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A structural, thermogravimetric and magnetic study of the WO_x–TiO_2 system

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TiO_2 unit cell parameter determinations, thermogravimetric measurements and magnetic susceptibility data (over the temperature range 78 to 300 K) were used to investigate samples of titanium dioxide containing a small percentage (up to 5% molar ratio) of tungsten dioxide. The samples were prepared by heating pellets of mixture of the appropriate dioxides in an evacuated silica tube at 1223 K. The results show that tungsten is incorporated in the rutile structure in the 4+ oxidation state and causes an expansion of the TiO_2 unit cell volume. The expansion is anisotropic: while *a* increases with the tungsten content, *c* decreases. The magnetic data as well as the distortion of the TiO_2 unit cell point out to the existence of metal–metal interactions among the tungsten ions that are not randomly incorporated in the TiO_2 matrix.

1. Introduction

The interest in TiO_2 and its solid solutions has recently increased. In fact, in addition to the well known scientific and technological importance of this material in several areas, such as solid state chemistry [1] and surface chemistry [2], titanium dioxide may play an important role in photocatalysis [3]. In particular, the influence of some parameters such as oxygen pressure and temperature conditions on the incorporation of tetravalent ions into the rutile structure was discussed [4]. It was also found that, depending on the nature of the dissolved species, the usual assumption of the random distribution of the dissolved species in the host matrix may not be verified, even in the case of dilute solid solutions [5, 6].

In the present paper, titanium dioxide with a small addition of tungsten dioxide is studied by X-ray diffraction, thermogravimetric and magnetic techniques in order to gain information on the solid solution formation and on the distribution of the incorporated species. Indeed, WO_2 has a monoclinic, rutile type distorted structure, where strong metal–metal bonds are present [7].

Few studies concerning the system tungsten oxides–titanium dioxide have been reported. In addition to a paper on WO_2–TiO_2 solid solutions analyzed by magnetic technique [8], the system tungsten dioxide–titanium dioxide has been investigated at high temperatures ($T > 1673$ K) to examine the melting relations against composition [9]. W(V) in TiO_2, single crystal, has been also studied by electron spin resonance (ESR) [10].

2. Experimental

2.1. Samples

The samples were prepared from WO_2 and titanium dioxide. WO_2 was prepared according to a previously described procedure [11]. Metallic tungsten (Merk) and WO_3 (Suchard) were mixed in the stoichiometric ratio. After grinding, the powder was pelleted $\simeq 5 \times 10^8$ Pa) and the pellets heated in an evacuated silica tube at 1273 K for a week. At the end of the thermal treatment the tube was quenched to room temperature in water and the samples exposed to air. From X-ray analysis the sample resulted to be WO_2 containing traces of W metal and $W_{18}O_{49}$. The latter was transformed to WO_2 by heating in a hydrogen stream at 723 K. At this temperature $W_{18}O_{49}$ is reduced to WO_2, but the dioxide is not reduced to metallic tungsten, as observed directly in a thermogravimetric apparatus in a hydrogen stream.

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The X-ray pattern of the sample after the reduction treatment showed the WO_2 reflections and traces of metallic tungsten.

