Localization of Conduction Band Electrons in Polycrystalline TiO_2 Studied by ESR

E. Serwicka *, M. W. Schlierkamp, and R. N. Schindler
Institut für Physikalische Chemie, Universität Kiel

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Adsorption of electron acceptors on partially reduced TiO_2 leads to the localization of mobile conduction band electrons which is indicated by the appearance of an ESR signal with $g = 2.003$. The localization process is accompanied by an electron transfer from donor centers in reduced TiO_2 (Ti^{3+} ions) to adsorbed molecules. The ESR spectra show a decrease of the Ti^{3+} signal intensity at $g = 1.96$. Additionally, in the case of O_2, SO_2 and $C_6H_5NO_2$ adsorption, the ESR signals of the respective anion radicals are observed. Illumination of samples with an electron acceptor adsorbed enhances the $g = 2.003$ signal. The activation energy corresponding to the temperature dependence of the localization process has been determined to be ~ 1 kcal/mole in the temperature range -140 to -40 °C. In the case of O_2 and N_2O the signal at $g = 2.003$ could be annihilated chemically by using propylene which reacted with the adsorbed electron acceptor and thus removed the species which reduced the electron mobility.

Introduction

The effect of localization and trapping of excess electrons has attracted much interest in recent years, specially in the field of radiation chemistry [1, 2]. The electrons produced in condensed media by irradiation are localized due to medium polarization which tends to stabilize them. These electrons show a sharp, structureless ESR absorption with a g factor close to that of free electrons [1].

ESR studies of semiconducting TiO_2 indicate that under special conditions a reduction in conduction band electron mobility may be brought about, which also leads to the appearance of the characteristic absorption with $g = 2.003$ [3]. There is a general agreement that the ESR signal at $g = 1.96$ observed in TiO_2 submitted to vacuum or hydrogen reduction is due to the formation of $Ti^{3+}(3d^1)$ ions [4]. The symmetric signal at $g = 2.003$ noticed by some investigators was attributed either to electrons trapped on oxygen vacancies and described as F- or S-centers [5, 6] or to carbon impurities [7].

Adsorption of oxygen on reduced TiO_2 leads to the appearance of an O_2^- ESR signal [4]. In a few cases also a singlet, symmetric line at $g = 2.003$, following oxygen treatment was observed [3, 8, 9]. Depending on the oxygen pressure, this line either dominated in the ESR spectrum or was superimposed on the g_3 component of the O_2^- radical. The assignment of this signal to the O^- species appears still to be controversial since it is inconsistent with the theoretical spectrum [4]. Tench et al. have shown that the line with $g = 2.003$ stays unaffected by treatment with oxygen enriched with the isotope ^{17}O and therefore cannot be assigned to O^- [3]. They attributed the signal to an absorption by conduction electrons being localized in the lattice by the adsorbed oxygen.

In the present paper the interaction is studied between mobile conduction band electrons of the semiconducting TiO_2 with adsorbed species which possess a high electron affinity and are often used as electron scavengers. Special attention is paid to the occurrence of the localization phenomenon and its sensitivity towards illumination.

Experimental

1. *Preparations*

For each experiment a new sample of polycrystalline TiO_2 (optipur Merck) weighing 0.025 g was used. After pretreatment in vacuo (10^{-5} to 10^{-6} Torr) at 500 °C the sample was inserted into the ESR cavity while staying connected to a vacuum line equipped with greaseless stopcocks.

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* On leave from Institute of Catalysis, Polish Academy of Sciences, Krakow, Poland.

Reprints request to Prof. Dr. R. N. Schindler, Institut für Physikalische Chemie, Olshausenstraße 40/60, Neue Universität Haus S 12c, D-2300 Kiel 1.

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2. Adsorption

The following gases and vapours of different electron affinities were used in the adsorption experiments: O_2, N_2O, CO_2, SF_6, SO_2, H_2S, $C_6H_5NO_2$, CCl_4, $CHCl_3$, CH_2Cl_2, CH_3Cl, CH_4, CF_4, C_2H_4, C_3H_6, H_2 and Ar. The majority of compounds were degassed at the vacuum line by repeated freeze-thaw cycles. A prolonged purging preceeded adsorption of noncondensable gases. The gases were introduced at room temperature in the pressure range 4—10 Torr and the ESR spectra were taken after cooling down the sample to −150 °C. Afterwards the samples were warmed up to room temperature and evacuated before further ESR spectra were taken to check on the influence of excess gas on the sample.

