bound water; (*b*) region B between 240 and 400 °C in which bound water is lost probably by the condensation of hydroxyl groups;[2] (*c*) region C which is near 450 °C is associated with a sintering process in which perhaps water is trapped in small pores or water is formed by the condensation of surface OH groups. The number of moles of water per mole of Cr_2O_3 lost in the various regions for the various

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† *Non-S.I. units employed:* 1 eV ≈ 1.60 × 10^{-19} J; 1 G = 10^{-4} T; 1 B.M. = 0.927 × 10^{-23} A m^2; 1 e.m.u. = $\frac{1}{4}\pi \times 10^6$ S.I. unit.

Table 1. Water content, $\mu_{eff.}$, and θ values of various chromium oxide samples

Sample	Water lost at various temperatures (moles of H_2O/g atom of Cr) <150 K	150—400 K	>400 K	$\mu_{eff.}$/B.M. (per g atom of Cr)	θ
110A	3.6	3.2	0.5	3.47	~0
200H	1.6	3.4	0.6	3.76	40
350H	6.2	0.2	0.6	3.87	120
400H	—	—	0.6	—	—

samples are shown in Table 1. The amount of water lost in region B by 110A and 200H is high (*ca.* 3 mol) and suggests a co-ordination of the type $[Cr(OH)_6]^{3-}$ or of the type $[Cr(H_2O)_3(OH)_3]$ proposed for the crystalline chromium hydroxide trihydrate by Giovanoli *et al.*[9]

D.S.C. Studies.—The d.s.c. studies of 110A showed a broad endothermic peak centred at 140 °C and an exothermic-type peak centred at around 240 °C. The strong exothermic peak was surprisingly absent in both d.s.c. and d.t.a. experiments even when the latter was carried out in air. These results are somewhat different from the d.t.a. results published earlier.[2,10] The complex β-CrO(OH) decomposes exothermally to Cr_2O_3,[11] and β-CrO(OH) has been proposed as an intermediate species in the conversion of the hydrous oxide to crystalline α-Cr_2O_3. Our d.s.c. studies themselves therefore seem to show that β-CrO(OH) is not necessarily an intermediate in the decomposition of 110A to α-Cr_2O_3.

I.r. Studies.—Infrared spectra of the samples in the region 1 000—2 000 cm^{-1} are shown in Figure 1. There is a strong band around 1 550 cm^{-1} in all samples heated below 400 °C. This band has been attributed to surface hydroxyl groups.[2] A band around 1 400 cm^{-1} has been attributed to carbonate groups on the surface.[2] The sharp band at 1 360 cm^{-1} is probably due to nitrate impurities. In none of the spectra do we find bands similar to any of the α- or γ-CrO(OH) species reported by Christensen.[5] We note that Ratnasamy and Leonard[2] observed only the band at 1 550 cm^{-1} for their crystalline sample (their sample A) which has an *X*-ray diffraction pattern similar to $Cr(OH)_3 \cdot 3H_2O$ reported by Giovanoli *et al.*,[9] which also has very short O–H–O bonds. Hence the band at 1 550 cm^{-1} may tentatively be assigned to the O–H stretching vibration in short O–H–O bonds of the amorphous hydrous oxides. The samples heated above 400 °C show features of molecular water which may have been physically adsorbed on the surface. The features near 1 050 cm^{-1} for 110A, 200H, and 350H could be associated with $[CrO_4]^{n-}$ species as proposed by Ratnasamy and Leonard.[2]

Magnetic Susceptibility Studies.—The inverse magnetic susceptibility (χ^{-1}) *versus T* plots ($T < 300$ K) of some of the samples are shown in Figure 2. The magnetic susceptibilities were normalised per gram atom of chromium in samples of the nominal formula $Cr_2O_3 \cdot nH_2O$ (see Table 1). The $\mu_{eff.}$ and θ (Weiss constant) values obtained from the χ^{-1} *versus T* plots below 300 K are given in Table 1. The 110A sample shows a near Curie-law-like behaviour. The $\mu_{eff.}$ value for this sample (3.47 B.M.) is considerably less than that expected theoretically (3.91 B.M.). The α-, β-, and γ-forms of CrO(OH) all show Curie-Weiss behaviour.[5] The 110A sample does not contain any of the forms of CrO(OH) to a significant extent.

