JOURNAL OF
Materials
CHEMISTRY
Communication

Magnetic properties of CrO_2 prepared by an ambient pressure TiO_2 support assisted synthesis

R. G. Egdell,* E. Brand and D. Kellett

Inorganic Chemistry Laboratory, South Parks Road, Oxford, UK OX1 3QR.
E-mail: russ.egdell@chem.ox.ac.uk

Received 12th August 1999, Accepted 20th September 1999

CrO_2 has been prepared on polycrystalline rutile (TiO_2) supports by thermal decomposition of impregnated $Cr(NO_3)_3$ under ambient pressure conditions to give a material whose saturation magnetisation per Cr ion and coercivity at 5 K are found to be comparable to those for commercial CrO_2 powder used in magnetic recording tape.

Chromium dioxide (CrO_2) is a ferromagnetic material of great commercial importance in magnetic recording media.[1,2] The compound adopts the tetragonal rutile structure, with lattice parameters[3] ($a=b=4.419$ Å; $c=2.917$ Å) somewhat smaller than those characteristic of TiO_2 itself ($a=b=4.593$ Å; $c=2.958$ Å). The transport properties are those of metal. The ferromagnetism is now known to involve complete spin polarisation of the 3d conduction electrons at temperatures below the Curie temperature of 390 K to give a so-called half metallic ferromagnet[4–8] with a saturation magnetisation of $2\mu_B$ per Cr ion. CrO_2 is a somewhat elusive compound, apparently with no range of thermodynamic stability under ambient oxygen partial pressure. Synthetic routes for preparation of CrO_2 involve decomposition of precursor compounds under high oxygen partial pressure,[9–11] often assisted by hydrothermal conditions.[3] It has been known for some time that CrO_2 thin films can be grown on TiO_2 and Al_2O_3 single crystal substrates,[12–14] but again only under high pressure conditions. On the other hand there are recurring reports in the catalytic literature that CrO_2 may be formed under ambient pressures of oxygen when Cr compounds impregnated on high area TiO_2 powder are decomposed under carefully controlled conditions.[15–23] In most of this work the support material is a mixture of the anatase and rutile polymorphs of TiO_2. The existence of CrO_2 supported on TiO_2 has been inferred from a range of techniques including electron paramagnetic resonance and ferromagnetic resonance,[15,19,21,23] XPS[17] and XANES.[22] However, to date the magnetic properties of this novel form of CrO_2 have not been investigated and the material is reported to be amorphous according to XRD.[19] Here, we describe optimised procedures for preparation of nano-crystalline CrO_2 supported on phase-pure rutile TiO_2 using only ambient oxygen partial pressures and present magnetisation measurements for the supported CrO_2. The saturation magnetisation observed at 5 K is about 75% of the limiting value of $2\mu_B$ per Cr ion found for macroscopic samples of CrO_2.

The phase–pure rutile (TiO_2) support material was prepared by heating high area anatase TiO_2 (Johnson Matthey 99.99%, measured BET surface area 16 $m^2\,g^{-1}$) at 800 °C for 24 h. The resulting material had a BET surface area of 1.9 $m^2\,g^{-1}$. This equates to a mean particle size of 760 nm, in agreement with observations of XRD line broadening. Impregnated samples with a Cr weight fraction in the final product ranging between 0.8 and 20% were made by mixing rutile powder with appropriate volumes of aqueous solutions of $Cr(NO_3)_3{\cdot}9H_2O$ (Johnson Matthey Putratonic Grade). The sample described in detail here was prepared from 5 g of rutile powder and 12.5 dm^3 of a solution 1 M in Cr(III), the chromium content of solutions being confirmed by inductively coupled plasma emission spectroscopy. The resulting slurry was stirred vigorously for 2 h and was then dried at 115 °C for 15 h. Decomposition of the $Cr(NO_3)_3$ was achieved by heating the dried powder under flowing N_2 at 320 °C for 12 h, cooling to 120 °C and then reheating to 320 °C for 12 h under flowing O_2. This heating cycle proved to be optimal in achieving a maximum magnetic susceptibility.

