

Influence of Vanadium and Tungsten Substitution on the Stability of Anatase

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A possible explanation of the stability of the TiO_2 rutile phase is given on the basis of crystal chemical reasoning and a mechanism of the anatase-rutile transformation in pure TiO_2 is suggested.

The effect of the substitution of Ti by another metal ion on the stability of anatase is considered. In particular the microstrains induced by tungsten when substituted in the anatase structure, calculated from XRD measurements, are reported and compared with the microstrains induced by the vanadium ions. W and V have similar electronegativity and ionic radii, but the former does not introduce microstrains in the anatase, while the effect of V is the opposite, as previously shown. The bond-valence empirical model is applied to evaluate the oxidation states of the metal ions and a structural explanation of the effect of vanadium and tungsten substitution in the anatase structure is proposed.

The problem of the effect of the substitution of Ti in the anatase-rutile transformation has been under investigation for a long time (1, 2). It has been suggested that the nature of the impurities regulates the stoichiometry of the TiO_2 and thus the oxygen vacancy concentration. In particular, ions with valence greater than four would lower the oxygen vacancy concentration and

therefore the transformation temperature. In fact, W was found to stabilize the anatase phase and the crystallite dimensions, but in the case of V the opposite effect is shown. Recently (3, 4) the influence of vanadium on the phase transition has been studied and the changes in particle sizes and microstrains obtained with different thermal treatments were considered in detail. An evident correlation between microstrains and the vanadium content in the $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ powder, obtained by laser-induced pyrolysis (5), was determined. Thermal treatments cause the relief of microstrains originally present in the powders and, in $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ samples with $x > 0.2$, the segregation of V_2O_5 was detected.

In this letter the structural mechanism of the anatase-rutile transformation in pure TiO_2 is proposed on the basis of the different coordination of O, since the coordination geometries of Ti are octahedral in both structures. Moreover, the results of thermal treatments on commercial catalysts, based on TiO_2 with WO_3 (about 10%), are given and compared with those obtained with pure TiO_2 and $\text{Ti}_{1-x}\text{V}_x\text{O}_2$ mixed oxides. The valence-bond model proposed by Brown and Altermatt (B-A) (6, 7) was used to calculate the oxidation states for the metal ions and, on this basis, a possible explanation of the

influence of V and W in the structure is given.

The (B-A) model is based on the valence-sum rule that states that the sum of the bond valences around an atom is equal to its atomic valence. The relationship between bond-valence (s_{ij}) of two atoms i and j and bond length (R_{ij}) is monotonic and, over the small range in which most bonds are found, it can be approximated by

$$s_{ij} = \exp [(R_0 - R_{ij})/B].$$

Here R_0 and B are fitted constants, R_0 being the length of a bond of unit valence. Values for these constants have been determined by many authors, by requiring that the values of s_{ij} obey the valence-sum rule in many different compounds (7). The value of B was found to be 0.37 Å and R_0 is equal to 1.815, 1.803, 1.921 Å for Ti, V, and W, respectively.

The TiO_2 anatase phase has a defective NaCl structure in which one-sixth of the sites for each type of ion are unoccupied. In Fig. 1 the octahedral coordination of an anion, characteristic of the NaCl type of structure, is shown. In TiO_2 , as in the related nonstoichiometric compounds, some metal is missing in the O coordination. In particular, in TiO_2 one metal ion in the O-coordination octahedron is missing. Likewise, for electroneutrality, one oxygen is missing for each metal of its coordination. At high temperature these anionic and cationic vacancies are randomly distributed in the structure (8), whereas in the anatase structure the three cation vacancies in the O coordination are ordered. The occupied Ti sites are indicated by solid circles in Fig. 1a. For this idealized coordination two Ti-O-Ti angles are equal to 90° and it was noted that this configuration for the O ions is not very suitable for an essentially ionic compound (8). Probably for this reason in the real structure these angles are increased to 102° , thus leading to an oxygen coordination geometry closer to the ideal trigonal case.

