JOURNAL OF MATERIALS SCIENCE 28 (1993) 1189–1193

# Real structure of $TiO_2$ in samples of the $TiO_2$–$V_2O_5$ system

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Measurements of electron spin resonance (ESR) spectra and X-ray structure analysis have been performed on samples of the $TiO_2$–$V_2O_5$ system, formed by anatase crystallites on the surface of which a thin layer of $V_2O_5$ was deposited by thermal decomposition of ammonium vanadate at 800 °C. It was found that the deposited $V_2O_5$ gives rise to a change in the modification of $TiO_2$ (anatase goes over to rutile) and to a decrease in the volume of the $TiO_2$ elementary cell. Bands corresponding to Ti atoms of oxidation state +III were identified in the ESR spectrum of the initial $TiO_2$. The intensity of these bands decreases with increasing content of $V_2O_5$ in the $TiO_2$–$V_2O_5$ samples; the ESR spectra of the samples with high $V_2O_5$ content exhibit only one band corresponding to vanadium atoms in oxidation state +IV in the rutile lattice. The experimental results allow one to form an idea on the changes of the real structure of $TiO_2$ in connection with the deposition of $V_2O_5$ thin films on $TiO_2$ crystallites and with thermal treatment of these materials.

## 1. Introduction

Published papers devoted to the study of samples of the $TiO_2$–$V_2O_5$ system can be divided into two groups. The first one includes communications reporting the influence of vanadium impurities on the properties of $TiO_2$ single crystals, in particular rutile. The second one comprises papers dealing with the characterization of polycrystalline preparations.

The first group of papers is dominated above all by analyses of the electron spin resonance (ESR) spectra of vanadium-doped $TiO_2$ single crystals [1–4]. The results reported [1–3] lead to identical conclusions on the way in which impurity vanadium atoms are incorporated into the $TiO_2$ crystal lattice: namely that vanadium atoms in the form of $V^{4+}$ ions, i.e. atoms of oxidation degree + IV, occupy titanium sites giving rise to substitutional defects. This view on the incorporation of $V^{4+}$ ions in the $TiO_2$ lattice was complemented by Kubec and Šourek [4] who observed the changes in ESR spectra of vanadium-doped $TiO_2$ single crystals due to various heat treatments. In the samples heat-treated at a higher temperature (900 °C) they assume, in agreement with the results reported by others [1–3], the formation of substitutional defects of $V^{4+}$ ions in titanium sites. Analysis of the ESR spectra of crystals heat-treated at 600 °C led these authors to the conclusion that in this case the $V^{4+}$ ions are preferentially located in the interstitial sites of the $TiO_2$ crystal lattice.

The second group of papers, i.e. the communications dealing with the study of polycrystalline $TiO_2$–$V_2O_5$ samples, is focused in the first place on the characterization of catalysts on the basis of these components, which find applications in a number of selective oxidations, reduction of nitrogen oxides by ammonia, etc. [5–10]. The phase composition of polycrystalline $TiO_2$–$V_2O_5$ samples, heat-treated at 500, 600 and 700 °C, is the object of a study reported by Sterligova *et al.* [11]; on the basis of the results of ESR spectra measurements and X-ray structure analysis the authors conclude that, in the $TiO_2$–$V_2O_5$ system under given conditions of treatment, no compound is formed and no mutual solution of components in the solid state takes place so that there are no solid solutions on the basis of either $TiO_2$ or $V_2O_5$. In contrast to this observation, the formation of solid solutions in the $V_2O_5$–$TiO_2$ system has been proved [12].

Since the catalyst efficiency is markedly influenced by surface area, the published results characterizing the above-mentioned $TiO_2$–$V_2O_5$ catalysts concern samples treated at relatively low temperatures not exceeding 500 °C. There are, however, few data in the literature on the properties of polycrystalline $TiO_2$–$V_2O_5$ samples prepared at higher temperatures.

