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Photoadsorption and Photodesorption of Oxygen on Titanium Dioxide

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An electron spin resonance study was made of the interaction of oxygen with titanium dioxide during photoillumination. Two paramagnetic signals were investigated: a triplet signal (*g* values of 1.984, 2.004, and 2.023) which is attributed to a solid state defect, and another signal (*g* value 2.009) which is attributed to an adsorbed oxygen species, probably O_2^-. When the TiO_2 is photoilluminated in the presence of oxygen, changes in the intensity of these signals are observed along with simultaneous changes of residual pressure at low values. The results indicate that the oxygen pressure determines whether photoadsorption or photodesorption of oxygen takes place, and that a solid state defect participates in these phenomena.

INTRODUCTION

Photoexcited adsorption and desorption of oxygen on zinc oxide have been the subject of numerous investigations (*1-3*), and we recently investigated the phenomenon using electron spin resonance (ESR) techniques (*4*) as an extension of studies of photocatalytic oxidation of carbon monoxide (*5*) and isopropyl alcohol (*6, 7*).

Titanium dioxide is also known to be photosensitive and to be involved in photochemical reactions that result in paint flaking and degradation of fabrics. In addition, photocatalysis on TiO_2 occurs; in particular, the oxidation of cumene to yield phenol and acetone takes place on TiO_2 when the solid in an atmosphere of oxygen is illuminated with ultraviolet light (*8*).

In spite of the interesting photochemical properties of TiO_2, the effect of light on the interaction of oxygen with TiO_2 has received less attention than has this effect with ZnO. The only report dealing with such photoeffects is that of Kennedy *et al.* (*9*), who reported that an irreversible uptake of oxygen takes place on films of TiO_2 illuminated at 25°C at wavelengths of about 365 mμ. As yet there is no experimental evidence to support the expectation that oxygen may photodesorb from TiO_2.

We have found that both photoadsorption and photodesorption of oxygen take place on TiO_2 and that a solid state defect participates in the phenomena. In this paper we report these results, which were obtained mainly through the use of ESR techniques. Recent ESR studies of TiO_2 powders are summarized in ref. (*10*).

EXPERIMENTAL

A TiO_2 sample was prepared by hydrolyzing $TiCl_4$ (Koso Chemical Co.) with ammonia and drying it at 130°C. A white sample was obtained by calcining the dried sample at 500°C in a stream of oxygen. X-Ray analysis indicated that the sample was of anatase type. An 80-mg sample was placed in a 2.5-mm id quartz tube, which was connected to a Pirani gauge near the tube, a trap cooled in liquid nitrogen, and a stopcock. This apparatus was attached to a vacuum system in order to outgas the sample at 500°C and subsequently expose it to oxygen. The apparatus was then removed from the vacuum line and the sam-

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ple tube was placed in the ESR cavity for measurements.

ESR measurements were carried out with a JEOL-P-10 spectrometer (100 kc/sec, X band). A 500-W high-pressure mercury lamp was employed as a light source in combination with appropriate Toshiba glass filters and a filter cell containing a solution of $CuSO_4$.

RESULTS

ESR Spectra

When the white TiO_2 sample was outgassed at a residual pressure of 10^{-5} torr at 500°C for 1 hr, its color at room temperature was bluish gray. This sample gave rise to two ESR signals. One was a narrow singlet signal ($g = 2.002$, $\Delta H = 4.6$ G) and the other a broad and asymmetric signal ($g = 1.93$, $\Delta H = 110$ G) observable only at low temperatures (e.g., −195°C). The intensity of the signal at $g = 2.002$ increased when a small amount of oxygen or of nitrous oxide was adsorbed on the outgassed TiO_2 at room temperature. An investigation of this signal which will be reported in a separate paper suggests that it is due to an O^- species adsorbed on the surface. The broad and asymmetric signal near $g = 1.93$ has been assigned to Ti^{3+} (*11*), in agreement with other investigations (*12–14*).