3. ESR Analysis

The ESR spectra were recorded in the temperature range −150 °C up to room temperature using a Varian E-line Century Series ESR spectrometer model E-112 operating in the X-band and a variable temperature accessory V-457. Spin densities were extimated by use of a $VOSO_4$ standard.

4. Illumination Experiments

The samples were illuminated in situ with a high pressure Xenon lamp, its light being focused onto an optical transmission cavity type 3-234. A set of cut-off filters was used to check on the wavelength dependence of the observed phenomena.

Results

1. Adsorption Experiments

The ESR spectrum of vacuum reduced TiO_2 is shown in Fig. 1 (solid line). It consists of two signals. As mentioned above the broad line with $g = 1.96$ and $\Delta H = 40$ G is characteristic for Ti^{3+} ions in a TiO_2 matrix. The other, with $g = 2.003$ is attributed to the electron trapped on an oxygen vacancy. The possibility of paramagnetic carbon impurities can be excluded in our case, as the signal was also observed when the sample prior to vacuum treatment was heated in air at 500 °C for two hours. Annealing of pretreated samples in oxygen removed all paramagnetic centers immediately.

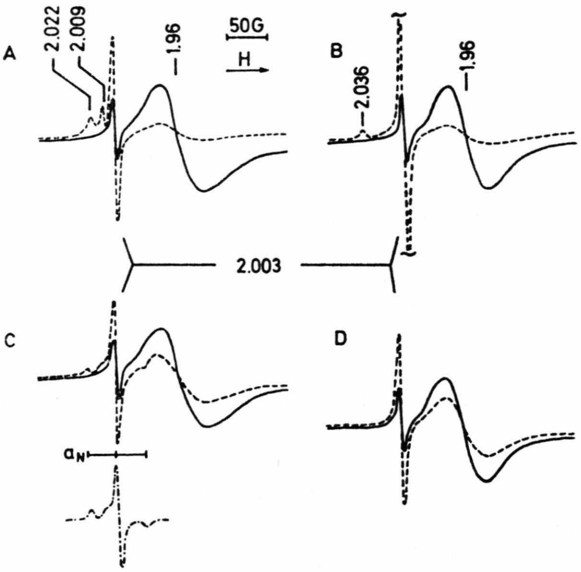

Fig. 1. ESR spectra of TiO_2 samples before (———) and after (– – – – –) adsorption of oxygen (A), sulphur dioxide (B), nitrobenzene (C), sulphur hexafluoride (D).

Adsorption of oxygen results in a strong increase of the signal with $g = 2.003$ accompanied by a decrease in Ti^{3+} ion signal intensity. Simultaneously the spectrum of O_2^- radical shows up (Fig. 1 A dashed line). Both new signals are strongly affected by the addition of air at atmospheric pressure. They drastically decrease upon introduction of air but are easily restored by subsequent evacuation. Such behaviour suggests surface character of species responsible for these signals. As the number of O_2^- radicals produced ($\sim 10^{15}$/g) is distinctly lower than the number of Ti^{3+} ions removed upon oxygen admission ($\sim 10^{17}$/g) it is suggested that oxygen adsorption at room temperature leads predominantly to the formation of diamagnetic O^{2-} ions which restore part of the initial oxide defect structure.

Adsorption of sulphur dioxide results in a very strong increase of the $g = 2.003$ singlet, its intensity being an order of magnitude higher than in the initial sample. Simultaneously the formation of a new paramagnetic radical with a low field g component equal to 2.036 is observed together with a decrease of the Ti^{3+} peak (Figure 1 B). The new spectrum around $g = 2.00$ is assigned in part at least to the formation of SO_2^- with possible contribution from SO_3^-. The g factors of both species are very close to each other and to the signal of the free electron and therefore cannot be distinguished under the given conditions [10, 11]. The weak signal at $g = 2.036$ is tentatively attributed to SO_4^- radicals since its position is close to the $g_\perp$ value of this anion radicals as reported in the literature [12, 13].