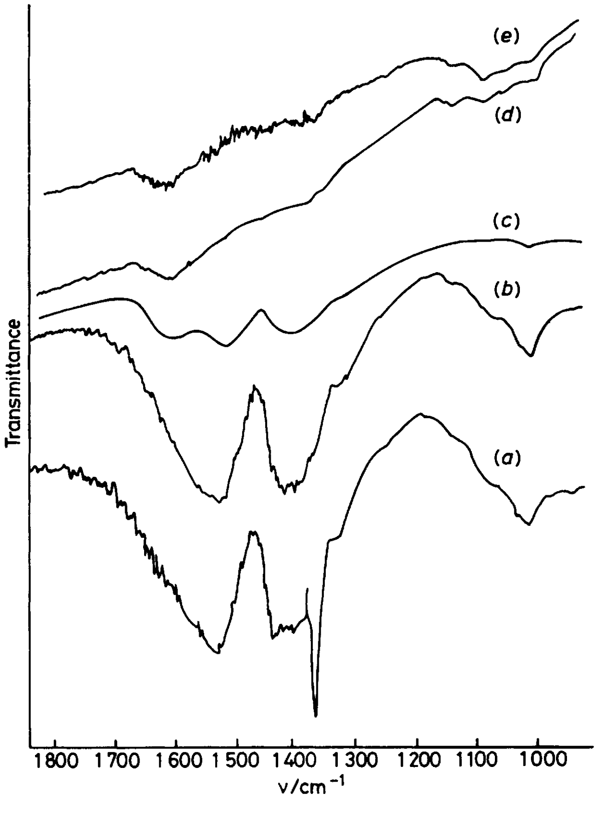

Figure 1. Infrared spectra of hydrous chromium oxide gels in the region 1 000—2 000 cm^{-1}. Samples (*a*) 110A, (*b*) 200H, (*c*) 350H, (*d*) 450H, and (*e*) 800H

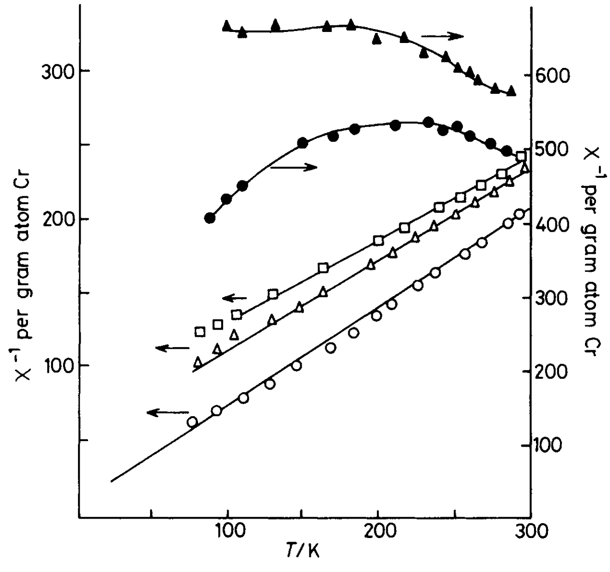

Figure 2. Inverse susceptibility (χ^{-1}) per gram atom of Cr *versus T* at $T < 300$ K for samples 110A (○), 200H (△), 350H (□), 600H (●), and 800H (▲)

The low $\mu_{eff.}$ value of this sample probably shows the presence of higher oxidation states of chromium and/or small amounts of CrO(OH) or microcrystalline aggregates of antiferromagnetic Cr_2O_3. The 200H and 350H samples show Curie–Weiss type behaviour with the $\mu_{eff.}$ values being rather close