When the bluish gray TiO_2 sample was heated at 500°C in oxygen, its color became pale yellow. The ESR spectrum of this yellow sample (but not of the bluish gray sample) gave at room temperature a triplet with g values of 1.984, 2.004, and 2.023, and the signal persisted in the presence of high-presure oxygen. In other words, this triplet spectrum showed no magnetic dipolar (i.e., oxygen pressure) broadening, which indicates that the signal is probably due to a bulk species. The intensity of the triplet signal depended on the residual oxygen pressure during the heat treatments, and the intensity was greatest when the oxygen pressure was in the range from 0.1 to 10 torr. However, the signal did not appear for pretreatments at 500°C either in vacuum or in 760 torr oxygen, or for any pretreatments tried at 700°C. We shall refer to this triplet signal as "signal-D." A typical spectrum is shown in Fig. 1 (left). This signal probably corresponds to the one which has been assigned to O_2^+ (*13*), and which has been reported recently to be produced by adsorption on TiO_2 of O_2, NO_2, or N_2O (*14*). Signal-D was readily saturated at a microwave power greater than 30 mW, while no saturation occurred at this level for signal-O.

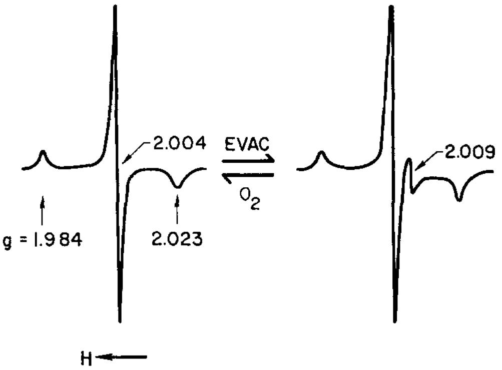

FIG. 1. Reversible effect of oxygen pressure on ESR spectra of TiO_2. Left: 40 torr. Right: 10^{-3} torr.

When our TiO_2 sample at room temperature was exposed to oxygen and then evacuated, another signal appeared around $g = 2.009$, which appears to agree with the result reported in a similar study (*14*). We found that increasing the oxygen pressure suppressed the new signal but that signal-D remained. This reversible behavior, illustrated in Fig. 1, indicates that the 2.009 signal is associated with a surface oxygen species which is subject to dipolar magnetic broadening by molecular oxygen.

We have already reported that when the bluish gray TiO_2 sample is exposed to oxygen at room temperature a triplet signal with g values of 2.003, 2.009, and 2.018 develops gradually, and we have tentatively assigned this triplet signal to O_2^- adsorbed on the surface (*11, 15, 16*). The $g = 2.009$ signal of Fig. 1 (right) is believed to be the central resonance line of this triplet while its other two lines are obscured by signal-D. We shall refer to

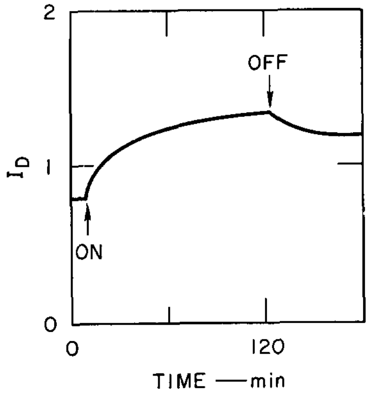

FIG. 2. The effect of illumination (300–410 mμ) on the intensity of signal-D (I_D) at an oxygen pressure of 40 torr.

the signal at $g = 2.009$ as "signal-O." The individual behaviors of signal-D and signal-O are separated by measuring the intensities I_D and I_O, of nonoverlapping lines, at g values of 2.009 and 2.004, respectively.

Both signal-D and signal-O disappeared after heating the sample at 500°C in high vacuum. However, we found that signal-D was restored upon subsequent exposure at room temperature not only to oxygen and to nitrogen dioxide, as reported by other workers (*10*), but also to sulfur dioxide. Signal-D was accompanied in the case of exposure to sulfur dioxide by a narrow and asymmetric singlet signal at $g = 2.002$, while in the case of nitrogen dioxide exposure we found that no additional signals were obtained, which agrees with the earlier work (*10*). It is of interest to note that these three gases which produced signal-D are usually considered to be electron acceptors. Also, the triplet signal (i.e., signal-D) has been reported to be produced by nitrous oxide when it decomposed on TiO_2 to give oxygen (*10*).