Also adsorption of nitrobenzene results in an increase of the $g = 2.003$ signal intensity. Simultaneously the spectrum characteristic for the $C_6H_5NO_2^-$ anion radical appears and Ti^{3+} signal intensity is reduced (Figure 1C). Formation of $C_6H_5NO_2^-$ is clearly demonstrated upon registration of the ESR spectrum at room temperature (see insert Figure 1C).

Adsorption of other gases or vapours known as electron acceptors also results in a strong increase of the singlet with $g = 2.003$. In each case a decrease in Ti^{3+} signal intensity is observed. No new signals appear which could be ascribed to new paramagnetic species. The picture was qualitatively the same for all electron acceptors applied, i.e. N_2O, CO_2, SF_6, H_2S, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4. The situation for SF_6 is depicted in Figure 1D. Within a set of similar compounds, the molecules with the higher affinity showed a more pronounced effect on the initial spectrum. Table 1 shows the results of adsorption experiments using the chloroderivatives of methane as electron trapping agents. Whereas CH_4 adsorption does not influence the signal intensity of both absorptions, the signal at $g = 2.003$ is increased with all halogenated species. The simultaneous reduction in Ti^{3+} signal intensity is the more ponounced the more effective the adsorbate is known to act as electron scavenger in the liquid as well as in the gas phase [14].

A comparison of the spectra obtained at different temperatures revealed that the $g = 2.003$ signal in samples containing the adsorbed scavenger results from at least two centers having different relaxation characteristics. The centers giving rise to the intensity increase upon scavenger adsorption relax faster than the centers present in the initial sample.

Adsorption of gases and vapours with no appreciable electron affinity such as Ar, H_2, C_3H_6, C_2H_4, CH_4 and CF_4 did not affect the $g = 2.003$ signal noticeably. Also, no increase was observed when the TiO_2 surface prior to electron scavenger adsorption was covered with adsorbed atoms or molecules which do not show electron acceptor properties, such as argon and propylene. Such pretreatment prevents also anion radical formation e.g. O_2^- upon oxygen adsorption.

The adsorption of all electron scavengers used was accompanied by a change of sample colour from grey to almost white.

2. *Test of Chemical Reactivity*

In order to check on the chemical reactivity of species responsible for the increase in signal intensity of the singlet at $g = 2.003$, the behaviour of this signal upon contact with propylene was investigated. Propylene has been chosen since its chemical affinity towards active forms of oxygen is well known [15]. The results are presented in Table 2. As it is seen, the $g = 2.003$ signal itself in the vacuum treated sample is not influenced by the adsorption of propylene. On the other hand, the additional signal intensity obtained from samples treated with O_2 and N_2O was removed upon subsequent contact with C_3H_6 reaching practically its initial value. The signal arising after SF_6 adsorption remained unaffected when the sample was exposed

Table 1. Changes in $g = 2.003$ and $g = 1.96$ signal intensity upon adsorption of chloroderivatives of methane (ESR intensity — arbitrary units).

Sample treatment	ESR signal intensity (arbitrary units)	
	$g = 2.003$ signal	$g = 1.96$ signal
initial sample	1.00	1.00
+ CH_4	1.01	1.00
+ CH_3Cl	1.09	0.86
+ CH_2Cl_2	1.21	0.81
+ $CHCl_3$	1.26	0.60
+ CCl_4	1.20	0.11

Table 2. The chemical reactivity towards C_3H_6 of the species responsible for the ESR signal with $g = 2.003$ (ESR intensity — arbitrary units).

Sample treatment	ESR signal intensity (arbitrary units)	
	before C_3H_6 adsorption	after C_3H_6 adsorption
initial sample	1.0	1.0
initial sample + O_2	1.7	1.2
initial sample + N_2O	1.9	1.1
initial sample + SF_6	1.5	1.5

to proylene. These observations demonstrate that different chemical species give rise to the increased absorption at $g = 2.003$.

3. *Illumination Experiments*

a) Photoresponse without Adsorbed Scavenger

The results of illumination experiments are presented in Figure 2. When the vacuum treated TiO_2 samples were illuminated at -150 °C the signal at $g = 2.003$ decreased distinctly (Fig. 2a) indicating a decrease in concentration of the centers responsible for this absorption. The process was reversible. When the light was switched off the signal was restored to its initial intensity.