In the present communication we report the results of measurements of ESR spectra and X-ray structure

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analysis of polycrystalline $TiO_2$–$V_2O_5$ samples formed by $TiO_2$ crystallites coated with a thin layer of $V_2O_5$ and heat-treated at 800 °C. On the basis of the changes in the character of the ESR spectra and in the lattice parameters of $TiO_2$ with increasing $V_2O_5$ content in the samples, we discuss the changes in the real structure of $TiO_2$ due to mutual interaction of $TiO_2$ and $V_2O_5$ taking place in the contact region of both components.

## 2. Experimental procedure

### 2.1. Preparation of polycrystalline samples of $TiO_2$–$V_2O_5$

The initial "pure" $TiO_2$ was prepared by calcination of the material obtained by hydrolysis of $TiOSO_4$ in a platinum crucible at a temperature of 800 °C for 4 h. The purity of the prepared product was verified by emission spectral analysis; it was found that it contains trace quantities of Al, Mg, Cu and Si.

The $TiO_2$–$V_2O_5$ samples were prepared in the following way. The calculated quantity of $V_2O_5$, of p.a. purity, was dissolved in ammonia solution, the resulting ammonium vanadate solution was diluted with redistilled water and mixed with 15 g of "pure" $TiO_2$. The suspension formed was thoroughly homogenized by mixing. After careful evaporation of water the solid residue was carried over into a platinum crucible and calcined at a temperature of 800 °C for 4 h. Samples of composition $TiO_2 + x$ (wt %) $V_2O_5$ were prepared in this way for $x = 0.5$, 1.0, 2.5, 4.0, 5.5, 7.0 and 9.5.

### 2.2. Determination of lattice parameters

X-ray powder diffractograms of the samples were obtained using a vertical X-ray diffractometer HZG-4B (VEB Freiberger Präzisionsmechanik, Freiberg, Germany) equipped with a goniometer of 50 cm diameter and a proportional detector. Cu$K_\alpha$ radiation was used with $K_\beta$ radiation eliminated with a nickel filter; in the range $2\theta = 10$ to 35° the interplanar spacing was calculated using Cu$K_\alpha$ radiation ($\lambda = 0.154178$ nm) and in the range $2\theta = 35$ to 90° Cu$K_{\alpha 1}$ radiation ($\lambda = 0.154051$ nm) was used.

Powdered silicon ($a = 0.54055$ nm) served as an internal standard. The lattice parameters were computed using the least-squares technique to increase the accuracy, the minimized quantity being $(2\theta_{exp} - 2\theta_{calc})^2$.

### 2.3. Measurement of ESR spectra

The ESR spectra of polycrystalline samples were measured using the ESR 221 apparatus (Akademie der Wissenschaften der GDR-Zentrum Wissenschaftlichen Geratebau) in the X-band ($\gamma \approx 9.5$ GHz) at room temperature.

## 3. Results

The results of the X-ray structure analysis of $TiO_2$–$V_2O_5$ samples are summarized in Table I and Fig. 1.

The ESR spectra of the investigated samples are presented in Figs 2 and 3. Beside the experimental curve corresponding to "pure" $TiO_2$, we give in Fig. 2 the integrated spectrum and illustrate its analysis.

## 4. Discussion

### 4.1. Characterization of "pure" $TiO_2$

With the aim of identifying the modification of "pure" $TiO_2$ prepared by heat-treatment at 800 °C, the X-ray structure analysis was carried out first. In view of the fact that the X-ray diffractogram contained only the lines corresponding to anatase, we can adopt the conclusion that the starting polycrystalline titanium oxide material treated at the given temperature is formed by anatase crystallites. The determined lattice parameters are given in Table I.