TiO_2 of different sources was used. A first material (A) was obtained by hydrolysis and oxidation of $TiCl_3$ as previously reported [12]. It resulted to be contaminated by iron at the 100 to 200 ppm level. A second material (B) was supplied by Tioxide Int. Ltd (stated impurities in ppm calcium < 20, $ZnO < 20$, iron $\simeq 10$, tin < 20, $Al_2O_3 < 100$, $SiO_2 < 100$, $P_2O_5 \simeq 110$, $SO_3 < 100$, $ZrO_2 \simeq 80$, lead $\simeq 20$, $K_2O \simeq 20$, $Nb_2O_5 < 10$, $Sb_2O_3 \simeq 50$, chlorine $\simeq 140$, sodium $\simeq 180$). In order to remove most of the water, both A and B samples were heated at 673 K for 2 h in air. The obtained products were used to prepare the tungsten-doped titanium dioxide samples. They were prepared by mixing weighed amounts of titanium dioxide and WO_2 in an acetone slurry by prolonged grinding in an agate mortar. After removal of the acetone by heating at 473 K in air for 2 h, the dried powder was pelleted (approximately 5×10^8 Pa). The pellets were sealed inside an evacuated silica tube and gradually heated at 873 K for 24 h, 1073 K for 24 h and then at 1223 K for 96 h. At the end of the thermal treatment, the silica tube was quenched to room temperature, dropping it in water and then the pellets were exposed to air. In order to remove the tungsten possibly present as a separate phase, both as metal and in the oxidic form, the samples were submitted to the following washing treatment. Each specimen was contacted with *aqua regia* for 0.5 h at a temperature at which a gentle evolution of gas was observed. In this way metallic tungsten and oxides containing tungsten with oxidation number lower than six were oxidized to WO_3 [13a]. After separation of the liquid fraction, the solid was rinsed with a NaOH solution of $1\ \text{mol dm}^{-3}$ in order to dissolve the WO_3 [13b]. The solid was then further washed with water and dried at 353 K in air. The samples appeared blue, with the colour intensity increasing with the tungsten content. Undoped TiO_2, both A and B preparation, was submitted to the same heating procedure and resulted slightly grey. The specimens containing tungsten are designated TW, the figure after the letters indicates the tungsten nominal content expressed as W atoms per 100 titanium atoms. The letters A and B after the figure, denote samples prepared by TiO_2 from hydrolysis or obtained from Tioxide.

2.2. Chemical analysis

Tungsten analysis was performed by atomic absorption [14]. A weighed portion of the sample was dissolved with 5 ml of hydrogen fluoride solution ($\simeq 40\%$) in a digestion bomb (Perkin Elmer Autoclave-3) at 423 K for 0.5 h. The tungsten standard solutions prepared by a standard 1000 ppm Na_2WO_4 (Ventron), contained TiO_2 (dissolved with HF) in a concentration comparable to that present in the solutions of the samples.

2.3. X-ray

A Debye-Scherrer camera, i.d. 114.6 mm, was used to obtain the powder diffraction patterns. Unit cell parameters of TiO_2 were measured with $\text{Co}K\alpha_1$ (Fe-filtered) radiation, as previously described [12]. Phase analysis was carried out with $\text{Cu}K\alpha$ (Ni-filtered) radiation.

2.4. Magnetic measurements

The magnetic susceptibility was measured by the Gouy method at 4000, 6000 and 8000 G in the temperature range 78 to 300 K. A semi-microbalance, reading to ± 0.05 mg was employed. The instrument was calibrated with $Hg[Co(CNS)_4]$ [15]. The magnetic susceptibility of undoped TiO_2 was determined with the same apparatus. For each measurement about 3 g of sample was used in order to have a reliably measurable change in weight. Details of the measurements were reported previously [12].

2.5. Thermogravimetric measurements

Thermogravimetric determinations were performed in flowing air ($25\ \text{ml min}^{-1}$) by a Cahn RG electrobalance. The temperature was raised linearly up to 1173 K ($3\ \text{deg min}^{-1}$).

3. Results

3.1. Chemical analysis

The results of the chemical analysis are shown in Table I. For all samples a tungsten content close to the nominal value was found.

3.2. X-ray

Undoped TiO_2 and tungsten-doped samples only showed the rutile reflections on the powder diffraction patterns. Table I gives the results of the determinations of the TiO_2 unit cell parameter a and the axial ratio $C = c/a$. Both A and B preparations of TiO_2 gave close values of a and C. For the doped specimens, as the tungsten content increases, the

TABLE I Analytical, thermogravimetric and X-ray diffraction data for TiO_2 containing tungsten dioxide

Samples*	[W]†	$\%\Delta^{exp.}_{973-1173}$	$\%\Delta^{calc.}$‡	a_{291} (nm)	C
TiO_2A	–	–	–	0.45928	0.6444
TW 0.5A	0.64	0.12	0.12	0.45948	0.6440
TW 1A	1.00	0.19	0.19	0.45953	0.6440
TW 3A	2.70	0.49	0.50	0.46013	0.6424
TW 4A	3.60	0.63	0.66	0.46044	0.6419
TW 5A	4.62	0.79	0.82	0.46065	0.6415
TiO_2B	–	–	–	0.45925	0.6443
TW 0.5B	0.50	0.09	0.09	0.45941	0.6441
TW 1B	0.96	0.19	0.19	0.45959	0.6436
TW 3B	2.88	0.53	0.54	0.46018	0.6426
TW 5B	4.56	0.84	0.81	0.46077	0.6413

*For samples designation see text.

