

Evidence for the Formation of an Anatase-Type V-Ti Oxide Solid-State Solution

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Received December 31, 1985; in revised form May 19, 1986

Samples of V-Ti oxides with V/Ti atomic ratios ranging from 0 to 0.01875 have been prepared by coprecipitation of VOCl_3 and TiCl_4 , followed by calcination in air up to 700°C . The samples have been characterized by X-ray diffraction, UV-visible diffuse reflectance, FT-IR and ESR spectroscopy, scanning electron microscopy, and surface area measurements. The results provide evidence for the formation of a well crystallized anatase-type V-Ti oxide solid-state solution characterized by a small but significant unit cell expansion and by the incorporation of V as a tetravalent species. © 1987 Academic Press, Inc.

Introduction

Vanadium-titanium oxides have been widely investigated as they represent commercial catalysts for a number of selective oxidation reactions (1) as well as for the NO reduction by NH_3 (2). Such systems have been also studied from the viewpoint of solid-state chemistry. Depending on the V/Ti atomic ratio (a.r.) and the preparation procedure different phases have been reported, namely pure TiO_2 anatase, pure TiO_2 rutile, V_2O_5 , lower V oxides, and substitutional solid-state solution of V^{4+} in TiO_2 rutile (3-5).

The possibility of formation of a solid-state solution of V in TiO_2 anatase has been proposed by Slinkard and DeGroot (6), but no clear evidence for its occurrence has been given.

During a systematic study of the vapor-phase methanol oxidation over V-Ti oxides (7) it has been found that the samples with low V/Ti a.r. are likely constituted by an anatase-type V-Ti solid-state solution. The present paper reports evidence for the occurrence of such a phase.

Experimental

Sample preparation. V-Ti samples with different V/Ti atomic ratios have been prepared by coprecipitation at room temperature from aqueous solutions of pure grade VOCl_3 (Fluka) and TiCl_4 (Carlo Erba) under continuous stirring. The coprecipitation was performed by addition of concentrated NH_3 (30% b.w.) up to a stable final pH value of 8. The filtered cake was washed

TABLE I
CELL PARAMETERS OF V-Ti SAMPLES (Å)^a

Parameter	Sample				
	V/Ti = 0	V/Ti = 0.00625	V/Ti = 0.01	V/Ti = 0.0125	V/Ti = 0.01875
<i>a</i>	3.7838 ± 0.0002	3.7839 ± 0.0002	3.7843 ± 0.0004	3.7834 ± 0.0001	3.7839 ± 0.0004
<i>c</i>	9.495 ± 0.001	9.511 ± 0.001	9.509 ± 0.002	9.508 ± 0.001	9.519 ± 0.002
<i>V</i>	135.94 ± 0.03	136.18 ± 0.04	136.18 ± 0.06	136.10 ± 0.02	136.29 ± 0.06

^a The regression has been performed on the eight most intense anatase reflections.

twice with boiling water, dried at 120°C, sieved to 35–52 Mesh, and calcined in air according to the following schedule: heating to 350°C (ramp 100°C/hr, hold 16 hr); heating to 700°C (ramp 50°C/hr, hold 3 hr); cooling down to room temperature (~50°C/hr).

Sample characterization. X-ray powder diffraction patterns were collected using a Philips PW 1050/70 vertical goniometer and PW 1730 generator. Ni filtered Cu K α radiation was employed, and pure silicon (SRM 640 from NBS, Washington, DC) was added to the samples as internal standard. Interplanar spacings were collected at 0.01° 2 θ increments. Cell parameters were calculated by a least-squares method using reflections from 35° to 70° 2 θ . Diffuse reflectance spectra were recorded by a Pye Unicam instrument using BaSO₄ as a reference. ESR spectra were obtained at 150 K using a Varian E4 X-band first derivative spectrometer. IR spectra were collected by a Nicolet MX1 Fourier transform spectrometer. Scanning electron micrographs were obtained using an ISI SS40 instrument. Surface areas were determined by a Carlo Erba Sorptomatic Series 1800 with a BET dynamic system. Ti and V nominal contents were checked by flame (Ti) and electrothermal (V) atomic absorption spectrometry after dissolution of the samples with concentrated sulfuric acid. In all cases the experimental and the nominal values were found in good agreement.