Photobehavior of Signal-D and Signal-O

After outgassing a TiO_2 sample at 500°C for 1 hr, the sample was pretreated with 8 torr of oxygen at the same temperature in order to produce signal-D. This pretreated sample was cooled to room temperature and then exposed to 40 torr of oxygen, and the intensity of signal-D remained unchanged in the absence of light. Upon photoillumination in the wavelength range from 300 to 410 mμ the intensity of signal-D increased, and during subsequent dark periods it decreased, as shown in Fig. 2. At this oxygen pressure, signal-O cannot be detected because of magnetic dipolar broadening. However, upon evacuation of such an illuminated sample, signal-O was observable and its intensity was greater than before the illumination. Measured in this way, illumination was found to result in about the same relative increase of both signal-O and signal-D. Hence the net effect of illumination in the presence of high-pressure oxygen is interpreted as oxygen photoadsorption.

Measurements similar to those described above were carried out on pretreated TiO_2 after the residual oxygen was pumped off at room temperature to a pressure of about 10^{-4} torr. The ESR spectrum under such conditions showed both signal-D and signal-O. The effects of illumination in the wavelength range from 300 to 410 mμ on the two signals and on the pressure are shown in Fig. 3. Under illumination the intensities of both signals decreased and the residual pressure increased. This behavior of signal-O and the pressure indicates that photodesorption of oxygen took place. When the light was turned off signal-O increased and the pressure de-

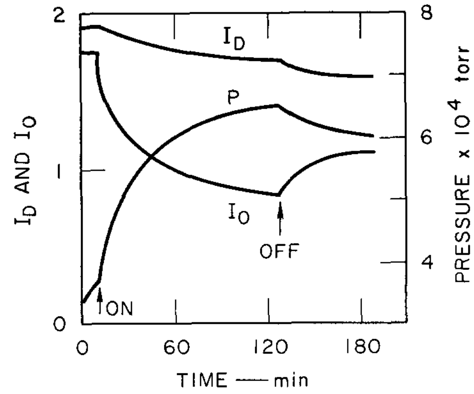

FIG. 3. The effect of illumination (300–410 mμ) on the intensities of signal-D (I_D) and of signal-O (I_O), and on the residual oxygen pressure (P). Before illumination the oxygen pressure was reduced from 8 to 10^{-4} torr.

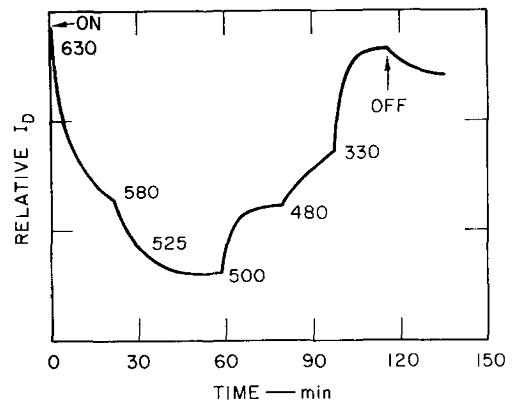

FIG. 4. Effect of wavelength (mμ) on the photoresponse of signal-D. Oxygen pressure, 50 torr.

creased. This behavior suggests that oxygen adsorption was occurring; also, signal-D decreased, as in the case of higher oxygen pressure (i.e., Fig. 2).

The photosensitivity of signal-D to illumination wavelength was investigated in greater detail for a pretreated sample under 50 torr oxygen. The data are shown in Fig. 4 for measurements made with filters passing successively shorter wavelengths. The direction of the photoresponse of signal-D reversed at about 525 mμ; wavelengths longer than this resulted in a decrease of intensity, while shorter ones caused an increase. When the light of any wavelength was switched off, intensity decreased.