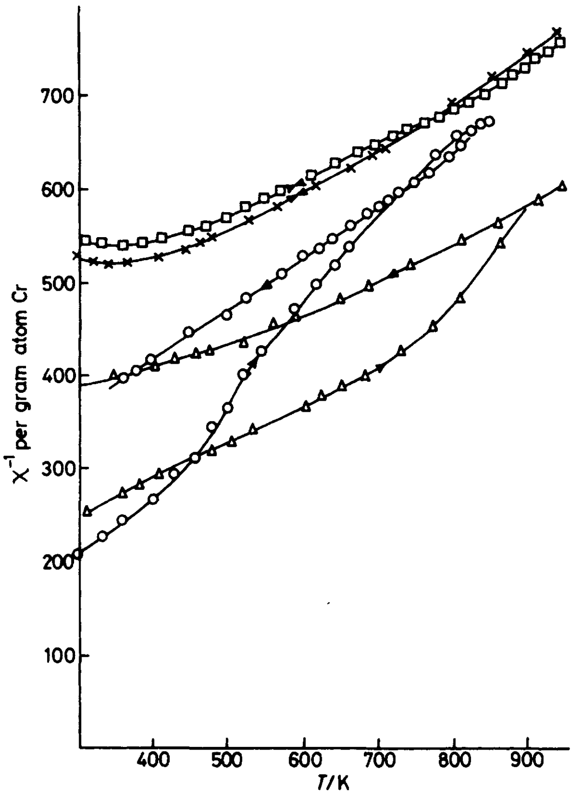

Figure 3. Inverse susceptibility (χ^{-1}) per gram atom of Cr *versus* T at T >300 K for samples 110A (○), 350H (△), 450H (×), and 800H (□)

to the theoretically expected value. Our i.r. studies rule out the possibility of the Curie–Weiss behaviour being attributed to a CrO(OH) phase. It is therefore likely that 350H has a highly defect Cr_2O_3 structure with a large number of Cr–O–Cr linkages which could give rise to superexchange interactions, as well as Cr–OH linkages which terminate these interactions. The fact that the $\mu_{eff.}$ value for 350H (3.87 B.M.) is close to that of the theoretical value suggests that the chromium ions all experience an effective uniform internal field so that the magnetic susceptibility may be represented by a Curie–Weiss law with a single θ value. Similar arguments hold for 200H. The samples heated above 400 °C resemble crystalline Cr_2O_3 in magnetic susceptibility behaviour. The increase in χ^{-1} with decreasing temperature suggests the presence of an ordered antiferromagnetic state. The Curie-like behaviour in the low-temperature range for 400H indicates the presence of isolated Cr^{3+} ions or superparamagnetic clusters. With increasing temperature the low-temperature behaviour of 400H is lost (see the plot of the 800H sample) indicative of sintering and long-range order.

Figure 3 shows the χ^{-1} *versus* T plots of some of the samples in the high-temperature range. The samples heated above 400 °C show reproducible behaviour on heating and cooling. The minimum in the χ^{-1} *versus* T plot around 320 K corresponds to the magnetic ordering temperature of Cr_2O_3. The 110A sample begins to show a rapid decrease in the susceptibility at about the same temperature (510 K) at which water is lost by the condensation of hydroxyl groups. The cooling curve diverges from the heating curve at around 700 K which corresponds roughly to the crystallisation temperature. The cooling curve shows Curie–Weiss type behaviour. These results support the conclusion that the condensation of hydroxyl groups lead to the formation of Cr–O–Cr linkages which could be responsible for the antiferromagnetic interactions. Sintering of the samples also affects the θ value as seen from the heating and cooling curves of the 350H sample.