The oxidation states for Ti and O in the anatase structure (9) were calculated by us-

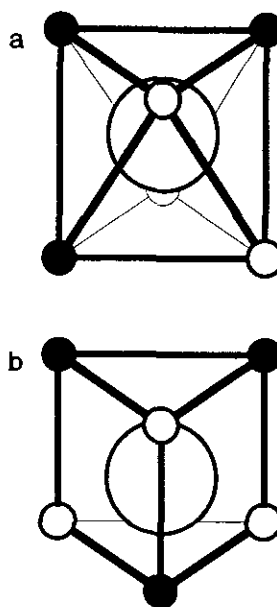


FIG. 1. (a) Octahedral coordination of the anion in the NaCl type of structure. The three cations in the O-coordination in anatase are indicated by the solid circles. (b) Prismatic coordination of the anion in the NiAs type of structure. The three cations in the O-coordination in the rutile are indicated by the solid circles.

ing the B-A model. The values are 4.2 and 2.1, respectively. A possible reason for these high values is the presence of vacancies in both the cation and the anion sites. In this hypothesis about one-third of the oxygens should be considered missing for each Ti in the structure; i.e., one-ninth of structural vacancies should be introduced. In any case, both the coordination and these high valence values are in agreement with the instability of the anatase structure with respect to that of rutile.

Indeed the (B-A) model applied to the TiO_2 -rutile structure, as reported in Ref. (9), gives for Ti and O valence values of 4.0 and 2.0, respectively. In this case the O coordination, shown in Fig. 1b, is derived from a NiAs type of structure, in which three metal atoms are missing. The three metals in the coordination are coplanar with the coordinating oxygen and ideally distrib-

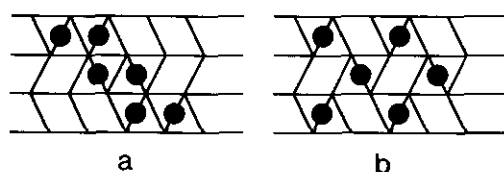


FIG. 2. (a) A chain of the anatase is shown in the idealized structure. (b) The idealized rutile structure. The ab plane is shown.

uted at the vertex of an equilateral triangle with the oxygen ion at the center.

Thus, from a structural point of view, the anatase-rutile transformation is promoted by local changes in the coordination geometry of O.

In Fig. 2 both anatase and rutile sections are shown in the idealized rutile structure. In these sections the transformation can be described as due to the jumping of cations into the interstitial octahedral sites. In Fig. 3 a possible model for the transformation is proposed. Starting from the zigzag chain of edge-sharing octahedral of Ti ions in anatase, the first step is the formation of linear chains, as shown in Fig. 3b, that can be caused by cooperative motion of cations in the anatase phase (Figs. 2 and 3). In a second step a shift of metal ions along the diagonal of the octahedron, as shown in Fig. 3c, determines the rutile structure (Fig. 3d).

Powder samples of pure titanium oxide (sample I), vanadium-titanium mixed oxides (sample II), obtained at CISE by laser-induced pyrolysis of titanium alkoxides (4), and the commercial catalyst, containing about 10% of WO_3 (sample III), were studied and compared. All the diffraction experiments were performed on a Philips MPD 1880 automated powder diffractometer with graphite-monochromated $CuK\alpha$ radiation and with flat samples in the Bragg-Brentano parafocusing geometry. In the "as received" samples pure anatase is detected, with traces of rutile in $Ti_{1-x}V_xO_2$, as previously reported (4).

A thermal treatment at a fixed temperature of $400^\circ C$ was performed for several days on the powder samples.

