

# Structural Changes of Titanium Oxide Induced by Chromium Addition as Determined by an X-Ray Diffraction Study

A. M. Venezia<sup>1</sup>

*Dipartimento di Chimica Inorganica dell'Università di Palermo, Via Archirafi, 26-28, 90123 Palermo, Italy*

and

L. Palmisano and M. Schiavello

*Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy*

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An X-ray diffraction study has been carried out on a series of polycrystalline TiO<sub>2</sub> (anatase) catalysts containing Cr(III) at different atomic concentrations (0.2–5.0 at.%), prepared by a coprecipitation method. Analysis of the variation of the unit cell parameters of chromium-doped anatase with respect to pure anatase has allowed us to estimate the solubility limit for the system at around 1.4 at.%. There is no evidence for the existence of a separate crystalline chromium oxide phase. Temperature effects on the cell parameter and on the anatase–rutile transformation rate were also analyzed. An increase in temperature produced release of the chromium from the solid solution. At the same time, an acceleration in the rate of the anatase-to-rutile phase transition was observed. © 1995 Academic Press, Inc.

## INTRODUCTION

The Cr<sub>x</sub>O<sub>y</sub>-TiO<sub>2</sub> system has received much attention, specifically in the field of photocatalysis (1–4). Doping with Cr(III) improves the charge separation of the photo-produced hole–electron pairs because a permanent electric field is present. Recently the surface atomic structure and the Lewis and Brønsted acid sites, important for photocatalytic activity, have been determined by UV, XPS, and IR studies (3–5). It has been concluded that the bulk of the catalysts contained essentially Cr(III), whereas their surfaces contained two species of chromium ions, Cr(III) and small amounts of Cr(VI). Chromium ions in the higher oxidation state, associated with surface Brønsted acid sites, increased with chromium concentration and were easily reduced to Cr(III) by X-ray bombardment. Addition of chromium to titanium oxide in the anatase or rutile phase modifies the bulk structure and the surface proper-

ties in a way which is dependent on the experimental procedure used for catalyst preparation (4, 5).

Several studies on the solid state chemistry of titanium oxide and chromium oxide have dealt with magnetic (6, 7), interdiffusion (8), solubility (9), electric (10), and spectroscopic properties (11). While these studies deal with high-temperature behavior, mainly in the rutile crystalline phase, a detailed structural characterization of the anatase–chromium system has not been carried out. For a better understanding of the photocatalytic behavior previously described, a complete structural characterization of this system is essential; in particular, the anatase phase has been shown to be more suitable than the rutile phase for several photocatalytic reactions (3, 4).

The present study deals with the X-ray diffraction analysis of chromia–anatase catalysts containing different amounts of chromium. Changes in the crystal structure of the host TiO<sub>2</sub> produced by chromium addition are related to the formation of a solid solution and provide information on the solubility limit of chromia in the anatase phase. The effect of chromium on the anatase-to-rutile phase transformation temperature has been also investigated.

## EXPERIMENTAL

Catalysts containing different amounts of chromium have been prepared by coprecipitation. Aqueous solutions of TiCl<sub>3</sub> (15% Carlo Erba) containing the required amount of Cr(III) (Cr(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O, Merck) were reacted with aqueous solutions of ammonia (25 wt% Merck). The solids were filtered, washed, and then left standing for 24 hr at room temperature. Then they were dried at 120°C for 24 hr and finally fired in air for 24 hr at 500°C. The coprecipitated catalysts are designated TC-CP followed

<sup>1</sup> To whom correspondence should be addressed.

by a number expressing the chromium concentration as number of Cr atoms/100 titanium atoms. The following concentrations were used: 0.2, 0.5, 1.0, 2.0, and 5.0 at.%.  $\text{TiO}_2$  anatase was obtained from  $\text{TiCl}_3$  with a procedure similar to that used for the TC-CP catalysts without the addition of chromium nitrate.

Separate samples of the catalysts TC-CP0.5, TC-CP5, and pure anatase underwent thermal treatment at 550, 600, 650, 700°C after being fired in air at 500°C. During the heat treatments, performed in air, the samples were placed in a horizontal furnace in a quartz tube. The temperature was controlled to within  $\pm 5^\circ\text{C}$ .