TABLE I Lattice parameters of titanium oxide in $TiO_2$–$V_2O_5$ polycrystalline samples, heat-treated at 800 °C.

| | $V_2O_5$ (wt%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0 | 0.5 | 2.5 | 4.0 | 5.5 | 7.0 | 9.5 |
| Anatase | | | | | | | |
| $a$(nm) | 0.378 34(2) | 0.378 38(1) | 0.378 35(6) | – | – | – | – |
| $c$(nm) | 0.951 72(9) | 0.951 32(5) | 0.951 0(2) | – | – | – | – |
| $c/a$ | 2.515 5(7) | 2.514 2(4) | 2.514 0(2) | – | – | – | – |
| $V$(nm$^3$) | 0.136 23(2) | 0.136 20(1) | 0.136 14(5) | – | – | – | – |
| $\Delta 2\theta^a$ | 0.006 | 0.004 | 0.006 | – | – | – | – |
| Content (wt %) | 100 | 100 | 5 | 0 | 0 | 0 | 0 |
| Rutile | | | | | | | |
| $a$(nm) | – | – | 0.459 13(1) | 0.459 07(1) | 0.458 93(1) | 0.458 91(1) | 0.458 85(1) |
| $c$(nm) | – | – | 0.295 85(1) | 0.295 87(1) | 0.295 85(1) | 0.295 88(1) | 0.295 85(1) |
| $c/a$ | – | – | 0.644 4(1) | 0.644 5(1) | 0.644 7(1) | 0.644 8(1) | 0.644 8(1) |
| $V$(nm$^3$) | – | – | 0.062 355(5) | 0.062 353(3) | 0.062 311(2) | 0.062 313(2) | 0.062 290(2) |
| $\Delta 2\theta^a$ | 0 | 0 | 0.003 | 0.002 | 0.002 | 0.002 | 0.002 |
| Content (wt%) | 0 | 0 | 95 | 100 | 100 | 100 | 100 |

[a] $\Delta 2\theta = (1/N)\sum_{1}^{N}(2\theta_{exp} - 2\theta_{calc})$, where $2\theta_{exp}$ is the experimental diffraction angle, $2\theta_{calc}$ is the angle calculated from lattice parameters and $N$ is number of investigated diffraction lines.

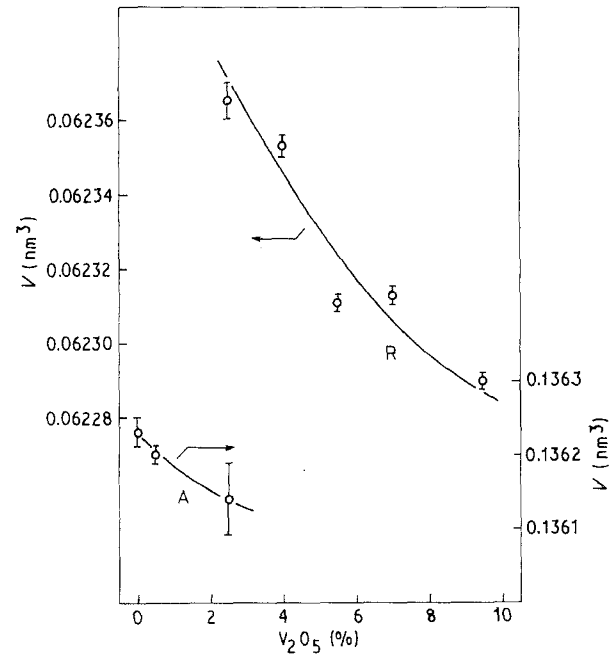

*Figure 1* Dependence of the volume of the elementary cell of $TiO_2$ crystal lattice on the content of $V_2O_5$ in polycrystalline $TiO_2$–$V_2O_5$ samples, heat-treated at 800 °C: (A) - anatase, (R) - rutile.