†Concentration expressed as W atoms per 100 Ti atoms.

‡Calculated from the analytical data (see text).

unit cell parameter a increases while the axial ratio C decreases. The variation of the TiO_2 unit cell volume $V = a^3C$ is linear with the analytically determined tungsten concentration, Fig. 1.

3.3. Thermogravimetric analysis

No appreciable weight variation was detected on thermograms of undoped TiO_2 A or B. For the tungsten-containing samples an increase in weight was observed in the temperature range 973 to 1173 K. The weight variation was found to be dependent on the tungsten content and is reported in Table I as a percentage, $\%\Delta^{exp}_{973-1173}$.

Thermogravimetric measurements in air were also carried out on pure WO_2 and WO_3. For WO_2 an increase in weight corresponding to the reaction

$$WO_2 + 1/2O_2 \longrightarrow WO_3$$

was found in the temperature range 773 to 973 K. For WO_3, no variation of weight was observed up to 1173 K. In both cases a slight loss in weight was observed at temperatures higher than 1173 K caused by WO_3 sublimation [16].

3.4. Magnetic measurements

Only specimens based on B-TiO_2 were considered for the magnetic study. In fact, due to iron impurities present in the TiO_2 obtained from $TiCl_3$ hydrolysis, the magnetic susceptibility of A-TiO_2 was field dependent.

For the samples prepared with TiO_2 from Tioxide, the specific magnetic susceptibility (magnetic susceptibility × specific volume) measured in the range 100 to 300 K was found to be very low of the order of 10^{-7} cgs units, practically coincident with that of undoped TiO_2 [5] and independent of the tungsten content.

4. Discussion

Several evidences point out that tungsten enters in

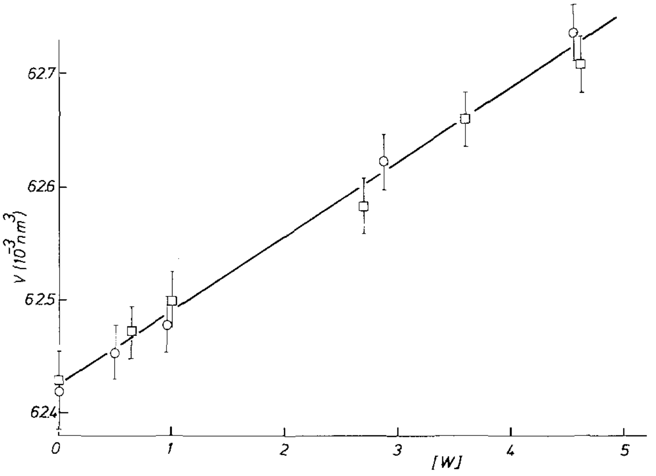

Figure 1 Variation of the TiO_2 unit cell volume V against the tungsten content. □ – TW A; ○ – TW B.

solid solution in TiO_2, rutile. First, the analytical results, Table I, show that, despite the treatment with *aqua regia* and subsequently with NaOH solution, for all samples the tungsten content is close to the nominal value. It is recalled that the washing treatment is able to dissolve the tungsten present as a separate phase, both as metal and in the oxidic form [13] but does not affect sintered TiO_2. The result is therefore a clear indication of the solid solution formation. Second, the X-ray diffraction analysis shows only the rutile reflections even in the patterns of the more concentrated specimens. Third, the TiO_2 unit cell parameter a and the axial ratio C change as the tungsten content increases, Table I.