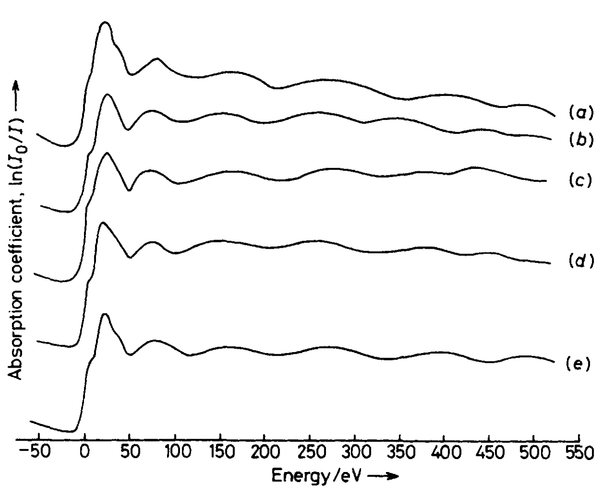

Figure 4. X-Ray K-absorption edge EXAFS of Cr in (*a*) Cr_2O_3, (*b*) 110A, (*c*) 350H, (*d*) 450H, and (*e*) 800H. EXAFS curves have been aligned for zero energy at their main edge inflection points. The energies of these inflection points for Cr_2O_3, 110A, 350H, 450H, and 800H samples are 5 998.0 ± 0.5, 5 995.0 ± 0.5, 5 995.5 ± 0.5, 5 996 ± 0.5, and 5 997 ± 0.5 eV respectively

EXAFS Studies.—Data analysis and results. The raw X-ray absorption data on chromia gels have been summarized in Figure 4, where we have plotted the K-absorption edge EXAFS of chromium in Cr_2O_3 and four chromia gels. During the present experiment we have been able to observe the EXAFS clearly up to ~ 525 eV only. However, beyond this value, the structure became very faint and diffused and it was difficult to obtain accurate values of absorption coefficients. Hence these data were truncated at ~ 525 eV.

For the purpose of data analysis, it is necessary to obtain the normalized fine structure as a function of the photoelectron wavevector, k, in Å^{-1}. We have calculated k by using the relationship $k = [2m/\hbar^2(E - E_0)]^{\frac{1}{2}}$, where E is the X-ray photon energy and E_0 is the X-ray energy corresponding to zero photoelectron energy, and m and $\hbar$ have their usual meaning. In the EXAFS data analysis E_0 has been consistently chosen as 6 010 eV which is beyond the first inflection points of the apparent X-ray absorption edges. An examination of other choices for E_0 showed that the accuracy of the distances obtained was not significantly affected by the choice of E_0 as long as the same value was used throughout.

To extract EXAFS from the raw absorption spectra, the background subtraction was carried out using the method of Lytle *et al.*[12] The data were then multiplied by the Hanning window function [13] in order to minimize the termination ripples, and by a weighting function, k^3, to compensate for amplitude reduction as a function of k. The integrations (integration limits k = 4.00 to k = 11.9 Å^{-1}) for the Fourier transforms, both for the real and imaginary components, were made using Simpson's rule. The modulus of the Fourier transform was obtained as the square root of the sum of the real and imaginary parts. In Figure 5 the Fourier transforms of the background subtracted data are presented. Commercially available crystalline Cr_2O_3 (99.9% pure) was used as the reference compound for the determination [14] of (*i*) the effective phase-shift α_{a-s} (determined as 0.38 Å) which is simply the difference between the observed Fourier-transform