Fig. 1 shows the X-ray powder diffraction pattern in the region of the (110) reflections of TiO_2 and CrO_2 from a sample with a 10.7% weight loading, corresponding to a Cr/Ti molar ratio of 0.17/0.83. The powder pattern clearly demonstrates the presence of CrO_2 although the peak is weaker than expected if all the Cr were present as crystalline CrO_2. The powder pattern for the material obtained by decomposing pure $Cr(NO_3)_3{\cdot}9H_2O$ under identical conditions contained only a broad hump centred at about $2\theta=26°$, characteristic of an essentially amorphous material. Similarly decomposition of $Cr(NO_3)_3{\cdot}9H_2O$ supported on the anatase form of TiO_2 gave a material in which no CrO_2 diffraction peaks were present and with a limiting magnetisation (see below) very much lower than that of CrO_2 supported on rutile with an identical CrO_2 layer thickness. These observations provide evidence that the rutile support exerts a well defined template effect in promoting

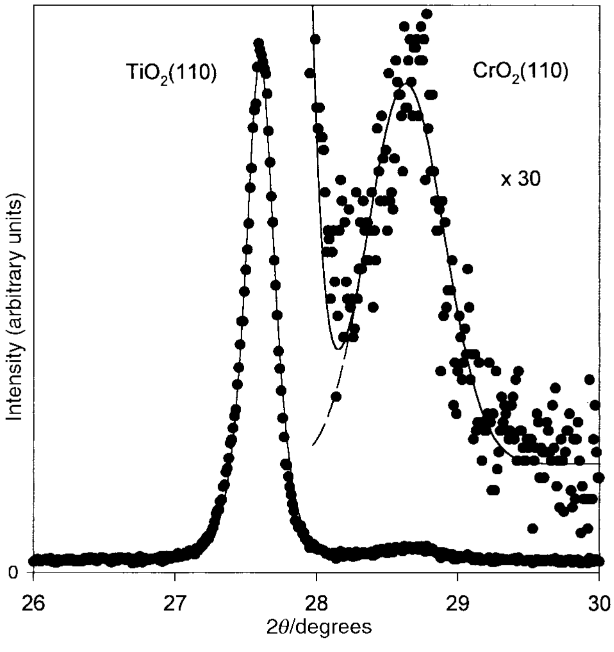

Fig. 1 X-Ray diffraction profile for 10.7% Cr loaded TiO_2, prepared as described in text in the region of the TiO_2 and CrO_2 (110) reflections. The dots are experimental data points and the solid line is fit to two Voigt profiles. The dashed line shows the Voigt profile for the CrO_2 reflection.

formation of CrO_2 under conditions where the oxide is not as thermodynamically stable as a bulk phase. As expected the $CrO_2(110)$ reflection became weaker and broader for lower Cr loadings, owing to the decreasing thickness of the CrO_2 overlayer. However, it was also found that the CrO_2 reflections became weaker at higher sample loading. Thus the loading of around 10% by weight of Cr is optimal in maximising the intensity of the CrO_2 diffraction peak. This suggests that templated growth of CrO_2 is only promoted over a limited range of thickness.

Assuming uniform coverage of the underlying TiO_2 substrate, the thickness of the CrO_2 layer should be about 25 nm. This thickness would produce 0.32° broadening in X-ray diffraction, as compared with 0.63° observed experimentally. A coherent and uniform film of this thickness would be expected to produce essentially complete attenuation of core level structure, owing to Ti, in Al-Kα X-ray photoelectron spectroscopy. In fact a weak Ti 2p doublet remained, with a cross-section corrected Cr 2p/Ti 2p area ratio of 9.9. This is almost a factor of 50 bigger than the value of 0.20 expected for a simple mixture of 17% CrO_2 and 83% TiO_2, indicating *almost complete* but *not perfect* encapsulation of the TiO_2 substrate. The Cr $2p_{3/2}$ peak was fitted to two components at binding energies of 577.0 and 579.2 eV. The former energy is intermediate between values[24] of 576.6 eV reported for Cr_2O_3 and 580.1 eV for CrO_3. We take the peak at 577.0 eV to be representative of the Cr(IV) oxidation state in CrO_2, although it should be recognised that the intrinsic peak-shape in CrO_2 will be complex owing to the narrow band metallic nature of the material.[25] The peak at 579.2 eV is attributed to chromate-like Cr(VI) species on the surface of the CrO_2. The relative intensity of this latter peak increased strongly for lower Cr loadings.