The X-ray diffraction measurements were carried out with a North American Philips X-ray diffractometer using  $\text{CuK}\alpha$  radiation. The diffracted beam was monochromatized with a focusing graphite monochromator. A proportional counter and a  $0.005^\circ$  step size in  $2\theta$  were used.

## RESULTS

The X-ray diffraction patterns of all catalysts were typical of the anatase phase, and no presence of crystalline chromium oxide was detected. The samples containing 2 and 5 at.% chromium exhibited slight evidence of the rutile structure.

To derive the anatase unit cell parameters  $a$  and  $c$ , the following reflections ( $hkl$ ) were recorded (the  $2\theta$  angles are given in parentheses): 004(37.86), 200(48.07), 215(75.10), 301(76.05), 316(107.53), and 400(109.01). For the rutile phase, the following reflections were considered: 200(39.31), 211(54.45), 220(56.70), 301(69.09), 112(69.93), 222(89.67), and 330(90.77). A graphical method of extrapolation versus  $1/2 (\cos^2\theta/\sin\theta + \cos^2\theta/\theta)$  followed by a least-squares technique was used (12). Three measurements were performed and the reproducibility of the lattice parameters  $a$  and  $c$  was  $\pm 0.0001$  and  $\pm 0.001$  Å, respectively. The higher accuracy in the determination of parameter  $a$  with respect to parameter  $c$  is due to the occurrence at a very high angle of one reflection, the 400, which is independent of parameter  $c$ . Consequently, the

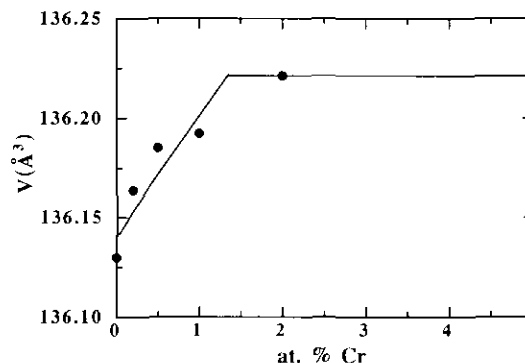


FIG. 1. Variation with chromium atomic percentage of the unit cell volume  $V$  of the anatase lattice; the dots represent the experimental points; the first region of the continuous line is the linear least-squares fit to the experimental points.

uncertainty in the volume  $V$  ( $V = a^2c$ ) of the unit cell was  $\pm 0.02$  Å<sup>3</sup>.

The anatase cell parameters  $a$  and  $c$  derived for the samples with different chromium atomic concentrations are listed in Table 1. The axial ratio  $C = c/a$  is also included. Whereas the  $a$  parameter in the catalysts increases with chromium content up to 1 at.%, the  $c$  parameter variations are within experimental error. In Fig. 1, the change in unit cell volume of anatase versus chromium concentration is plotted. There is an initial increase of catalyst volume with chromium concentration up to 1 at.%; thereafter, a constant value is observed.

As mentioned before, in contrast to the pure anatase and from the low chromium concentration catalysts, the samples TC-CP2 and TC-CP5, showing constant unit cell volume, exhibited a small amount of the rutile phase. Therefore it was interesting to investigate the effect of chromium on the phase transition temperature and, at the same time, to observe any variation of the unit cell parameters of the TC-CP5 sample with temperature. Separate samples of the TC-CP5 catalyst were heated for 3 hr at 550, 600, 650, and 700°C. Table 2 lists the unit cell parameters  $a$  and  $c$  of the heat-treated TC-CP5 sample at

TABLE 1  
Unit Cell Parameters  $a$  and  $c$  and Axial Ratios  $C$  for Pure Anatase and Chromium-Doped Catalysts

Sample	$a$ (Å)	$c$ (Å)	$C$
$\text{TiO}_2$	3.7846	9.504	2.5112
TC-CP0.2	3.7857	9.501	2.5097
TC-CP0.5	3.7856	9.503	2.5103
TC-CP1	3.7861	9.501	2.5094
TC-CP2	3.7861	9.503	2.5099
TC-CP5	3.7861	9.503	2.5099