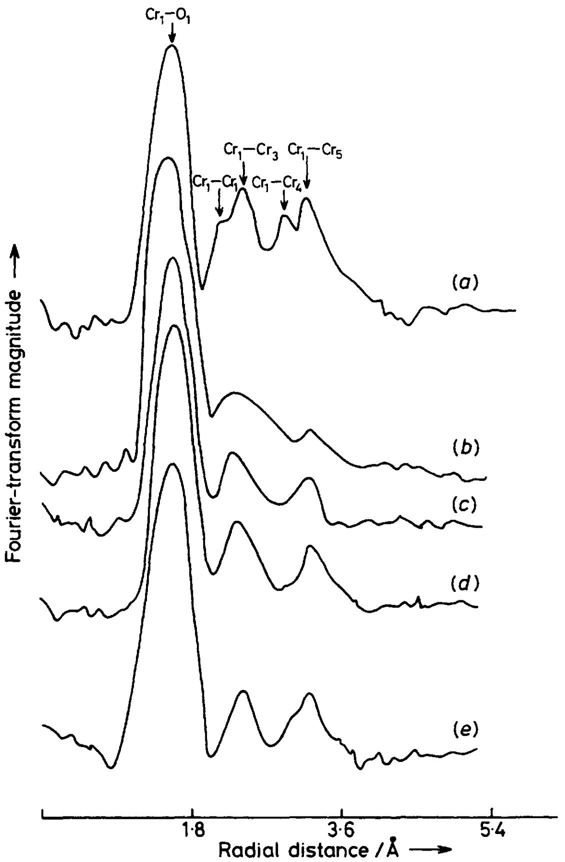

Figure 5. Fourier transforms of EXAFS data on (*a*) Cr_2O_3, (*b*) 110A, (*c*) 350H, (*d*) 450H, and (*e*) 800H

peak position $R_{obs.}$ (1.615 Å) and the known absorber-scatterer distance R_{a-s} (1.995 Å); and (*ii*) the effective per atom magnitude M_{a-s}, which is the observed peak height normalised to the number of scatterers N_s and their distance: $M_{a-s} = (M_{obs.}R_{a-s}^2)/N_s$. The values of α_{a-s} and M_{a-s} for the first co-ordination shell of Cr in Cr_2O_3 are determined from the known values of R_{a-s} and N_s.[11] These values are then used to obtain structural parameters from the Fourier transforms of unknown spectra through simple inversion of the above relations.

The Fourier transforms of the standard crystalline material and some of the investigated samples are shown in Figure 5. The various corrected distances and co-ordination numbers for the samples are given in Table 2. Changes in the integration limits did not shift the positions of the peaks in Figure 5 so that we feel sure that the distances in Table 2 are not computational artefacts. Uncertainties in the peak positions were found to be ±0.03 Å.

From Table 2 all the distances obtained from the reference crystalline Cr_2O_3 samples are in excellent agreement with those obtained by standard crystallographic techniques.[11] The 110A sample shows a first-co-ordination distance of 1.95 Å which is slightly smaller than the corresponding distance in Cr_2O_3,[11] or the Cr−OH distance in α-[4] or γ-CrO(OH).[5,6] The shorter distance could be due to a Cr−OH bond in the sample or due to the presence of Cr^{6+} ions.[1] The second broad peak in this sample (Figure 5) at 2.76 Å probably represents an envelope of the expected[11] Cr_1−Cr_1 (2.65 Å) and Cr_1−Cr_3 (2.89 Å) distance in Cr_2O_3. The broad nature of this peak and rather low intensity is probably due to ill-defined distances outside the first-co-ordination shell in the amorphous material.

Table 2. Chromium–oxygen distances in chromia gels (primed symbols refer to the unknown compounds)

Samples	$R_{obs.}$/Å [a]	$R'_{a-s} = (R'_{obs.} + \alpha_{a-s})$/Å [b]	$M_{obs.}$	$N'_s = (M'_{obs.}R'^2_{a-s})/M_{a-s}$ [c]
Cr_2O_3	1.615	—	10.5	—
110A	1.573	1.953	11.4	6.24
350H	1.601	1.981	11.0	6.19
450H	1.610	1.990	11.1	6.30
800H	1.613	1.993	11.0	6.27

[a] From Fourier-transform methods. [b] Determined from EXAFS; $\alpha_{a-s} = 0.38$ Å. [c] Determined from EXAFS. M_{a-s} was calculated assuming the co-ordination number of Cr^{3+} in Cr_2O_3 to be six. M_{a-s} (normalized) = 6.97 for Cr_2O_3.