Results

X-Ray Diffraction

X-ray patterns of V-Ti samples show the presence of the anatase phase as major component. Traces of the rutile phase become detectable starting from a.r. = 0.0125 (appearance of the [110] reflection). The concentration of rutile increases with V/Ti a.r., and reaches a value of about 12% for V/Ti a.r. = 0.01875, as estimated from the intensities of [110] rutile and [101] anatase reflections (8). No other phases are detected.

The cell parameters of the anatase phase, obtained by least squares refinement, are reported in Table I. The increase of V/Ti a.r. results in a small but significant increase of the *c* parameter of the anatase cell, while the *a* parameter is almost completely unaffected. Small deviations from a monotonic trend of *c* vs V/Ti a.r., if any, could possibly be due to uncontrolled slight changes in the preparation procedure.

The relative intensities of the anatase reflections are unaffected by the V-Ti a.r. The width of the X-ray lines is representative of a large crystallite size (>3000 Å) and does not account for the measured values of surface area (see below).

UV-Visible Diffuse Reflectance

The spectra of the V/Ti samples are shown in Fig. 1a along with that of pure TiO₂. Figure 1b shows the spectra recorded

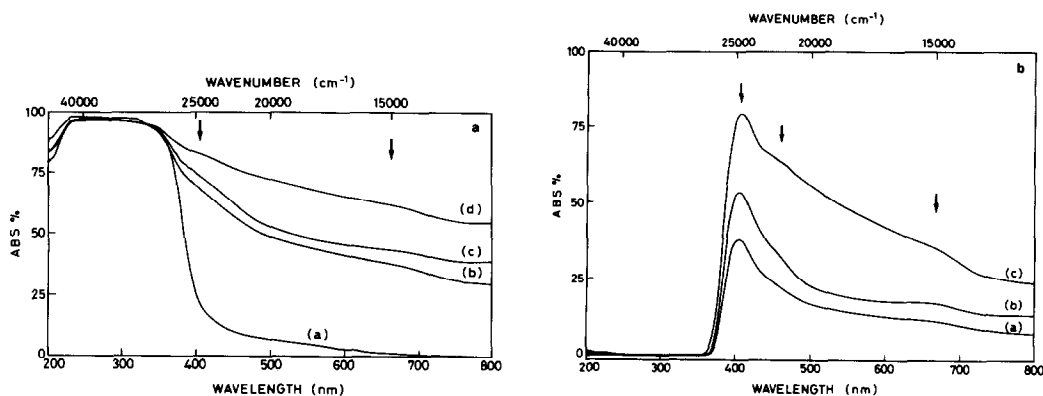


FIG. 1. (a) UV-visible reflectance spectra of TiO_2 anatase (a) and of the samples with V/Ti a.r. = 0.00625 (b), 0.0125 (c), and 0.01875 (d). (b) UV-visible reflectance spectra of V-Ti oxide samples recorded after replacing the BaSO_4 reference sample with TiO_2 anatase. V/Ti a.r. = 0.00625 (a), 0.0125 (b), and 0.01875 (c).

by replacing the BaSO_4 reference sample with TiO_2 anatase. Two additional absorptions centered near $24,700 \text{ cm}^{-1}$ (strong) and at about $15,000 \text{ cm}^{-1}$ (less intense) are evident. The intensity of both absorptions increases with the amount of V in the V/Ti a.r. range 0–0.01875. A further weak absorption centered at $21,700 \text{ cm}^{-1}$ is apparent for the highest V loading. We remark that V^{5+} in octahedral environment is characterized by a broad charge transfer absorption in the region $25,000\text{--}21,000 \text{ cm}^{-1}$, while in the case of tetrahedral environment an absorption occurs above $28,500 \text{ cm}^{-1}$ (9, 10). On the other hand, V^{4+} in the form of Vanadyl VO^{2+} is characterized by two or three weak absorptions in the region $20,000\text{--}10,000 \text{ cm}^{-1}$ associated with forbidden $d\text{--}d$ electron transitions (11, 12), and by a strong absorption near $25,000 \text{ cm}^{-1}$, which is assigned either to a $b_2 - a_1$ electron transition (11, 13), or to a charge transfer transition (14).

Therefore, the occurrence of a strong band near $24,700 \text{ cm}^{-1}$ and of a less intense band near $15,000 \text{ cm}^{-1}$ clearly indicates the presence of V^{4+} in the form of vanadyl VO^{2+} species, while the preferential occurrence of a very weak band near $21,700 \text{ cm}^{-1}$

for high V loadings indicates that V^{5+} ions are present in traces.

