An ESR Investigation of Illuminated Polycrystalline TiO_2

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(Z. Naturforsch. **32 a**, 501–504 [1977]; received March 19, 1977)

Formation of paramagnetic centers in polycrystalline TiO_2 samples and changes thereof upon heat treatment, addition of oxygen, and illumination, respectively, are described. From the temperature dependence of the disappearance of a photoproduced Ti^{3+} signal with $g=1.96$ an apparent activation energy of $\sim$1 kcal/mole is estimated for the electron annihilation processes.

Introduction

Titanium dioxide has recently attracted the attention of several authors [1–5] as a semiconductor active in the process of the photoassisted decomposition of water. On the other hand, the photosorption of several gases, especially oxygen on TiO_2 was extensively studied by investigators interested in catalytic properties of this oxide [6–12]. Some of the data obtained in the latter studies may be helpful in the elucidation of the photoelectric properties of TiO_2. In the presence of excess oxygen the ESR observation of surface centres, which are formed upon illumination of the polycrystalline TiO_2 material may be difficult if not impossible. It seems therefore reasonable to undertake an investigation of the effect of oxygen on these centres and of the temperature dependence of their lifetime in thermally pretreated polycrystalline material.

Experimental

Polycrystalline TiO_2 (optipur, Merck) was used in all experiments. Samples without any pretreatment in vacuo are designed as samples A. Samples heated in vacuo at different temperatures are denoted as samples B and labeled with a number indicating the temperature at which the heat treatment was performed, e. g. B-200 denotes preparation of TiO_2 in vacuo at 200 °C.

The ESR spectra were recorded in the temperatures range from -160 °C up to 20 °C by using an E-12 Varian spectrometer operating in the X-band and a variable temperature accesory V-4557.

The samples were illuminated in situ with light from a high pressure xenon lamp.

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Results and Discussion

1. ESR Spectra of Thermally Unpretreated TiO_2

Unpretreated polycrystalline TiO_2 (sample A) shows at -160 °C an ESR spectrum, in which a strongly asymmetric signal dominates with a g-factor near 2.00 (Figure 1 a). The spectrum is evidently composed of several overlapping lines arising from defects in the TiO_2 crystal lattice and from other paramagnetic species adsorbed at the surface. According to data in the literature ESR signals of the crystal defects in TiO_2 show g-factors ranging from 1.94 to 2.00. The signal with $g=1.96$ is usually considered as most characteristic for defects in TiO_2. The adsorbed oxygen species are responsible for the absorption around $g=2.00$.

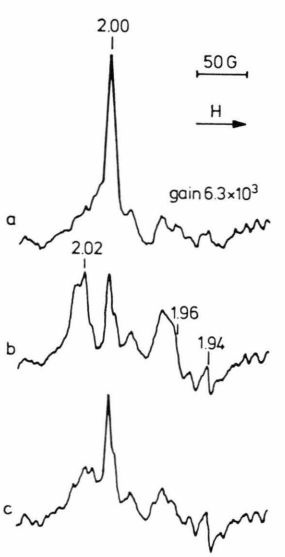

Fig. 1. ESR spectrum of unpretreated TiO_2 (sample A): a) before illumination, b) in the course of illumination, c) 10 min after ceasing of the illumination.

In the presence of air the ESR spectrum undergoes significant changes upon irradiation with light from a xenon-lamp at $-160\,^{\circ}C$ (Figure 1 b). The signal at $g = 2.00$ diminishes, whereas some new lines appear with g-factors equal to 1.94, 1.96 and 2.02 respectively. The ease of formation of the centre with $g = 1.96$ might be related to the presence of impurities in the polycrystalline material. After ceasing of the illumination the primary specrum is slowly restored. The time necessary for signal recovery is different for the individual lines of the spectrum. Most of the changes are removed after 10 min. The signal with $g = 2.00$ however does not reach the same intensity as before illumination any more within the period of our investigations (Figure 1 c).

2. *ESR Spectra of Thermally Pretreated TiO_2*

a) Heat Treatment in Vacuo

Treatment in vacuo at 10^{-6} Torr for 1 hr at temperatures up to $250\,^{\circ}C$ does not change the ESR spectrum of TiO_2. At temperatures around $300\,^{\circ}C$ the asymmetric composite signal converts into an intensive, almost symmetric line. Simultaneously a signal with a g-factor equal 1.96 is observed, which usually is ascribed to the presence of Ti^{3+} ions in the TiO_2 lattice [6–12]. The intensity of this signal is lower by a factor of ca. 10 than that of the signal with $g = 2.00$. Prolonged outgassing at $300\,^{\circ}C$ results in an increase in the intensity of the signal with $g = 2.00$, whereas the signal attributed to Ti^{3+} ions remains unchanged.