There is also a distance at 3.66 Å which is also of very low intensity and which corresponds to the Cr_1−Cr_5 distance in Cr_2O_3.[11] In the case of 350H and 450H the last two peaks are considerably more intense and sharp indicating the onset of crystallisation with considerable short-range order although the Cr_1−Cr_4 line is still absent. The 800H sample shows the appearance of all the distances in Cr_2O_3 although the peaks are not as well resolved. There is no distance around 2.98 Å in any of the samples corresponding to the Cr−Cr distance in CrO(OH).[4-6]

We note from the last column in Table 2 that the co-ordination number as calculated for the first-co-ordination shell is six in all cases. These results clearly indicate (*i*) that the chromium hydrous oxide sample 110A can be written as $Cr[Cr(OH)_6]{\cdot}nH_2O$ or $[Cr(H_2O)_3(OH)_3]{\cdot}nH_2O$ as postulated from t.g.a. studies; (*ii*) the Cr−OH groups condense to form Cr−O−Cr bonds without a loss in the co-ordination number of the central chromium ion; and (*iii*) the hydroxides are dehydrated to microparticulate Cr_2O_3 in a manner similar to the decomposition of crystalline chromium trihydroxide trihydrate studied by Giovanoli and Stadelmann[3] without the formation of a CrO(OH) phase as an intermediate.

We conclude from the above studies that formation of a CrO(OH) phase is not *essential* in the dehydration of hydrous chromium oxides to crystalline Cr_2O_3. The exothermic transition around 400 °C reported by earlier authors and generally associated with crystallisation may instead be associated with the decomposition of β-CrO(OH) to Cr_2O_3, which is known to be exothermic. The origin of β-CrO(OH) in the dehydration sequence of earlier workers is not clear. As mentioned by Giovanoli and Stadelmann,[3] hydrothermal conditions such as the presence of static water vapour (probably condensed in micropores) seem to be necessary. Thus heating in a nitrogen or hydrogen stream (as done by us) could prevent the formation of β-CrO(OH). The similarity of our results with those of Giovanoli and Stadelmann[3] seems to suggest that chromium trihydroxide trihydrate is the species which is first formed in the hydrous chromium oxide precipitates.

Acknowledgements

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References

1 J. Fenerty and K. S. W. Sing, Proc. 1st. Eur. Symp. Therm. Analysis, ed. D. Dollimers, Heyden, London, 1966, p. 304 and refs. therein.

2 P. Ratnasamy and A. J. Leonard, *J. Phys. Chem.*, 1972, **76**, 1838.

3 R. Giovanoli and W. Stadelmann, *Thermochim. Acta*, 1973, **7**, 41.

4 R. M. Douglas, *Acta Crystallogr.*, 1957, **10**, 423.

5 A. Noerlund Christensen, *Acta Chem. Scand., Ser. A*, 1976, **30**, 133.

6 A. Noerlund Christensen, *Mater. Res. Bull.*, 1971, **6**, 691; *Inorg. Chem.*, 1966, **5**, 1452.

7 J. Turkevich, H. Fehrer, and H. S. Taylor, *J. Am. Chem. Soc.*, 1941, **63**, 1129.

8 P. R. Sarode, K. J. Rao, M. S. Hegde, and C. N. R. Rao, *J. Phys. C*, 1979, **12**, 4119.

9 R. Giovanoli, W. Stadelmann, and W. Feitknecht, *Helv. Chim. Acta*, 1973, **56**, 839.

10 S. K. Battacharya, V. S. Ramachandran, and J. C. Ghosh, *Adv. Catal.*, 1957, **9**, 114 and refs. therein.

11 R. E. Newnhem and Y. M. De Hean, *Z. Kristallogr. Kristallgeom., Kristallphys., Kristallchem.*, 1962, **117**, 235.

12 F. W. Lytle, D. E. Sayers, and E. A. Stern, *Phys. Rev., Sect. B*, 1975, **11**, 4825 and refs. therein.

13 G. H. Via, J. H. Sinfelt, and F. W. Lytle, *J. Chem. Phys.*, 1979, **71**, 690.

14 S. P. Cramer, K. C. Hodgson, E. I. Stiefel, and W. E. Newton, *J. Am. Chem. Soc.*, 1978, **100**, 2748 and refs. therein.

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