Magnetisation curves for a 10.7% Cr loaded sample taken in a SQUID magnetometer at 5 and 300 K are shown in Fig. 2(a). At 5 K the magnetisation approaches 1.5 μ_B per Cr ion at high field. This is 75% of the saturation magnetisation for bulk CrO_2. The approach to saturation magnetisation is somewhat slower as a function of field than for ferromagnetic CrO_2 powder used in magnetic recording media, but the magnetisation even at low field is clearly much larger than for a simple paramagnetic system. We are probably in a regime intermediate between simple bulk ferromagnetism and the superparamagnetism exhibited by finely divided ferromagnetic materials whose particle size becomes very much smaller than the domain size characteristic of the ferromagnetic state.[26] The limiting magnetisation at room temperature is 0.838 μ_B per Cr ion. Fig. 2(b) and (c) show the magnetisation at low field in greater detail. Significant hysteresis is observed at 5 K. At this temperature the remanent magnetisation is 0.345 μ_B per Cr ion and the coercive field H is such that $\mu_0 H = 0.045$ T. This latter value compares with typical values of $\mu_0 H$ of *ca.* 0.1 T for CrO_2 powder used in commercial magnetic recording tape:[27] this material typically consists of acicular grains of dimension 300 × 40 nm. However at 300 K the remanent magnetisation has decreased to only 0.045 μ_B per Cr ion and the coercivity shows a comparable order of magnitude decrease such that $\mu_0 H = 0.005$ T. This behaviour contrasts with the bulk CrO_2 powder where the room temperature coercivity is usually about 0.05 T *i.e.* roughly half the value at 5 K. The hysteresis of the composite material at 5 K decreased rapidly with decreasing Cr loading. This again appears to be an effect related to the layer thickness: sufficiently thin layers should exhibit superparamagnetic behaviour wherein the magnetisation is much higher than for a simple paramagnetic system but the hysteresis characteristic of the true ferromagnetic state tends toward zero even at low temperatures.

In summary, we have demonstrated that CrO_2 supported on TiO_2 exhibits saturation magnetisation and magnetic hysteresis at 5 K comparable to those of bulk CrO_2. However, the new material becomes much softer magnetically at 300 K than conventional CrO_2 powder. The method of synthesis allows for considerable flexibility in tuning the magnetic properties: both the thickness of the CrO_2 overlayer and the particle size in the TiO_2 support are easily controlled. The dependence of the magnetisation behaviour on these and other parameters will be reported in greater detail elsewhere.

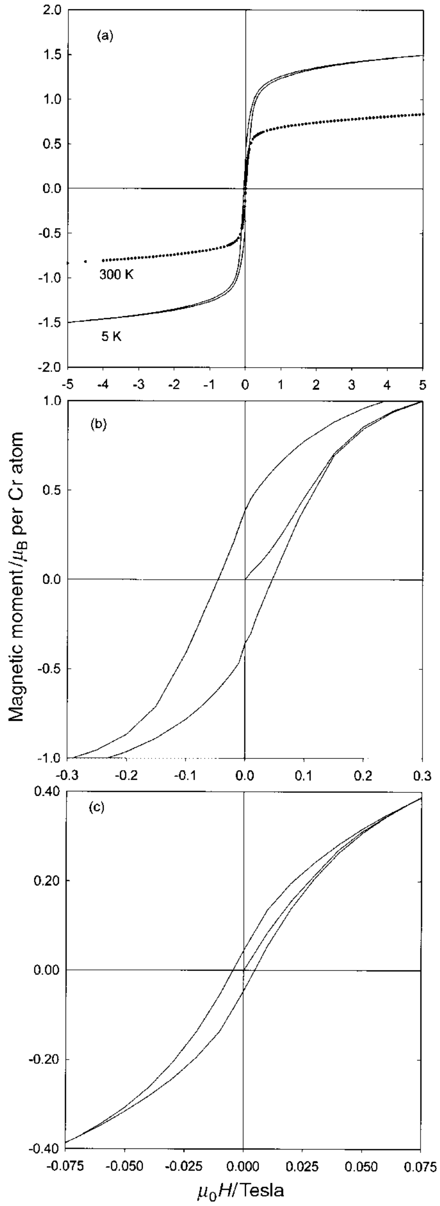

Fig. 2 (a) Magnetic hysteresis loops for 10.7% Cr loaded TiO_2 at 300 K (dotted line) and at 5 K (solid line). (b) Expanded view of the low field hysteresis loop at 5 K. (c) Expanded view of the low field hysteresis loop at 300 K. Note that the scales are different to those in (b).