Simultaneously a photoresponse of the $g = 1.96$ signal, attributed to Ti^{3+} ions, was observed. Its behaviour was similar, i.e. on illumination the signal intensity went down, while in the dark it came back to the initial level.

Experiments were carried out using cut-off filters to obtain information on the energy of the states involved in these photoinduced changes. They show clearly that no transition across the band gap is responsible for our observations, since the elimination of light with energy $E \geqq 3.0$ eV does not affect the observed phenomenon at all. Even with the longest wavelengths $\lambda \geqq 700$ nm ($E \leqq 1.8$ eV) accessible to us, the photoresponse of the sample was the same as using the full light of the lamp. Small changes observed in the amount of signal decrease are attributed to a light intensity effect.

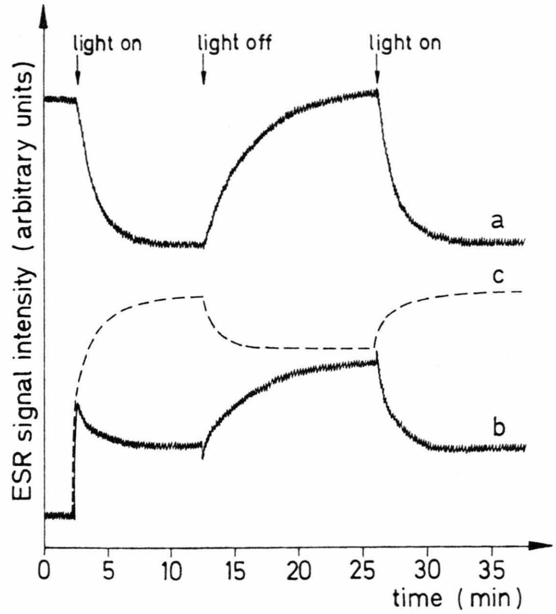

Fig. 2. Photoresponse of ESR signal with $g = 2.003$:
a) vacuum treated TiO_2 sample,
b) after electron acceptor adsorption,
c) net curve obtained by subtracting curve a) and b).

b) Photoresponse in the Presence of Adsorbed Electron Scavengers

A different photoresponse was observed in the presence of an electron acceptor on the surface of TiO_2. When these samples were submitted to illumination at -150 °C, the $g = 2.003$ signal first increased immediately, then slowly decreased again (Figure 2b). When the light was switched off an increase of the signal was observed. Subsequent on/off cycles gave qualitatively the picture as in case (a), except of the small spikes in the beginning of each light and dark period. The signal intensity never went down to its initial value. This could only be reached by warming the sample up to room temperature and subsequent cooling down to -150 °C.

The behaviour of the $g = 1.96$ line was the same as for the TiO_2 samples without adsorbed scavenger, i.e. on illumination the Ti^{3+} signal went down, but was restored when the light was off.

Two sets of experiments were carried out to determine the temperature dependence of the photoeffect for samples with adsorbed scavenger. The intensity changes of the signal at $g = 2.003$ for vacuum treated samples under illumination were measured in the range $-140\ °C < T < -40\ °C$

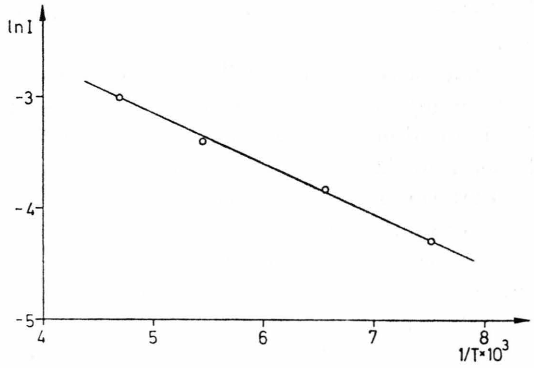

Fig. 3. Temperature dependence of the photoeffect at $g = 2.003$ for TiO_2 sample containing adsorbed SF_6.

prior to and after admission of SF_6. The difference in intensity was taken as a measure of scavenger contribution. The results are shown in Figure 3. The graph of ln ΔI, where I describes the line intensity, versus reciprocal temperature shows a linear decrease of the photoeffect due to the presence of adsorbed scavenger. Since the additional signal appears always at $g = 2.003$ independent of the chemical nature of the adsorbate it is suggested that the center is connected to the adsorber TiO_2 rather than to the adsorbed layer.