As far as the oxidation state of the incorporated species is concerned, the thermogravimetric data indicate that tungsten is dissolved into the TiO_2 structure as W(IV). In fact, the experimental increase in weight in the temperature range 973 to 1173 K, $\%\Delta^{\text{exp.}}_{973-1173}$, Table I, agrees very well with the values, $\%\Delta^{\text{calc.}}$, calculated on the basis of the following reaction:

$$Ti_{(1-x)}W_xO_2 + x/2\,O_2 \longrightarrow (1-x)TiO_2 + xWO_3.$$

It may be noted that the oxidation of the W(IV) in TiO_2 occurs at higher temperatures and in a wider range than in the case of pure WO_2. This fact is a further indication of the solid solution formation. Indeed, as shown previously for several cases [17, 18], the host structure has a protective effect on the guest species against redox processes. The tungsten incorporation in the 4+ oxidation state is also in agreement with the extent of the TiO_2 unit cell volume expansion. As Fig. 1 shows, the TiO_2 unit cell volume V increases as the tungsten content in solid solution increases. This behaviour is accounted for by considering the ionic radii of the involved species, i.e. $r_{\mathrm{Ti(IV)}} = 0.0605\,\mathrm{nm}$, $r_{\mathrm{W(IV)}} = 0.066\,\mathrm{nm}$ [19]. It must be also added that if tungsten were incorporated as W(V) an expansion of the TiO_2 unit cell volume should also be expected. In fact the value 0.062 nm has been reported for the ionic radius of this species and, because of the electroneutrality requirements, an equivalent amount of Ti(III), $r_{\mathrm{Ti(III)}} = 0.067\,\mathrm{nm}$ [19], should be considered. However, the data allow to rule out the latter possibility. In fact it has been shown [20] that the following relation,

$$\Delta V_{1\%} = K(r_i^3 - r_{\mathrm{Ti(IV)}}^3)$$

holds between the variation on V caused by the incorporation of 1% atomic of species i, $\Delta V_{1\%}$, and the difference of the cubes of the ionic radii of the involved species. Since $K \simeq 1$, using the values of the ionic radii reported by Shannon [19] the following values for $\Delta V_{1\%}$ are obtained: for the incorporation of W(IV) replacing Ti(IV) $\Delta V_{1\%} = 0.66 \times 10^{-4}\,\mathrm{nm}^3$ while in the case of W(V) + Ti(III) replacing two Ti(IV), $\Delta V_{1\%} = 0.96 \times 10^{-4}\,\mathrm{nm}^3$. From Fig. 1 an experimental value of $\Delta V_{1\%} = 0.65 \times 10^{-4}\,\mathrm{nm}^3$ is obtained, in very good agreement with that calculated for the incorporation as W(IV).

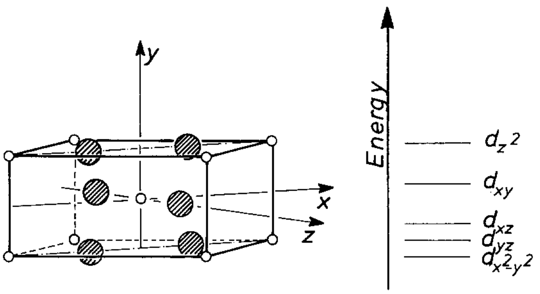

Figure 2 TiO_2 unit cell with the definition of the axes and schematic energy-level splitting for the central ion *d*-orbitals.

In order to account for the magnetic behaviour, it may be recalled that W(IV) is a $5d^2$ ion and that in TiO_2, rutile, the Ti(IV) site is only approximately octahedral, being in fact D_{2h}. With reference to the x, y, z axes shown in Fig. 2, the splitting of the d-orbitals is schematically indicated [21]. If the W(IV) are randomly dispersed in the TiO_2 matrix, the two electrons per tungsten ion should be unpaired. On the contrary, if the tungsten ions are incorporated in pairs in adjacent sites along the c-axis, metal–metal interactions may occur causing the pairing of the two electrons. Indeed, the two lowest energy orbitals are oriented in such a way to be particularly suitable for interaction between W(IV) ions along the c-axis, Figs. 3a and b. The situation is analogous to that reported for pure WO_2 [22, 23]. It must be noted, however, that the cation–cation separation along the c-axis is 0.296 nm. Such a distance, though larger than that corresponding to W–W bonds present in pure WO_2 (0.249 nm [24]), may be short enough for a metal–metal interaction to be present. In fact it has been shown [5, 6] that a similar metal–metal interaction exists in the case of the isoelectronic Mo(IV) incorporated in TiO_2, even at high dilution [6]. In comparison with the molybdenum case, in the present situation a much stronger metal–metal