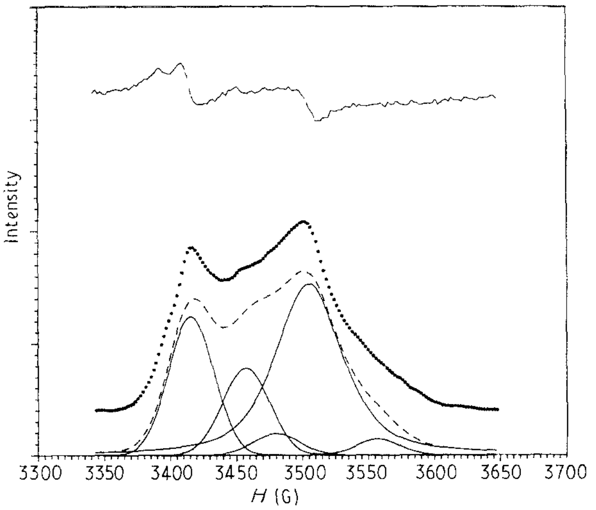

*Figure 2* ESR spectrum and its analysis for a polycrystalline sample of "pure" $TiO_2$, heat-treated at 800 °C: (—) experimental spectrum, (. . .) integrated experimental spectrum, (- - -) fitted spectrum. Microwave frequency = 9.523 GHz.

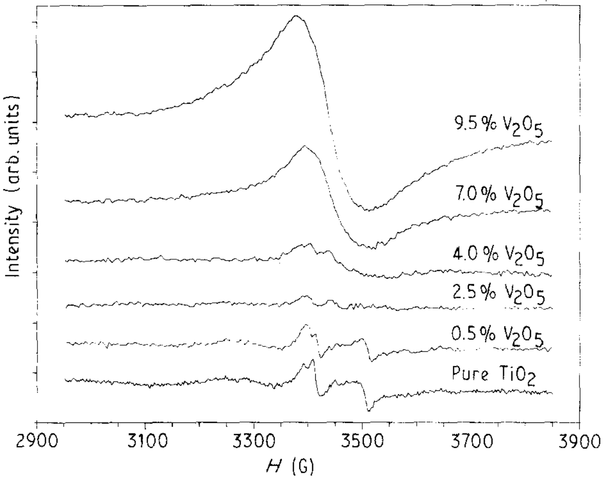

*Figure 3* ESR spectra of polycrystalline $TiO_2$–$V_2O_5$ samples, heat-treated at 800 °C. Microwave frequency = 9.523 GHz.

The starting "pure" $TiO_2$ material was further characterized by ESR measurements. The measured ESR spectrum (Fig. 2) contains several bands. In order to characterize them, the spectrum was integrated and the absorption spectrum obtained was fitted by decomposition into individual bands. The number of bands and their positions (or their $g$-factors) were estimated using a standard numerical treatment. It was found that the spectrum is formed by five bands; their position ($H_0$), $g$-factor and relative intensity are given in Table II. A good agreement between the calculation and the experimental result is clearly seen in Fig. 2.

Comparing the values of the $g$-factors of identified bands with published values of the $g$-factors of ESR spectra of $TiO_2$ we come to the following conclusions. The most intense bands, whose $g$-factors equal 1.992 and 1.942, are identical with values of $g_\perp = 1.99$ and $g_\parallel = 1.94$, which – according to Kera *et al.* [6] – correspond to Ti atoms in the oxidation state of + III in the crystal lattice of anatase. The first most intense band showing $g = 1.968$ and the band with $g = 1.955$ can be assigned to interstitial $Ti^{3+}$ ions in rutile crystal lattice. In fact, according to Gashieva and Anufrienko, [13], interstitial $Ti^{3+}$ ions in rutile are characterized by bands with $g_\perp = 1.99$, $g_\parallel^{(1)} = 1.967$ and $g_\parallel^{(2)} = 1.960$ (according to the Gashieva and Anufrienko [13], the existence of two bands, $g_\parallel^{(1)}$ and $g_\parallel^{(2)}$, is connected with ambiguity of the interstitial site in the rutile crystal lattice). The presence of these bands in the spectrum testifies that the prepared $TiO_2$ material contains rutile in quantities that escape X-ray structure analysis. The existence of a certain admixture of rutile structure is also pointed to by a weak band showing $g = 1.913$, which can be connected with titanium atoms in the + III oxidation state in rutile lattice sites (according to Gashieva and Anufrienko [13], Ti( + III) atoms built as substitutional impurities into the crystal lattice of rutile show a weak band with $g_\parallel = 1.913$ and $g_\perp = 1.906$).