TABLE 2  
Unit Cell Parameters  $a$  and  $c$  for the TC-CP5 Sample Treated at Different Temperatures

$T$ (°C)	$a$ (Å)	$c$ (Å)
500	3.7860	9.503
550	3.7855	9.502
600	3.7849	9.502
650	3.7849	9.507
700	3.7842	9.509

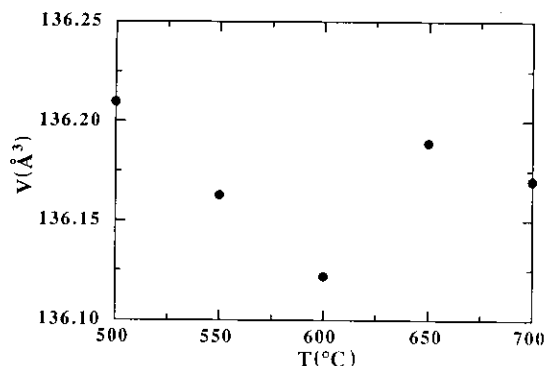


FIG. 2. Variation with temperature of the unit cell volume  $V$  of the anatase lattice in the TC-CP5 catalyst.

different temperatures. The parameter  $a$  decreases steadily, whereas the parameter  $c$  is constant up to 600°C; thereafter, it increases. The variation of the unit cell volume of the TC-CP5 sample with temperature is plotted in Fig. 2. For temperatures up to 600°C, the volume decreases until it reaches a value close to that of pure anatase (136.12 Å<sup>3</sup>). Above 600°C, the volume starts to increase.

As observed from the diffraction patterns taken after each temperature treatment, in the TC-CP5 catalyst the increasing temperature favored the anatase-to-rutile transition. An estimate of the forming rutile was determined using the equation of Spurr and Mayers (13) to calculate the weight fraction of anatase,  $f_A$ ,

$$f_A = (1 + 1.26 I_R/I_A)^{-1}, \quad [1]$$

where  $I_R$  and  $I_A$  are the intensities obtained from the areas of the peaks relative to the 110 and 101 reflections of rutile and anatase, respectively, which are the most intense reflections in the spectra. For comparison, the variation of the weight fraction of rutile,  $f_R$  ( $f_R = 1 - f_A$ ), with temperature in pure anatase and in the TC-CP5 and TC-CP0.5 catalysts is reported in Fig. 3. At 700°C and in air

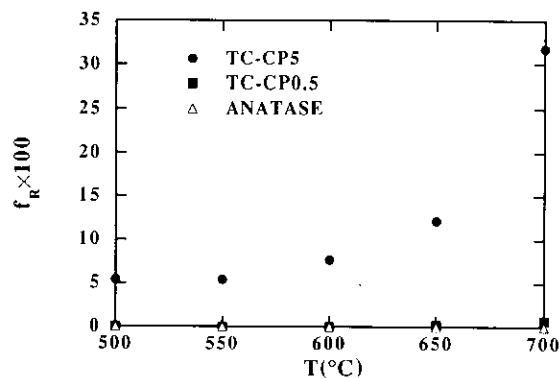


FIG. 3. Rutile weight fraction  $f_R$  versus temperature in the TC-CP5 catalyst.

TABLE 3  
Unit Cell Parameters  $a$  and  $c$   
for Pure Rutile and for the TC-CP5 Sample Treated at 700°C

Sample	$a$ (Å)	$c$ (Å)
TiO <sub>2</sub>	4.5929	2.962
TC-CP5	4.5941	2.958

the rate of anatase-rutile transition for pure anatase is so low (14) that no rutile phase was detected after the sample had been heated for 3 hr. The TC-CP0.5 sample hardly transforms at 700°C, whereas the most concentrated sample, TC-CP5, which at 500°C already exhibited 5% rutile, transforms rapidly above 650°C, and at 700°C presents about 32% rutile.