Additional treatment in vacuo at temperatures around $550\,^{\circ}C$ results in a slight intensity reduction of the $g = 2.00$ signal. Interestingly the signal with $g = 1.96$ is distinctly lowered. A similar effect was observed by other authors [6, 14, 15]. In several cases the strongly reduced and colored samples of TiO_2 did not even show any signal with $g = 1.96$. This effect is explained by the formation of narrow defect bands resulting from a large number of overlapping donor levels in strongly reduced TiO_2 in which the mobility of electrons is too high to enable the observation of an ESR signal at room or liquid nitrogen temperature. It was noticed in our experiments, that the quality factor Q of the cavity was markedly reduced by samples treated at the higher temperatures apparently due to the large number of mobile charge carriers in the sample.

The symmetric sharp line with $g = 2.00$ observed also by other authors in the ESR spectra of reduced TiO_2 was attributed either to surface carbon impurities [7, 12] or to defects like O^- in the bulk of TiO_2 lattice [9].

b) Adsorption of Oxygen

Upon introduction of oxygen or air to samples of TiO_2 pretreated in vacuo at temperatures higher than $250\,^{\circ}C$ different changes in the ESR spectrum are observed depending on the temperature at which the gases were added. Introduction at $-160\,^{\circ}C$ results in a small decrease of the symmetric signal at $g = 2.00$ and in the appearance of an absorption with $g = 1.96$. The observations made at $20\,^{\circ}C$ are discussed separately for the two resonances.

After addition of air at $20\,^{\circ}C$ a signal is obtained which is similar around $g = 2.00$ to that of the untreated sample (Figure 1 a). Figure 2 shows the ESR spectrum of TiO_2 before (a) and after (b) introduction of air to yield a partial oxygen pressure 70 Torr at $20\,^{\circ}C$. Subsequent outgassing of the sample at $20\,^{\circ}C$ down to 10^{-3} Torr reveals, that the changes of the signal are irreversible. The central signal with g around 2.00 diminishes considerably and a signal due to O_2^- species appears [11, 13] (Figure 2 c). The signal of the

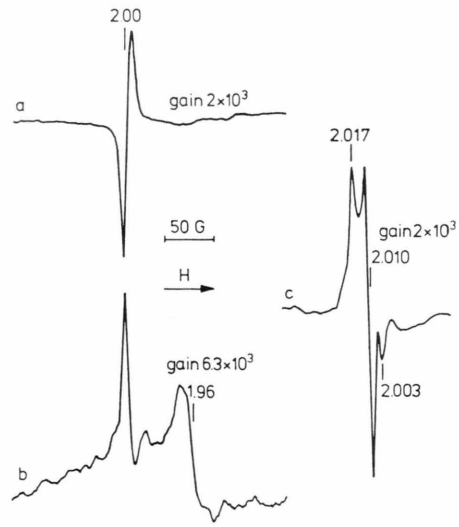

Fig. 2. ESR spectrum of vacuum pretreated TiO_2 (sample B-450): a) ESR spectrum of TiO_2 pretreated at $450\,^{\circ}C$, b) as above after admission of air at $20\,^{\circ}C$ corresponding to a partial oxygen pressure of 70 Torr, c) as above after evacuation to the pressure 10^{-3} Torr.

O_2^- radical is not seen before removing of the excess oxygen from the gas phase due to dipolar broadening which confirms surface character of the species responsible for this signal.

As mentioned above the spectrum shown in the Fig. 2 b is in the region $g = 2.00$ similar to that of unpretreated TiO_2. However, the spectrum of the untreated sample does not change upon outgassing in the temperature range $20\,^{\circ}C < T < 250\,^{\circ}C$. If similar paramagnetic species are responsible for the particular overlapping ESR signals in the observed spectrum they should be situated predominantly in the bulk of the unpretreated TiO_2 crystal, which makes them unsensitive towards changes in oxygen pressure in the gas phase.

The signal of Ti^{3+} with $g = 1.96$ was only barely observable in samples heated to 450 °C before the admission of oxygen. After exposure to air at 20 °C the spectrum shown in Fig. 2 b was obtained. Under these conditions the signal with $g = 1.96$ shows a reasonable intensity. A weak resonance at $g = 1.96$ was already detected after admission of oxygen at $-160\,^{\circ}C$.

Two mechanisms are conceivable for the appearance of the signal with $g = 1.96$ upon oxygen admission: Oxygen adsorption results in O_2^- ion formation and thus traps on localized sites part of the highly mobile electrons present in the heat treated TiO_2. The concentration of the charge carriers in TiO_2 is markedly descreased this way. It is suggested, that the critical free carrier concentration necessary for the formation of defect bands is not attained any more. Thus the remaining electrons stay localized [16] and form the Ti^{3+} centres.