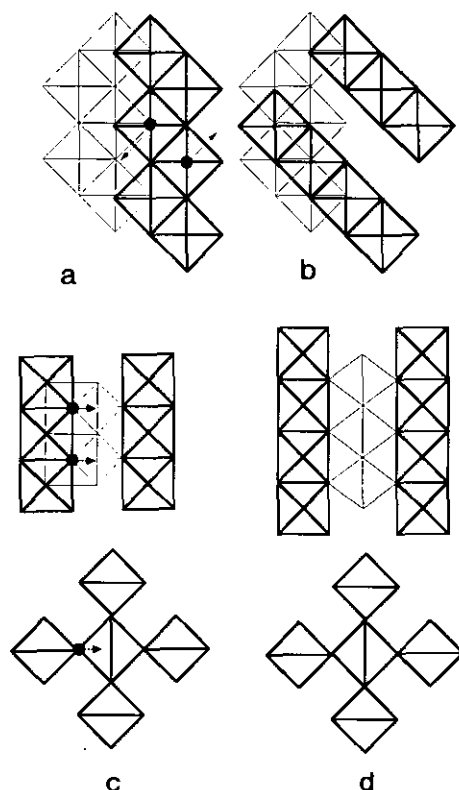


FIG. 3. (a) The idealized anatase structure is shown. The arrows indicate the possible shifts of two cations. (b) These shifts cause the formation of linear chains. (c) Two projections are shown of a possible intermediate structure. The arrow indicates the motion of a cation that eventually could produce the rutile structure. (d) Two projections of the idealized rutile structure as could be eventually obtained by steps (a), (b), and (c).

The profiles of the 110 reflections of anatase were Fourier analyzed as described in previous papers (2, 3). The microstrain values and the crystallite sizes are shown in Figs. 4a and 4b as a function of the time of treatment. Before the thermal treatments the crystallite sizes of pure TiO_2 and $Ti_{1-x}V_xO_2$ are similar. The treatments cause an increase of the crystallite sizes in the mixed oxides, while in the commercial catalyst and in the pure anatase the sizes remain almost constant (Fig. 4a). The effects of W and V are evident in the microstrains calculated before the thermal treatments. In W-containing anatase the microstrain is about

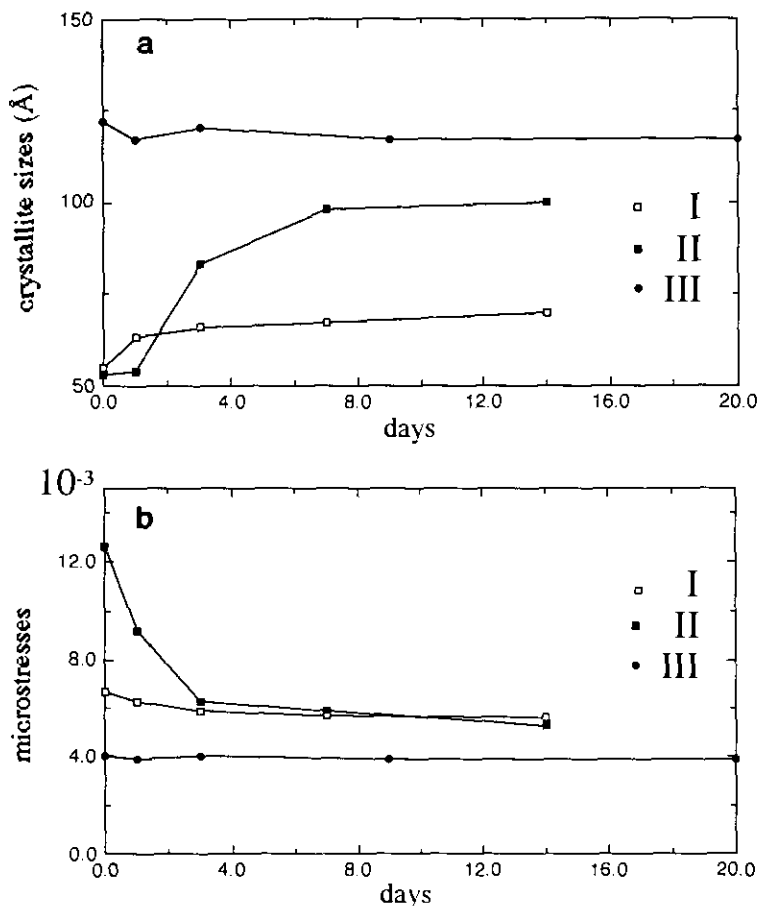


FIG. 4. The crystallite sizes (a) and the microstrains (b) of the analyzed powders are shown as a function of the period of the thermal treatment at 400°C. I are samples of pure TiO_2 , II are V-Ti mixed oxides samples, and III are commercial catalysts (see text).