On the basis of the X-ray and ESR characterization of the $TiO_2$ material prepared by heat-treatment at 800 °C for 4 h we can state that the prepared $TiO_2$ is predominantly anatase with a slight admixture of rutile, showing an oxygen deficit in the crystal lattice which is manifested by the presence of titanium atoms in oxidation state + III, i.e. by $Ti^{3+}$ ions. This non-stoichiometry is probably connected with the release of a certain amount of oxygen from the $TiO_2$ crystal lattice during the heat-treatment, and is not in contradiction with the published data on non-stoichiometry of $TiO_2$ [14, 15].

TABLE II Parameters of bands in the ESR spectrum of "pure" $TiO_2$, heat-treated at 800 °C ($H_0$ = band position in the spectrum)

| $H_0$ (G) | $g$ - factor | Relative intensity |
|---|---|---|
| 3415 | 1.992 | 0.246 |
| 3457 | 1.968 | 0.160 |
| 3480 | 1.955 | 0.040 |
| 3505 | 1.942 | 0.526 |
| 3557 | 1.913 | 0.028 |

## 4.2. Characterization of $TiO_2$–$V_2O_5$ samples

In this section we present views on the mutual interaction of the components of $TiO_2$–$V_2O_5$ samples that takes place in the course of the heat-treatment.

First, we can evaluate the data that we obtained by X-ray structure analysis of the investigated materials. The diffractograms of the samples of "pure" $TiO_2$ and $TiO_2$ containing 0.5 wt % $V_2O_5$ showed only the lines corresponding to anatase structure. However, the diffractogram of a sample with 2.5 wt % $V_2O_5$ showed, in addition to anatase lines, also the lines corresponding to rutile structure. Comparing the line intensities, we estimated the relative proportion of both modifications in the given sample and arrived to a value of about 5 wt % of rutile. The diffractograms of samples with higher $V_2O_5$ content showed only the lines of the rutile modification. Therefore, we can adopt a conclusion that addition of $V_2O_5$ in the form of a thin layer formed on the surface of anatase crystallites by decomposition of ammonium vanadate gives rise to a change in crystal modification: under given conditions anatase is transformed into rutile.

The values of the lattice parameters of the studied samples, as shown in Table I, and the variations of the volume of the elementary cell of $TiO_2$ crystal lattice with increasing $V_2O_5$ content (see Fig. 1), further testify that beside the change in the crystallographic modification due to deposition of a thin $V_2O_5$ layer, an interaction of both oxides takes place which results in a change in the lattice parameters of the $TiO_2$ crystal lattice. It is clear from Fig. 1 that with increasing content of $V_2O_5$ in the samples the volume of the $TiO_2$ elementary cell decreases, for both the anatase modification in the range of low $V_2O_5$ concentrations and the rutile modification in the samples with higher $V_2O_5$ content. In our opinion, this effect can be explained as follows.

Heat-treatment of the samples formed by $TiO_2$ crystallites provided with a thin deposited $V_2O_5$ layer can give rise to the diffusion of vanadium atoms, or ions, into the $TiO_2$ crystal lattice. It is quite plausible to assume that these atoms, or ions, at temperatures of 800 °C will preferentially occupy titanium sites in the $TiO_2$ lattice, giving rise to substitutional defects [4]. Owing to the fact that vanadium atoms are smaller than titanium atoms, this substitution will result in a decrease of the elementary cell volume, which is in agreement with the experiment.