ESR Spectroscopy

An intense ESR signal was recorded on all the V-Ti oxide samples. The ESR spectrum of the sample with a.r. = 0.00625 is shown in Fig. 2. The spectrum is characterized by two anisotropic components with eightfold hyperfine splitting, which assigns the signal to isolated V^{4+} centers ($S = \frac{1}{2}$, $I = \frac{5}{2}$). The following parameters were estimated by a second-order fitting of the experimental line position field:

$$g_{\perp} = 1.940; \quad |A_{\perp}| = 59.4 \text{ G}; \\ g_{\parallel} = 1.938; \quad |A_{\parallel}| = 165.0 \text{ G}.$$

These features, characterized by $g_{\perp} \sim g_{\parallel}$ and $\langle A \rangle_{\text{iso}} = 95 \text{ G}$, are roughly intermediate between those of inorganic vanadyl VO^{2+} species in distorted octahedral or square pyramidal coordination ($g_{\perp} > g_{\parallel}$; $\langle A \rangle_{\text{iso}} \sim 90\text{--}110 \text{ G}$) (11, 12, 15) and those of more symmetrical octahedral V^{4+} in substitutional position inside rutile-like oxides, e.g., TiO_2 , GeO_2 , and SnO_2 ($g_{\parallel} > g_{\perp}$; $\langle A \rangle_{\text{iso}} = 75 \text{ G}$) (16–18). On the other hand we notice that the difference $g_{\perp} - g_{\parallel}$ related to

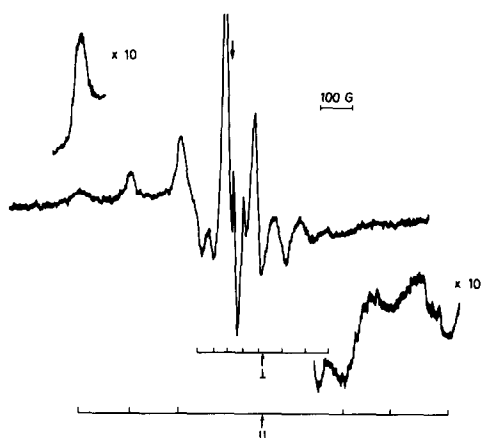


FIG. 2. ESR spectrum of the sample with V/Ti a.r. = 0.00625 recorded at 150 K.

the coordination sphere surrounding the d_1 centers is known to decrease markedly on increasing the basic character of the axial ligand in vanadyl complexes (12). Values of $g_{\perp} \sim g_{\parallel}$ have also been reported for a number of V^{4+} complexes (19). Accordingly, the spectrum of the sample with V/Ti a.r. = 0.00625 points to the presence of paramagnetic V^{4+} centers in a coordination sphere intermediate between those of symmetrical octahedral V^{4+} and square pyramidal Vanadyl VO^{2+} species; its features differ strongly from those reported for vanadyl species on the surface of both anatase and rutile TiO_2 (20, 21). Indeed, the observation that introducing gaseous oxygen into the ESR cell does not affect the spectrum confirms that V ions are located in the bulk. The incorporation of V^{4+} in the bulk is further consistent with the detection of V by UV-visible reflectance primarily as V^{4+} in spite of the calcination in air at $700^{\circ}C$, which would result in the oxidation of surface V to V^{5+} .

FT-IR Spectroscopy

The FT-IR spectra of TiO_2 anatase and of the sample with V/Ti a.r. = 0.00625 are given in Fig. 3 along with the ratioed spectrum. The presence of V causes the appear-

ance of a single broad band slightly asymmetrical toward lower frequencies and centered at 1005 cm^{-1} . On increasing the V/Ti a.r. the feature of the spectrum is essentially unaltered. The band at 1005 cm^{-1} can be assigned to the stretching mode of $V=O$ double bond, which is typically observed in the $950\text{--}1050\text{ cm}^{-1}$ region for both V^{4+} and V^{5+} compounds (22, 23). It is worth mentioning that the $\nu(V=O)$ frequency is more sensitive to changes in the coordination sphere of the vanadyl center than to the oxidation state of V. Besides, $\nu(V=O)$ frequencies very close to 1000 cm^{-1} have been reported for V^{4+} compounds with vanadyl species in distorted octahedral or square pyramidal coordination, such as $VO(acac)_2$, $VO(OH_2)_5^{2+}$, and VO_2 oxides (22, 24–26).