one-third of that in the V-containing anatase. The microstrains obtained by analyzing the profile of the 110 reflection of the phase W-containing are smaller than those in pure TiO_2 , indicating that this phase is probably more stable than that of the pure TiO_2 . Thermal treatments cause a relief of the strain in the V-containing powder and this relief coincides with a segregation of V_2O_5 (4). The W-containing powder does not show any change with thermal treatments. From these results it is evident that the presence of W reduces the microstrains in the structure and, on the contrary, the presence of V causes microstrains.

Using the B-A model the oxidation state

of the W in the Ti site of anatase was found to be +5.6. The stabilization effect of the W can be connected to the reduction of the microstrains while from the structural point of view, the stabilization can be related to the fact that the W-coordination octahedra are not distorted. The opposite effect is induced by the V ion, as previously shown (10), since by increasing its oxidation state in Ti sites it induces a distortion in its coordination polyhedron, changing it, for example, to a square pyramidal or to a tetrahedral geometry. This effect can explain both the lower temperature of the anatase-rutile transformation and the important microstrains in the structure shown above and in

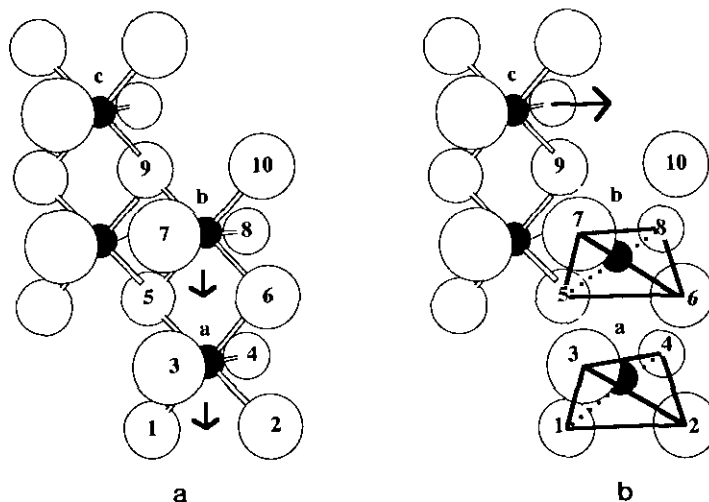


FIG. 5. Possible transformation from the anatase structure, idealized in (a), due to the tetrahedral distortion of Ti sites shown in (b).

Refs. (3, 4). The segregation of V_2O_5 that appears even at 400°C (4) proves that V has a very high mobility in the anatase structure. This mobility makes the formation of linear chains easy, which is a fundamental step in the anatase–rutile transformation as described in Fig. 3. A possible model for explaining this mechanism is shown in Fig. 5. When V is in a Ti site, it may cause a tetrahedral distortion of the octahedral geometry. In this hypothesis the cation comes closer to oxygens 1 and 2 (see Fig. 5a). The two oxygens 5 and 6 will be less bound and will also induce cation b to undergo a tetrahedral distortion. The requirements of oxygens 9 and 10 to coordinate a metal ion could cause c to jump into the interstitial octahedral site, thus determining a linear chain and starting the transformation.

In conclusion, one may suggest that the anatase–rutile transformation is determined by the coordination requirements of O. In fact, while the Ti ions have an octahedral geometry in both phases, O has a “more symmetric” coordination in rutile. Anatase can be seen as a phase derived from TiO . When the number of metal vacancies is too high the phase becomes unstable. The en-

ergy required for the transformation is due to the need of a metal ion to jump into interstitial sites.

The stabilization effect of W in the anatase structure is experimentally proved on the basis of the XRD profile analysis. The lower transformation temperature observed in the V-containing samples is justified by the high mobility of V in the structure (shown by segregation of the V_2O_5) and also by a possible tetrahedral distortion that V could induce, causing the formation of linear chains, typical of the rutile phase. These distortions may explain the high microstrain values observed in the nonthermally treated samples.

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