Notes and references

1 D. Jiles, *Introduction to Magnetism and Magnetic Materials*, Chapman and Hall, London, 1991.
2 G. Bate, in *Ferromagnetic Materials*, ed. E. P. Wohlfarth, North Holland, Amsterdam, 1980, vol. 2.
3 T. J. Swoboda, P. Arthur, N. L. Cox, J. N. Ingraham, A. L. Oppegard and M. S. Sadler, *J. Appl. Phys.*, 1961, **32**, 374S.
4 P. A. Cox, *Transition Metal Oxides*, Clarendon Press, Oxford, 1992.
5 K. Schwarz, *J. Phys. F: Met. Phys.*, 1986, **16**, L211.
6 K. P. Kämper, W. Schmitt, G. Güntherodt, R. Gambino and R. Ruf, *Phys. Rev. Lett.*, 1987, **59**, 2788.
7 S. P. Lewis, P. B. Allen and T. Sazaki, *Phys. Rev. B: Condens. Matter*, 1997, **55**, 10 253.

8 T. Tsujioka, T. Mizokawa, J. Okamoto, A. Fujimori, M. Nohara, H. Takagi, K. Yamura and M. Takano, *Phys. Rev. B*, 1997, **56**, R15509.

9 B. Kubota, *J. Phys. Soc. Jpn.*, 1960, **15**, 1706.

10 B. Kubota, *J. Am. Ceram. Soc.*, 1961, **44**, 239.

11 B. L. Chamberland, *CRC Crit. Rev. Solid State Mater. Sci.*, 1977, **7**, 1.

12 R. C. DeVries, *Mater. Res. Bull.*, 1966, **1**, 83.

13 H. Brändle, D. Weller, S. S. P. Parkin, J. C. Scott, P. Fumagalli, W. Reim, R. J. Gambino, R. Ruf and H. J. Güntherodt, *Phys. Rev. B: Condens. Matter*, 1992, **46**, 13 889.

14 L. Ranno, A. Barry and J. M. D. Cooey, *J. Appl. Phys.*, 1997, **81**, 5774.

15 K. Köhler, C. W. Schlapfer, A. von Zelewsky, J. Nickl, J. Engweiler and A. Baiker, *J. Catal.*, 1993, **143**, 201.

16 J. Engweiler, J. Nickl, A. Baiker, K. Köhler, C. W. Schlapfer and A. von Zelewsky, *J. Catal.*, 1994, **145**, 141.

17 U. Scharf, H. Schneider, A. Baiker and A. Wokaun, *J. Catal.*, 1994, **145**, 464.

18 H. Schneider, U. Scharf, A. Wokaun and A. Baiker, *J. Catal.*, 1994, **147**, 545.

19 K. Köhler, M. Maciejewski, H. Schneider and A. Baiker, *J. Catal.*, 1995, **157**, 301.

20 H. Scheider, M. Maciejewski, K. Köhler, A. Wokaun and A. Baiker, *J. Catal.*, 1997, **157**, 312.

21 K. Köhler, J. Engweiler, H. Viebrock and A. Baiker, *Langmuir*, 1995, **11**, 3423.

22 T. Schedel-Niedrig, T. Neisius, C. T. Simmons and K. Köhler, *Langmuir*, 1996, **12**, 6377.

23 K. Köhler, W. Mörke and T. Bieruta, *Colloids Surf. A*, 1998, **144**, 81.

24 D. Briggs and M. P. Seah, *Practical Surface Analysis*, Wiley, Chichester, 2nd edn., 1990.

25 N. Beatham, P. A. Cox, R. G. Egdell and A. F. Orchard, *Chem. Phys. Lett.*, 1980, **69**, 475.

26 D. L. Leslie-Pelecky and R. D. Rieke, *Chem. Mater.*, 1996, **8**, 1770.

27 J. M. D. Coey, A. E. Berkowitz, L. Balcells, F. F. Putris and A. Barry, *Phys. Rev. Lett.*, 1998, **80**, 3815.

Communication 9/06556C