Based on the above observations and also considering that V is mostly present as V^{4+} , a likely conclusion is that the band at 1005 cm^{-1} originates from the same VO^{2+} species responsible for UV-visible and ESR

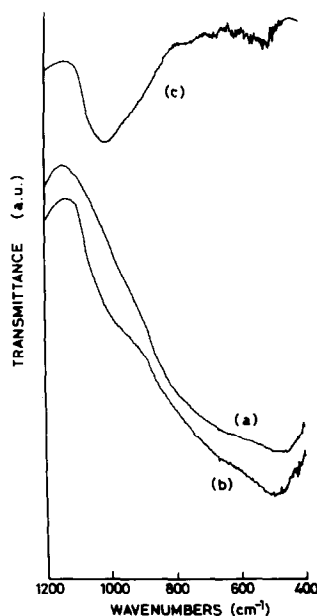


FIG. 3. FT-IR spectra (KBr pressed disks) of (a) pure TiO_2 anatase; (b) sample with V/Ti a.r. = 0.00625; (c) ratio (b)/(a).

absorptions. The broadness of this band is unusual as compared to pure vanadyl compounds, and points to a structural effect of the matrix on the V=O vibrator. Furthermore, it is worth noticing that the ratioed spectrum of Fig. 3 does not show any additional absorptions in the 900–500 cm^{-1} region, where $\nu(\text{V—O—V})$ bands of bulk V oxides typically occur. Thus, the IR technique, which is known to be more sensitive than XRD, as well as sensitive to amorphous phases, confirms the absence of pure V oxides in detectable amounts.

Scanning Electron Microscopy and Surface Area

Electron micrographs of TiO_2 and V-Ti oxide samples (a.r. = 0.01875) are shown in Fig. 4. Inspection of the figure indicates that the surface roughness and the concentration of small particles (200–500 Å) on the grain surface decreases on increasing the V/Ti a.r. in line with the decrease in surface area shown in Table II.

Discussion

Based on the above results, the following points can be taken as evidence for the formation of a solid-state solution of V in TiO_2 anatase.

(1) The XRD investigation has shown that our Ti-V samples are constituted by a well-crystallized anatase phase characterized by a small but significant expansion of the unit cell along the *c* axis on increasing the V/Ti atomic ratio.

(2) The UV-visible results, showing that V is mostly present as V^{4+} with only traces of V^{5+} in spite of the calcination in air at

high temperatures suggest that V is incorporated in the lattice of TiO_2 anatase.

(3) ESR spectroscopy has shown the presence of isolated V^{4+} centers located in the bulk. Based on the values of the ESR parameters, it can be ruled out that these centers are associated either with vanadyl species on the surface of anatase and rutile TiO_2 or with substitutional or interstitial V^{4+} in TiO_2 rutile.

The formation of a solid solution of V in TiO_2 anatase is also consistent with the absence of pure V oxides as detected both by XRD and IR, with the appearance of a new IR absorption at 1005 cm^{-1} , and possibly with the observed changes in surface morphology.

Our data do not allow to discriminate between an interstitial and a substitutional solid-state solution. Indeed, the presence of three types of interstitial sites, one of which has larger dimensions than the reticular sites (27), might allow for the formation of an interstitial solution resulting in a unit cell expansion. On the other hand, in spite of the cell contraction reported for $\text{V}_x\text{Ti}_{1-x}\text{O}_2$ rutile-like solid-state solutions (3, 4) the substitution of the $d_0\text{Ti}^{4+}$ cations by the $d_1\text{V}^{4+}$ cations could produce a deformation of the structure due to the different geometry of the coordination sphere of TiO_2 anatase, which again could result in a cell expansion.

As a final note, we remark that the coprecipitation method, providing an intimate contact of the constituents, and the high final calcination temperature, which ensures high crystallinity of the samples, could possibly favor the formation of a detectable well-crystallized solid-state solution in our samples.

TABLE II
SURFACE AREAS OF V-Ti SAMPLES (m^2/g).

Sample	V/Ti = 0	V/Ti = 0.00625	V/Ti = 0.01	V/Ti = 0.0125	V/Ti = 0.01875
Surface area	20.0	15.6	16.0	9.5	3.5

