An ESR Study on Oxygen Adsorption and Illumination of Vacuum Treated V_2O_5/TiO_2

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Oxygen adsorption on vacuum treated TiO_2 doped with vanadium results in the formation of O_2^- species. It is argued that substitutional V^{3+} ions act as electron donors. The oxygen radicals are stabilized in the neighbourhood of titanium ions. Depending on the oxygen pressure photoadsorption or photodesorption of oxygen is observed.

Introduction

It is well known that surface as well as bulk properties of solids can be drastically changed by the presence of structural defects. In particular the existence of surface anion vacancies formed upon vacuum reduction of metal oxides is regarded as a factor promoting the creation of stable radicals on these compounds [1].

In the present paper results are described obtained upon oxygen adsorption on vacuum treated V_2O_5/TiO_2. The formation of radical oxygen species is demonstrated by means of ESR. Their behaviour upon illumination is investigated.

Experimental

Samples containing different vanadium concentrations were obtained by impregnation of TiO_2 (anatase, optipur Merck) with suitable amounts of ammonium metavanadate solution (Merck, pro analysis). The preparations were calcinated in air at 250 °C for 2 hours and submitted to vacuum treatment (10^{-5}–10^{-6} Torr) at 600 °C for different periods of time. After pretreatment in vacuo the samples were inserted into the ESR cavity while staying connected to a vacuum line equipped with greaseless stopcocks.

Oxygen was introduced to the samples at room temperature. The excess gas was pumped off down to 10^{-3} Torr and the ESR spectra were registered at 77 K using a Varian E-line Century Series ESR spectrometer model E-112 equipped with an optical transmission cavity type E-234. Further details are given elsewhere [2].

Results

Undoped TiO_2 submitted to vacuum treatment at 600 °C yields the spectrum shown in Figure 1a. It consists of a strong line with $g = 2.003$ being attributed to electrons trapped at anion vacancies and a broad signal with $g_{\mathrm{av}} = 1.96$ due to Ti^{3+} ions [3]. From samples containing vanadium the spectrum given in Fig. 1b (continuous line) is obtained. The parameters $g_{\parallel} = 1.909$, $g_{\perp} = 1.973$ and the well resolved hyperfine splitting with $A_{\parallel} = 190$ G are close to those of vanadium ions in vanadyl coordination, i.e. V^{4+} in close association with O^{2-} [4, 5]. The narrow line centered at $g = 2.003$ is possibly connected with an electron trapped at a lattice defect, e.g. an oxygen vacancy. The spectrum of vanadyl ions is observable also at room temperature, which indicates a rather long relaxation time of these paramagnetic centers. The comparison of the spectrum presented in Fig. 1a with the corresponding part in the spectrum 1b indicates that in samples doped with vanadium no detectable amounts of Ti^{3+} ions are present. Prolonged reducing treatment at this temperature results in diminishing of the vanadyl ion spectrum.

Oxygen Adsorption

A significant change in the low-temperature ESR spectrum is observed upon oxygen adsorption on doped vacuum treated TiO_2 at room temperature.

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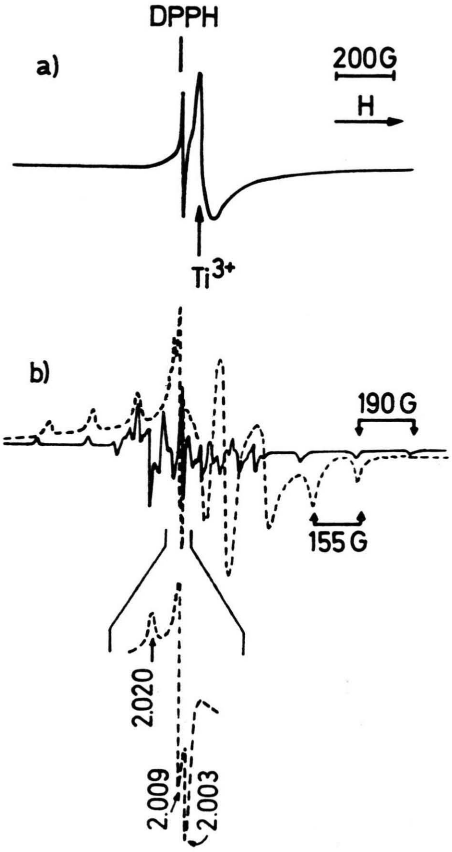

Fig. 1. a) ESR spectrum of pure TiO_2 after vacuum treatment at 600 °C for 2 hours. b) ESR spectrum of TiO_2 doped with 0.1% V: —— after vacuum treatment at 600 °C for 2 hours ---- after oxygen adsorption at room temperature, 10^{-2} Torr.