As far as the present results of X-ray structure analysis are concerned, it has to be mentioned here that the diffraction patterns of all samples, i.e. even of the sample with the highest content (9.5 wt %) of $V_2O_5$, showed only the lines corresponding to anatase or rutile structure; no lines due to vanadium oxide were detectable in the diffractograms. This fact is probably connected with a very thin layer of vanadium oxide being deposited on the surface of $TiO_2$ grains. In addition, one cannot exclude a possibly substantial reduction of the vanadium oxide content on the surface of the samples in consequence of the above discussed diffusion of vanadium atoms or ions into the $TiO_2$ crystal lattice.

Important information on the interaction of $V_2O_5$ with titanium oxide is provided by the ESR spectra of the studied samples. The influence of increasing $V_2O_5$ content on the character of ESR spectra is evident from Fig. 3. The spectra of samples with a low $V_2O_5$ content clearly show that the interaction between both oxides leads to a suppression of the bands in the spectral region corresponding to the presence of titanium atoms in the + III oxidation state, i.e. $Ti^{3+}$ ions, in the crystal lattice of $TiO_2$. The suppression of these bands is most pronounced in the sample containing 2.5 wt % $V_2O_5$, where the most intense band of "pure" $TiO_2$ at a value of $H = 3500$ G ($g = 1.942$) is completely missing. This band, as mentioned before, corresponds to titanium atom in the + III oxidation state, i.e. to $Ti^{3+}$ ion, in the anatase lattice. The spectra of samples with higher $V_2O_5$ contents are then of a completely different character to those of "pure" $TiO_2$. It is evident that the spectra of the samples containing 7.0 and 9.5 wt % $V_2O_5$ are composed of a single pronounced band corresponding to the value of $g = 1.979$. The value of the $g$-factor of this band is virtually identical with the $g$ value of the band corresponding to the presence of vanadium atoms in oxidation state + IV, i.e. to $V^{4+}$ ions, in the rutile crystal lattice; according to Kera *et al.* [6], this value equals 1.983. These data allow us to complement the ideas about the interaction of the two oxides in the samples, based on the results of X-ray structure analysis, in the following way.

During the heat-treatment of the samples formed by anatase crystals whose surface is provided with a deposited layer of ammonium vanadate, in the first stage, vanadate thermally decomposes giving rise to $V_2O_5$. It is known that at elevated temperatures vanadium oxide releases oxygen easily; according to Kofstad [14], the oxygen deficit in the $V_2O_5$ crystal lattice is characterized by the presence of $V^{4+}$ ions. Therefore, one can well accept the idea that the $V_2O_5$ produced by decomposition releases some oxygen, which diffuses from the $TiO_2$–$V_2O_5$ interface towards the crystal lattice of $TiO_2$ where it obviously occupies oxygen vacancies, but is also responsible for oxidation of titanium atoms from oxidation state + III to + IV, or drives the diffusion of $Ti^{3+}$ interstitials at the interface of the two oxides. Here, as a result of oxidation of these ions, growth of $TiO_2$ takes place. Thus, the oxygen released from $V_2O_5$ brings about a suppression of the concentration of titanium atoms in the + III oxidation state, i.e. $Ti^{3+}$ ions, in the crystal lattice of $TiO_2$, as seen from the changes in the ESR spectra.

Beside diffusion of released oxygen into the $TiO_2$ crystal lattice, one can, under given conditions of heat-treatment of the samples, assume that the diffusion of vanadium atoms takes place too. Most probably, in accordance with the results of ESR spectra of the samples with higher $V_2O_5$ contents, they diffuse into the $TiO_2$ lattice, forming substitutional defects of vanadium atoms in the + IV oxidation state, i.e. $V^{4+}$ ions. The resulting defects are responsible for the reduction of the volume of the $TiO_2$ elementary cell, which is also in agreement with the results of X-ray structure analysis.

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*Received 2 September 1991*
*and accepted 24 July 1992*