An alternative way to interpret our result rests on the assumption, that paramagnetic and diamagnetic defect centres exist in highly reduced TiO_2. The paramagnetic centres are too mobile for ESR detection. The presence of diamagnetic defect centres is well known for Ta_2O_5 and Nb_2O_5 [17, 18]. Experimental observations of the diamagnetic centres in these oxides in the presence of efficient electron acceptors indicate, that only one electron is transferred to the acceptor. The diamagnetic centre is converted into a paramagnetic centre which can be detected by ESR [19]. Oxygen as electron acceptor traps not only part of the electrons from the originally paramagnetic centres but is also able to convert in part at least the diamagnetic centres into paramagnetic defects which are then seen als Ti^{3+}.

3. Photolysis Experiments

The ESR spectra of illuminated TiO_2 were investigated by other authors mainly with respect to the photoadsorptive properties of this oxide. Changes of the ESR signal of adsorbed oxygen species and of bulk defects with a g-factor around 2.00 are observed by Fukuzawa et al. [8] in the course of photoadsorption of oxygen on TiO_2. Kazansky et al. [6] interpreted these changes as the formation of oxygen radicals O^-. Their results were obtained by illuminating TiO_2 on SiO_2 in the presence of oxygen. According to others [11] chemisorption of oxygen on TiO_2 is generally accompanied by a decrease in the intensity of the signal with $g = 1.96$ attributed to the Ti^{3+} ions.

Our own investigations concentrate on the behaviour of the signal with $g = 1.96$. In the present work no significant changes of the ESR spectrum were observed upon illumination of TiO_2 samples $B > 250$ before admission of oxygen. However, a distinct increase in the intensity of the signal wit $g = 1.96$ is achieved if these samples B were illuminated at $-160\,^{\circ}C$ in the presence of oxygen.

It appears that the photoinduced electrons are trapped by Ti^{4+} ions forming Ti^{3+} centres and/or by oxygen molecules creating O_2^- species. At $-160\,^{\circ}C$ in the presence of oxygen, formation and stabilization of Ti^{3+} centres occurs much more rapidly than their annihilation in the dark leading to a stationary Ti^{3+} concentration (Figure 3). At $-160\,^{\circ}C$ 80% of the photoinduced centres are formed in the period of a few seconds, whereas annihilation of 50% of them takes ca. 2.5 minutes. Presumably centres in a range of stabilities are formed in this polycrystalline material. This seems to be indicated by the complex kinetics for both the formation and the disappearance of these species, the more stable centres having a lifetime of many minutes at $-160\,^{\circ}C$.

With the light intensity available in these experiments there is no chance to detect these centres at room temperatures. In Fig. 4 are plotted the changes of the stationary state concentration of the centre with $g = 1.96$ as function of the inverse temperature. Samples pretreated at 200 °C and at 450 °C were investigated.

On the assumption that the stationarity in Ti^{3+} signal intensity indicates equilibrium between the rate of formation of these centres ($\vec{k}$) and the rate of their

disappearance ($\overleftarrow{k}$), the temperature dependence of the equilibrium constant $K = \vec{k}/\overleftarrow{k}$ can be obtained. If the rate of centre formation had no temperature dependence, or at least a dependence much smaller than the rate of centre annihilation, an apparent activation energy of ~ 1 kcal/mol could be calculated for the latter process from the slope of the straight lines in Figure 4.

Acknowledgements

The authors are indepted to Dr. Svejda for a helpful discussion.

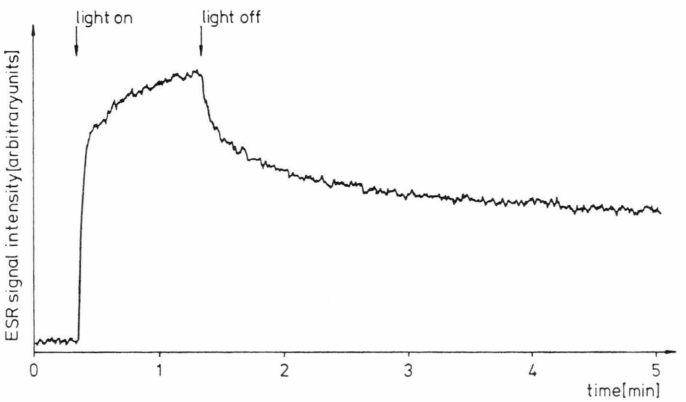

Fig. 3. Rate of the formation and annihilation of photo-induced centres responsible for ESR signal with $g=1.96$ at -160 °C on the sample B-450.

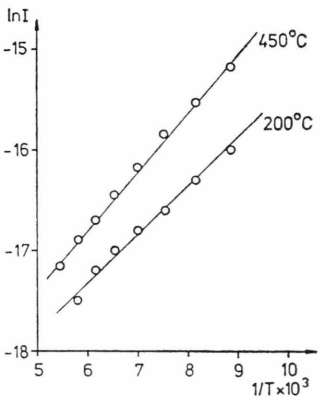

Fig. 4. Temperature dependence of the annihilation for centres with $g=1.96$.

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