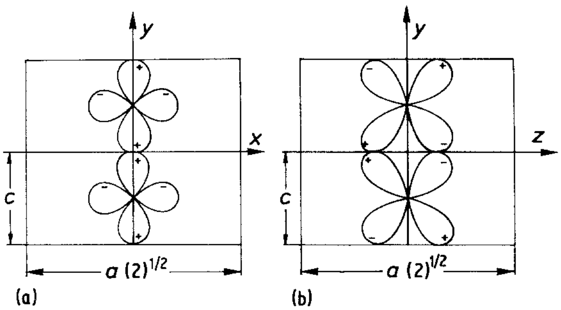

Figure 3 Cross section of the rutile double unit cell showing the interaction between two tungsten ions. (a) cross section in the xy plane: $d_{x^2-y^2}$ orbital. (b) cross section in the zy plane: d_{yz} orbital.

interaction is operating. In fact, whereas for the $Ti_{(1-x)}Mo_xO_2$ system a decrease on the magnetic moment at increasing molybdenum content was found [5], in the present case no appreciable paramagnetic contribution was measured. On the other hand, a stronger metal–metal interaction for tungsten compared to molybdenum should be expected since the former has more expanded d-orbitals.

The formation of WO_2–TiO_2 solid solution in the range of a small percentage of W(IV) is in agreement with the results of Aryia and co-workers [8]. However, they report somewhat different results concerning the magnetic behaviour. In fact a magnetic moment approaching the spin-only value ($2.84\,\mu_B$) was reported. Furthermore for this sample a linear variation of χ^{-1}_{molar} against T (Curie law) was observed. In our case, for the specimen TW 0.5B as well as for the more concentrated ones a specific susceptibility coincident with that of undoped TiO_2 and practically independent of the temperature was measured. At the moment no explanation is given for the difference. It may be only noted that in the present case the incorporation in pairs takes place even at low tungsten content. Finally, the formation of pairs, due to the metal–metal interaction along the c-axis, explains the contraction of the c parameter determined for samples with increasing tungsten content, Fig. 4.

In conclusion, by the combined use of X-ray diffraction, thermogravimetric, analytical and magnetic susceptibility data, it was shown that tungsten is incorporated as W(IV) in the rutile structure. However, the solid solution formed is not random. A similar situation has been found for other d^2 ions such as V(III) in α-Al_2O_3 [25] and Mo(IV) in TiO_2 [5, 6]. However, for $Al_{2-x}V_xO_3$ and $Ti_{(1-x)}Mo_xO_2$ systems the value of x affects the degree of pairing, as deduced from the variation of the magnetic moment values observed at different content of the magnetic species. In the present case, stronger metal–metal interactions are observed, since no paramagnetic contribution to the magnetic susceptibility was measured even for the less concentrated specimen, (TW 0.5B).

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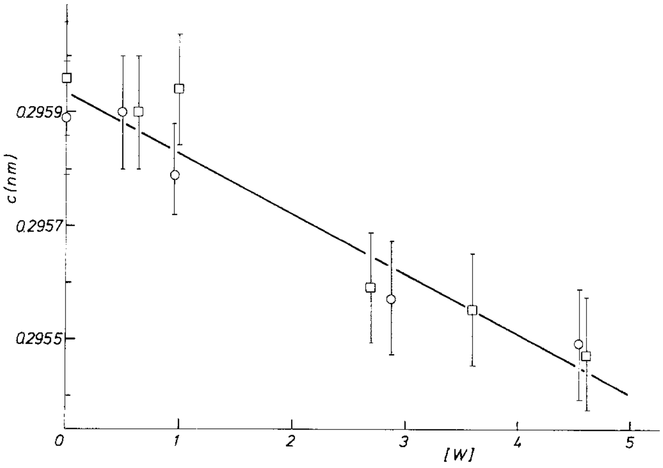

Figure 4 Variation of the TiO_2 unit cell paraeter c against the tungsten content. □ – TW A; ○ – TW B.

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