The unit cell parameters for the rutile phase observed in the TC-CP5 catalyst treated at 700°C were calculated and compared with the pure rutile parameters. The experimental values are listed in Table 3. The  $c$  parameter does not change significantly, whereas the  $a$  parameter value increases.

## DISCUSSION

The lack of any diffraction peaks of separate phases, besides the appearance of small peaks in the TC-CP2 and TC-CP5 assigned to the rutile phase, excludes the presence of significant amounts of chromia or any other chromium-containing crystalline phase.

As shown in Table 1, the unit cell parameter  $a$  increases with Cr concentration, and the parameter  $c$  is nearly constant within experimental error. The variation of the parameter  $a$  of the TC-CP1 sample is equal to  $15 \times 10^{-4}$  Å, a value similar to that found for samples of rutile containing 1 at.% chromium(III) (15).

The observation of changes of the unit cell volume of TiO<sub>2</sub> versus chromium concentration (Fig. 1) indicates that chromium is combining with the TiO<sub>2</sub> lattice, producing an expansion of the cell volume and leaving the diffractogram of the anatase phase unchanged. Since the ionic radii of Cr(III) and Ti(IV) (16) are very close, it is reasonable to assume that chromium ions substitutionally replace the Ti(IV) ions. Indeed, this idea is confirmed from previous visible-ultraviolet diffuse reflectance studies of the same system, which indicated the location of Cr(III) at well-defined octahedral sites (3, 4). The change in unit cell volume between anatase and TC-CP1 as obtained from the fitted line of Fig. 1 is  $\Delta V_{\text{exp}} = 0.059$  Å<sup>3</sup>. This variation is larger than the value of 0.038 Å<sup>3</sup> found for the same concentration of chromium (1 at.%) in the rutile system (6). There, the volume change was related to the

ionic radii of Ti(IV) and Cr(III) by the elastic matrix model (17, 18) based on the equation

$$\Delta V = K(r_{\text{Cr(III)}}^3 - r_{\text{Ti(IV)}}^3), \quad [2]$$

where  $K$  is an empirical parameter related to the number of guest ions present in 100 titanium atoms and to the elastic features of the materials,  $r_{\text{Cr(III)}}$  and  $r_{\text{Ti(IV)}}$  are the ionic radii for Cr(III) and Ti(IV); these radii are equal to 0.615 and 0.605 Å, respectively, according to the compilation by Shannon (16) for octahedral coordination around metal atoms, as in the rutile and anatase structures. The model is based on the assumption that the guest ions are incorporated into substitutional sites and that the crystal behaves as an elastic continuum. It ignores the effect of vacancies on the lattice parameters. Indeed, the substitution of a Ti(IV) ion by a Cr(III) ion can be electrically compensated for by oxygen vacancies (19). In the absence of any crystal deformation, missing ions in ionic crystals cause expansion of the unit cell volume (20, 21). Even though TiO<sub>2</sub> is not purely ionic, a positive contribution to the cell expansion may arise from the oxygen vacancies and, in chromium-doped anatase, could account for the larger increase in the unit cell volume. In rutile, this oxygen deficiency does not have an appreciable effect on the unit cell volumes, probably because easily formed shear planes remove the local stress caused by the anion vacancies (22).

Moreover, the increase in the cell volume indicates that chromium is present in the bulk as Cr(III) instead of Cr(VI). In the latter case, given the small radius of Cr(VI) (0.44 Å), its substitution for Ti(IV) in the anatase structure would have produced an appreciable decrease in the unit cell volume. The finding that Cr(VI) is present mainly on the surface and Cr(III) in the bulk is in agreement with a previous FT-IR study (5) where surface Brønsted acid sites were associated with chromium in its higher oxidation state, while Lewis sites were associated with Cr(III).