The formation of two paramagnetic species is detected (Fig. 1b dashed line). One spectrum with $g_1 = 2.020$, $g_2 = 2.009$ and $g_3 = 2.003$ corresponds apparently to the O_2^- radical. This part of the spectrum is reproduced as insert in Figure 1b. The parameters of the other species, i.e. $g_{\|} = 1.956$, $g_{\perp} = 1.912$, and the well resolved hyperfine splitting with $A_{\|} = 155$ G are characteristic for V^{4+} incorporated substitutionally into the rutile matrix. The signal due to $(VO)^{2+}$ ions disappears. Also, when the sample was annealed in air at 600 °C for a short time a strong signal was obtained due to V^{4+} ions built substitutionally into the rutile matrix [2a]. No O_2^- formation was observed under these circumstances [2].

Illumination Experiments

The photoresponse of the O_2^- radical signal upon illumination with light from a high pressure Xenon lamp depended on the oxygen pressure in the vessel.

a) Residual oxygen pressure $\sim 5 \times 10^{-4}$ Torr.

Figure 2a shows the photobehaviour of O_2^- radicals upon illumination in the case when the vessel was evacuated down to $\sim 5 \times 10^{-4}$ Torr. As shown the intensity of the signal decreased upon illumination. Simultaneously an increase of the residual oxygen pressure in the vessel was observed. This behaviour indicates that oxygen photodesorption from the sample takes place. When the light was turned off, the signal corresponding to O_2^- radicals increased again and the pressure in the system simultaneously decreased. This behaviour suggests readsorption of oxygen in the dark period.

b) Residual oxygen pressure $\sim 10^{-1}$ Torr.

The photobehaviour of O_2^- radicals at higher oxygen pressure is presented in Figure 2b. Under illumination the signal corresponding to O_2^- increased. The subsequent dark period practically did not influence the concentration of photoproduced O_2^-.

In order to check whether the observed photoresponse is connected with the formation of excitons across the band gap, illumination experiments were carried out using cut-off filters. It was found that the photodesorption is connected with

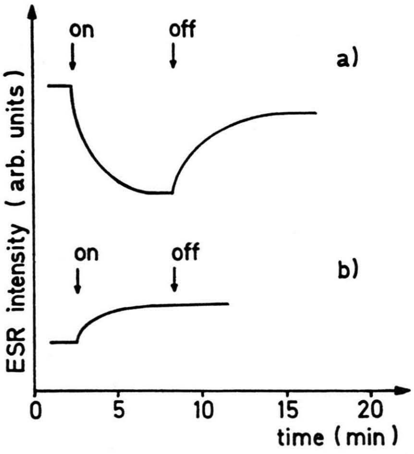

Fig. 2. Photoresponse of the O_2^- radical. a) oxygen pressure 5×10^{-4} Torr; b) oxygen pressure 10^{-1} Torr.

electron-hole photoproduction, since it did not occur upon irradiation with light of wavelenghts $\lambda > 415$ nm ($E < 3.0$ eV).

On the other hand, the photoproduction of O_2^- occurred in a much broader range of wavelenghts. Even with the longest wavelenghts accessible to us ($\lambda > 700$ nm) the effect was still observed.

Discussion

During the last years the interaction of oxygen with TiO_2 as well as with V_2O_5 has been extensively studied, since both oxides are important for the catalytic oxidation of hydrocarbons. It is argued that the speciation of the adsorbed oxygen is one of the major factors influencing the pathway of the catalytic reaction [6].

It was found that in the case of TiO_2 most of the oxygen is chemisorbed as O_2^- species. The ESR experiments demonstrated that pretreatment in vacuo results in the formation of Ti^{3+} ions. Upon contact with oxygen these centers were depleted, and simultaneously the formation of O_2^- radicals was observed [3, 7].