Discussion

1. Adsorption Experiments

The experiments reported in the present paper show that adsorption of each of the electron scavengers used on TiO_2 leads to a strong increase of the signal with $g = 2.003$. The analysis of the spectra obtained at different temperatures indicates that the $g = 2.003$ line in samples with adsorbed electron scavengers is a superposition of at least two separate signals having different relaxation characteristics.

In a paper concerned with the identification of adsorbed oxygen species on reduced anatase powder Tench et al. [3] observed a symmetrical line at $g = 2.003$ arising after oxygen adsorption. The line was superimposed on the high field g component of the O_2^- radical spectrum. Although the line appeared upon oxygen adsorption no hyperfine splitting was observed when oxygen enriched with ^{17}O was used. Since at 77 K a rapid exchange with oxide ions of the lattice is unlikely, it is argued that the signal could not be attributed to an oxygen species such as O^-. The authors suggested that the symmetric line arises from the localization of the conduction band electrons in the lattice by the adsorbed oxygen.

Our results strongly support Tench's assignment. All our findings can be interpreted in terms of localization and/or reduced mobility of conduction band electrons in TiO_2. The experiments show clearly that this signal is not connected with any adsorbed oxygen species, since it appeared also with acceptor molecules which do not contain oxygen, like SF_6 and H_2S. Also, the adsorption experiments with a series of chlorine containing methanes show that the localization phenomenon gradually increases with the electron affinity of the adsorbate.

It is consistent with the above assignment that no increase of the signal with $g = 2.003$ was observed in experiments with gases which do not show electron acceptor properties such as Ar, H_2, CH_4, C_2H_4, C_3H_6 and CF_4.

It is of interest to point out that localization was also not observed when the TiO_2 surface prior to electron acceptor adsorption was covered with atoms or molecules which possess no electron affinity like Ar and C_3H_6. Such behaviour indicates a strong dependence of the localization phenomenon on the adsorbate — TiO_2 surface distance.

The results reveal that the process of localization of conduction band electrons in accompanied by an electron transfer to the adsorbed molecules upon admission of electron acceptors. The observed change in colour from grey to almost white indicates Ti^{3+} oxidation. Spectroscopically a decrease of the ESR signal due to these ions is observed showing the depletion of these donor centers in the transfer reaction (see below).

In the case of oxygen, sulphur dioxide and nitrobenzene the formation of stable paramagnetic anion radicals is shown. In other cases the products of the electron transfer process were not detected in ESR. This may be due e.g. to their short life or relaxation times or to diamagnetic properties of adsorbed species. Also, the occurrence of dissociative chemisorption is possible whereby a variety of species may be formed. This concerns specially the chloroderivatives of methane. It is well known that CCl_4 reacts with TiO_2 already at room temperature leading to the chlorination of the surface [16]. The particulary strong decrease of the $g = 1.96$ signal for samples treated with CCl_4 (Table 1) indicates that chemisorption involving electron transfer from Ti^{3+} ions plays here an important role.

2. Test of Chemical Reactivity

The results of the reactivity test using C_3H_6 lend further support to the assumption that the increase in signal intensity obtained after scavenger adsorption on semiconducting TiO_2 is due to the localization of conduction band electrons.

TiO_2 is known as a catalyst for hydrocarbon oxidation. Propylene is a compound which easily reacts with oxygen on the catalyst surface. Reactive oxygen species are supposed to be formed when O_2 or N_2O is adsorbed on n-type semiconducting oxides. In the case of N_2O a unimolecular decomposition occurs on the oxide surface [15, 17]. The exposure of TiO_2 samples containing preadsorbed oxygen or nitrous oxide to propylene leads to a reactive removal of the oxygen species. In consequence the surface concentration of adsorbed scavenger is reduced. This results in a decrease of the signal attributed to the localized conduction electrons (see Table 2). On the other hand, propylene has no influence on the $g = 2.003$ signal arising after SF_6 adsorption. Here, the scavenger is not reactively removed and thus keeps the conduction band electrons localized.