There is a limit to the amount of chromium that can dissolve into the anatase structure; when this limit is reached, no further increase in the unit cell volume is observed (Fig. 1). The solubility limit can be set in a concentration region around the intersection of two lines drawn through the experimental points of the plot in Fig. 1; a value of about 1.4 at.% is obtained. This value is smaller than the solubility limit of 2.6 at.% found for chromium in rutile (6). A direct comparison with that case is not appropriate since a different catalyst preparation procedure was used; the rutile compounds were prepared by mixing the titanium and chromium oxides, which were then heat treated in air at 950°C (6). However, within a series of samples prepared by the same procedure, a higher solubility of chromium in rutile than of chromium in anatase was found by electron spin resonance (23). The

difference was attributed to the presence in rutile of open channels along the  $c$ -axis which allow diffusion of the ions into the lattice (24). In the anatase, which has a different crystal structure, this preferential route for the migration of ions is not present.

In contrast to the chromium-anatase samples prepared by impregnation, in which chromium occurs mainly at the surface at temperatures below or equal to 500°C (5, 23), the coprecipitated samples analyzed here have the chromium incorporated into the anatase bulk structure for chromium concentrations below 2 at.% even at 500°C.

These X-ray diffraction data agree with the XPS results obtained previously (5) for the same catalysts. For chromium concentrations below 2 at.%, the XPS data were fitted by a theoretical model describing a uniform distribution of chromium through the anatase matrix. A failure of the model for chromium concentrations higher than 2 at.% was considered indicative of surface segregation processes which are detrimental to the photoactivity of the species (3). It is worth noting that the more active catalysts were those with Cr concentration  $\leq 2$  at.% as has been reported (3). Therefore, since the solubility limit found here is at a chromium concentration of 1.4 at.%, it is reasonable to consider that segregation did not occur in the more active catalysts.

The decrease in the unit cell volume with temperature, shown in Fig. 2 for the TC-CP5 catalyst, is consistent with chromium separating from the solid solution formed at 500°C. When the temperature is 600°C, the value of the unit cell volume decreases to the pure anatase value; thereafter, it starts to increase again. The increasing volume above 600°C is attributed to expansion of the anatase cell in proximity to the transition of the rutile phase (14).

Changes in the rutile/anatase fraction with temperature are shown in Fig. 3. In the temperature range and for the heating times used in this study, the pure anatase powder does not undergo a phase transformation to rutile. The TC-CP5, already presenting a small fraction of rutile at 500°C, transforms rapidly between 600 and 700°C. Comparison with the small fraction of rutile obtained in the TC-CP0.5 catalyst with the same heat treatments indicates that the effect of chromium addition on the anatase-to-rutile transformation temperature is dependent on the dopant amount. Similar results were found for the iron-titania system (25).

A possible explanation for the effect of Cr(III) on the rate of the anatase-to-rutile transition could be that during the phase transition the elongated anatase crystal rearranges itself into the more compact rutile form. This process involves the rupture of two of the six Ti-O bonds in the unit cell to form new bonds (26). When Cr(III) replaces Ti(IV), the titanium cation produced by the rupture of a Ti-O bond is stabilized by the excess negative charge in the lattice. This explanation is analogous to the

one given for the effect of reducing conditions on the anatase-to-rutile transition rate (27).

The change in the *a* and *c* parameters of the rutile phase contained in the TC-CP5 catalyst treated at 700°C with respect to the pure rutile phase, listed in Table 3, suggests that some chromium which was separating from the anatase solid solution may have dissolved into the rutile matrix.

### CONCLUSION

This study has confirmed, for the series of catalysts prepared by coprecipitation, that chromium in the bulk of TiO<sub>2</sub> anatase is present as Cr(III). Through a direct analysis of the variation of the unit cell parameters, the concentration limit for the solid solution formation of chromium oxide and the anatase phase has been estimated to be approximately 1.4 at.% Cr. This fact may explain the higher photoactivity shown by the samples with Cr concentrations < 2 at.%.

The analysis of the effect of increasing temperature on the anatase unit cell parameters has indicated that chromium, previously incorporated at 500°C, starts to separate from the solid solution. When the temperature is 600°C, the value for the pure anatase volume cell is obtained. Above this temperature, the anatase cell expands. This expansion is likely to be due to the increased rate of the anatase-to-rutile transition, which as indicated by the increased rutile/anatase fraction, is caused by the presence of chromium.

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