The results of the ESR investigation reported here demonstrate that the spectra of vanadium doped TiO_2 depend on the extent of vacuum pretreatment. Samples show the presence of small amounts of vanadium ions in vanadyl coordination. The intensity of the $(VO)^{2+}$ absorption decrases with the time of vacuum reduction. The majority of vanadium, however, is revealed after annealing in air, in the form of substitutional V^{4+} ions. The observed appearance of V^{4+} ESR signal upon sample oxidation is most probably due to the fact that during vacuum treatment, which leads to a loss in oxygen, the incorporated vanadium undergoes reduction to V^{3+} ions. These centers are non-Kramers ions and do not give an ESR signal. Reoxidation transforms them into V^{4+} ions giving rise to the observed strong ESR absorption being characterized by the values $g_{\parallel} = 1.956$, $g_{\perp} = 1.912$ and the well resolved eight line hyperfine structure with $A_{\parallel} = 155$ G. No detectable amount of Ti^{3+} was found in the vacuum treated vanadium doped TiO_2, in agreement with data reported by others [8, 9]. Evidently the excess electrons are preferably located on dopant ions. Only the $+4$ oxidation state is detectable by ESR.

Oxygen Chemisorption

The room temperature chemisorption of oxygen on vacuum treated doped TiO_2 containing 0.1 or 0.3at.% vanadium results in the formation of O_2^- oxygen radicals (Fig. 1b-insert). From the simultaneous appearance of V^{4+} ions at substitutional sites it is concluded that V^{3+} ions were acting as electron donors to the adsorbed oxygen. The lack of hyperfine structure and the g-values similar to those obtained for O_2^- adsorbed on pure TiO_2 [10] suggest, however, that the oxygen radicals are located in the neighbourhood of titanium rather than vanadium ions. A similar effect was observed for V_2O_5 supported on MgO [11], where O_2^- radicals created were stabilized on Mg^{2+} ions. It is argued that the adsorptive properties of vanadium ions depend strongly on their coordination in the lattice. The octahedral surrounding, which exists in the V_2O_5/TiO_2 as well as in the V_2O_5/MgO systems prevents the stabilization of O_2^- radicals at the dopant ions. On the other hand the tetrahedral coordination existing in the V_2O_5/SiO_2 system provides suitable conditions for oxygen radicals to be stabilized on vanadium centers [12].

Photobehaviour of the O_2^- Radical

The illumination experiments demonstrated that, depending on the oxygen pressure in the vessel, an increase or a decrease in the O_2^- absorption can be obtained. A similar observation is reported for pure TiO_2 [13, 14].

Assuming formally that O_2^- is the only chemisorbed oxygen species, the following equations may be considered to relate the observed effects upon illumination to the oxygen pressure:

$$(TiO_2) + h\nu \rightleftarrows p^+ + e^- , \tag{1}$$

$$O_{2\,(g)} \rightleftarrows O_{2\,(ads.)} , \tag{2}$$

$$O_{2\,(ads.)} + e^- \rightarrow O_2^- , \tag{3}$$

$$O_2^- + p^+ \rightarrow O_{2\,(ads.)} . \tag{4}$$

Reactions (3) and (4) are considered irreversible. According to this scheme, the oxygen pressure determines the surface coverage with adsorbed oxygen. That is why at high oxygen pressures the enhancement or photoadsorption is expected. On the other hand at low oxygen pressures photodesorption should be favoured. The resulting low surface coverage of oxygen will limit the contribution of reaction (3). As a result the recombination of the photoproduced holes with surface oxygen radicals, according to reaction (4), will dominate in the net effect.

The experimental results reported here are in agreement with the above consideration. Reversible photodesorption of oxygen was observed at a residual oxygen pressure of $\sim 5 \times 10^{-4}$ Torr. The net photoadsorption effect was only observed at the higher oxygen pressure of $\sim 10^{-1}$ Torr.

The use of cut-off filters demonstrated that the photodesorption effect depends on the transition across the band gap. This is understandable since, according to (4), the photodesorption is due to the recombination of O_2^- radicals with photoproduced holes. On the other hand the photoadsorption occurred in a much broader range of wavelengths. Thus it may be concluded that not only electrons from excitons, but also electrons from donor levels below the conduction band are effective in the formation of the O_2^- species.

Conclusions

Adsorption of oxygen on vacuum treated vanadium doped TiO_2 leads to the formation of O_2^- radical species.

Electron transfer is discussed to occur from substitutional V^{3+} non-Kramers centers turning them into V^{4+} ions which become detectable in the ESR spectrum. The lack of hyperfine structure indicates that the oxygen radicals are stabilized on the titanium rather than on vanadium ions.

Upon illumination at low oxygen pressure photodesorption of oxygen is observed, whereas at higher oxygen pressure the photoadsorption is favoured.

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