3. *Illumination Experiments*

The illumination of TiO_2 samples without electron acceptor adsorbed and in the presence of a scavenger showed different photoresponse of the $g = 2.003$ signal (Figure 2).

a) Photoresponse without Adsorbed Scavenger

The absorption of light quanta by the vacuum treated TiO_2 leads to a reversible decrease of the $g = 2.003$ signal (Figure 2a). As pointed out above, this signal is attributed to electrons trapped on oxygen vacancies.

Since light can be absorbed by the electrons in the valence band and/or by the defects, two possible reasons for the observed behaviour should be taken into consideration.

If the valence band electrons absorb light and are lifted to the state of singly ionized vacancies which turn diamagnetic, the signal at $g = 2.003$ would decrease. If singly ionized vacancies were involved in the electron transfer upon absorption of quanta, doubly ionized states would result, which also leads to a decrease of the $g = 2.003$ ESR absorption. There is a number of investigations reported on the energetic position of oxygen vacancies [18—20]. It is generally agreed that oxygen vacancy states in TiO_2 are located ~ 2.2 eV above the valence band. Our experiments with cut-off filters showed that even light with energy lower than 1.8 eV decreases the $g = 2.003$ signal. Thus absorption by the valence band electrons does not seem to be responsible for the observed photobehaviour of the $g = 2.003$ line. On the other hand, the energy distance between oxygen vacancy states and the bottom of the conduction band amounts to ~ 0.8 eV. This energy gap is small enough to make the electron transfer possible in our experiments even with the longest wavelengths used. It is suggested that the latter process is responsible for the observed photoresponse of the $g = 2.003$ signal in reduced TiO_2. Also a decrease in Ti^{3+} signal intensity is observed upon illumination. Light absorption by these centers may occur, whereby electrons are transferred to the conduction band. The energy difference between the Ti^{3+} state and the conduction band edge is considered to be 0.1—0.2 eV [20, 22]. Dissipation of light quanta in the lattice would provide ample energy to make such process possible.

b) Photoresponse in the Presence of Adsorbed Electron Scavenger

The photobehaviour of the $g = 2.003$ signal in TiO_2 samples with adsorbed electron acceptor is represented in Figure 2b. Upon illumination a rapid increase of the line intensity is observed followed by its decrease. Subsequent on/off cycles give qualitatively the picture as in case a). The photoresponse of the Ti^{3+} centers was not affected by the presence of adsorbed scavenger.

It is suggested that curve b) represents a superposition of two processes: one is given by curve a), the other by a hypothetical curve c). The former is attributed to the signal from the vacuum treated sample. Its intensity decrease when the light is on. The other has to be ascribed to the photoresponse of species becoming apparent after scavenger adsorption. For these species illumination must lead to an immediate increase of the signal with $g = 2.003$ whereas in the dark the centers responsible for it are partially annihilated again.

The results of these photolysis experiments can again be understood in terms of the localization phenomenon occurring in the presence of adsorbed scavenger. Illumination of the sample brings about an immediate rise of the electron concentration in the conduction band. This increase is paralleled by the decrease in Ti^{3+} signal intensity as pointed out in the previous section. In the presence of adsorbed electron scavenger part of the electrons becomes localized. As a result of this the signal at $g = 2.003$ shows an initial increase.

In competition to the localization process also photoreactions of the singly ionized vacancies in the reduced TiO_2 take place. These processes reduce the signal intensity. The superposition of both competing steps, which apparently occur at different rates, is observed as curve b). After an initial rapid formation the concentration of conduction band, electrons localized by the scavenger reaches a stationary value under illumination. The stationarity in the photoproduced signal intensity indicates an equilibrium between the rate of center formation and the rate of their disappearance. The equilibrium concentration decreases with increasing temperature. Since the center formation is light induced the temperature dependence of the equilibrium concentration will be related to the annihilation processes. From the concentration changes measured in the temperature range −140 to −40 °C an apparent activation energy of ~ 1 kcal/mole for the annihilation processes is calculated. This value is in reasonable agreement with data reported by others for the thermal decay of the localized electrons [23].

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