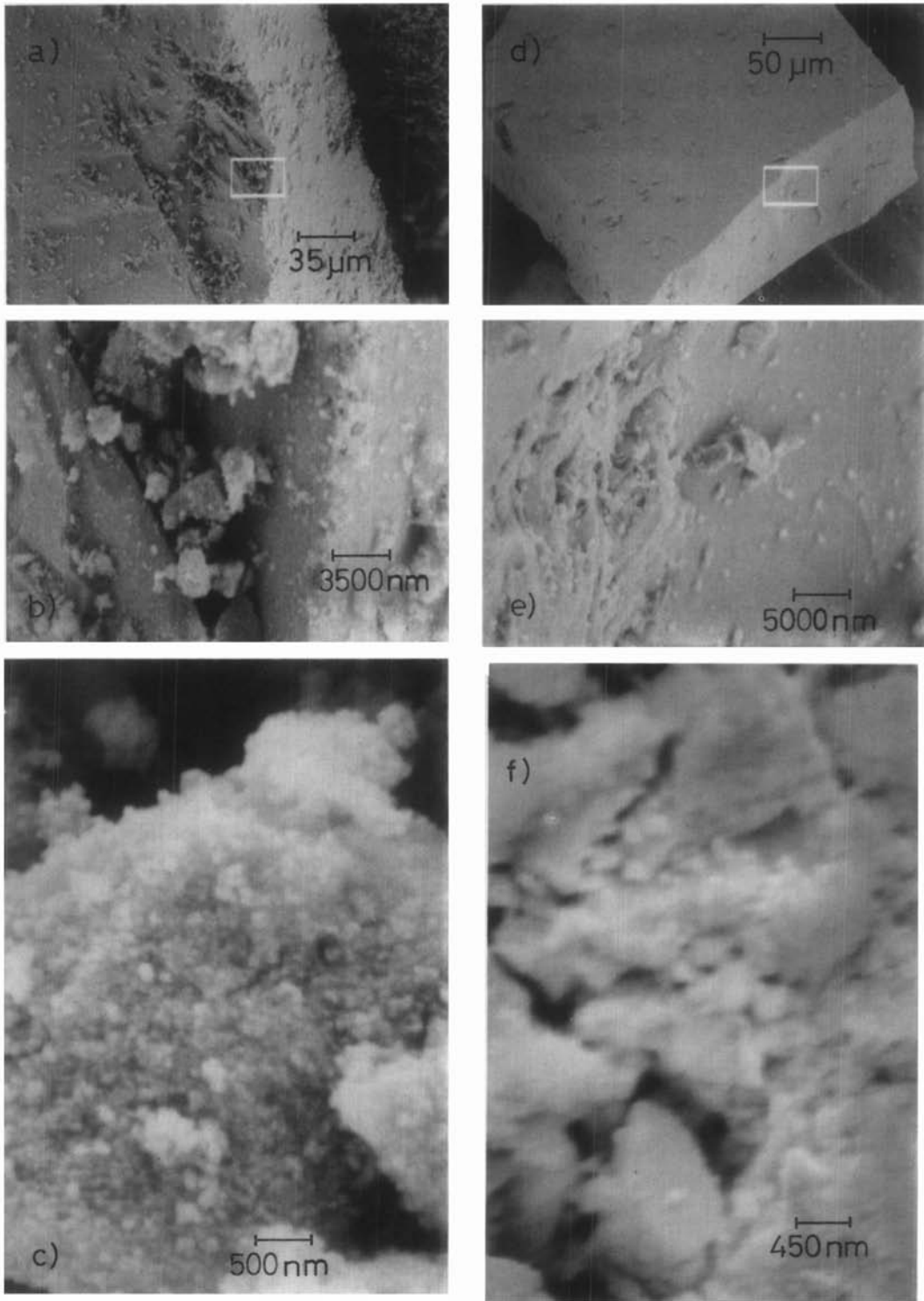


FIG. 4. Electron micrographs of the TiO₂ sample (a,b,c) and of the sample with V/Ti a.r. = 0.00625 (d,e,f).

Conclusions

The main conclusions of the present work are the following.

(1) A formation of well-crystallized solid-state solution of V^{4+} in TiO_2 anatase has been obtained by coprecipitation of $TiCl_4$ and $VOCl_3$ in H_2O (final pH 8) followed by calcination up to $700^\circ C$, for V/Ti a.r. less than or equal to 0.0125.

(2) The solid-state solution is characterized by (a) a small expansion of the anatase TiO_2 unit cell along the c axis; (b) the incorporation of V as paramagnetic species in a coordination sphere intermediate between those of square pyramidal vanadyls VO^{2+} and of symmetrically octahedral V^{4+} .

Acknowledgments

The authors thank Mr. Federico Fenu for performing the S.E. micrographs. This work was supported by Ministero Pubblica Istruzione (Roma) (Gruppo Nazionale "Struttura e Reattività" delle Superfici")

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