DISCUSSION

In order to understand the photoeffects on the two ESR signals, it is convenient to discuss the expected effects of photoillumination on a semiconductor with sorbed oxygen, and to provide an interpretation of signal-D. The photoproduced electrons, $\ominus$, and holes, $\oplus$, tend to recombine at surface recombination centers such as those resulting from oxygen chemisorption. The recombination process may be summarized by the following reactions:

$$O_2(g) \rightleftarrows O_2(a) \tag{1}$$

$$O_2(a) + \ominus \rightarrow O_2^- \tag{2}$$

$$O_2^- + \oplus \rightarrow O_2(a) \tag{3}$$

where O_2^- represents one of several possible oxygen species which are chemisorbed by the transfer of electrons from the solid. Reactions (2) and (3) are usually irreversible except at sufficiently high temperatures, at which oxygen desorption will occur by the reverse of reaction (2). According to these reactions, oxygen pressure will control the oxygen surface coverage and thereby affect photoadsorption but not photodesorption. Therefore, photoadsorption is favored at high oxygen pressures. Photoadsorption is also favored by conditions which provide efficient trapping of photoproduced holes and hence minimize the contribution of reaction (3), which leads to desorption. Photodesorption will be favored at low oxygen pressures at which the resulting low surface coverage of oxygen limits the importance of reaction (2).

We postulate that signal-D is associated with a solid state defect because the signal is not broadened by paramagnetic gases such as oxygen or nitric oxide. Furthermore, we postulate that this paramagnetic defect, $\uparrow$, is formed when a nonparamagnetic bulk defect, $\downarrow\uparrow$, is ionized, for example, by transfer of an electron to the surface where it is trapped by sorbed electron acceptors such as oxygen, nitric oxide, or sulfur dioxide. In this way the development of signal-D can be accounted for without recourse to the suggestion that dissociative chemsorption of the gases to produce oxygen must occur (*10*), except of course of a gas, e.g., N_2O, which may need to dissociate to provide an electron acceptor. Moreover, if dissociative chemisorption is a requirement for the development of signal-D, then in order to account for the absence of pressure-broadening we must imagine that the product of dissociative chemisorption diffuses into the bulk. However, such a diffusion would be very slow at room temperature, at which the sorptions and measurements have been made, and therefore would not be a likely mechanism for the production of the defect.

In general the ionization of such defect states may occur according to the following reactions:

$$\downharpoonleft\!\upharpoonright \rightarrow \uparrow + \ominus \tag{4}$$

$$\downharpoonleft\!\upharpoonright + \oplus \rightarrow \uparrow \tag{5}$$

Reaction (4) represents the ionization of the defect states either by a thermal process, for example during the pretreatment in oxygen, or by direct photopromotion of an electron from the defect state to the conduction band. Reaction (4) may also represent the equilibrium population of the defect states in the space charge region at the surface of a semiconductor, and this population will depend upon the bending of the bands with respect to the Fermi energy. Upward bending of the bands, resulting from chemisorption or photoadsorption of an electron acceptor, tends to increase the density of ionized defect states as they are raised above the Fermi energy. On the other hand, downward bending of the bands, resulting from photodesorption, will tend to decrease the density of ionized defect states. Reaction (5) represents the capture of photoproduced holes by unionized defects.

The density of ionized defect states may be decreased by several possible mechanisms, which can be represented by the reaction

$$\uparrow + \ominus \rightarrow \downharpoonleft\!\upharpoonright \tag{6}$$

These mechanisms are the transfer to the defect states of photoproduced electrons from the conduction band or of electrons from desorbed chemisorbed species, or the capture by the defects of photopromoted electrons from the valence band.

These considerations lead to the conclusion that the net photosorption process will depend qualitatively upon parameters such as oxygen pressure, the surface state energies of chemisorbed species, and the participation of holes and electron traps. The experimental results demonstrate the influence of some of these parameters.

In the case of low oxygen pressure, photoillumination results in net photodesorption, as judged from the increase of oxygen pressure and the decrease of signal-O (Fig. 3). The concurrent decrease of signal-D is in accordance with a process whereby an electron is transferred to the surface and captured by oxygen, i.e., reactions (2) and (4). The subsequent behavior when the light is turned off is interpreted as a process of readsorption of some oxygen. The concurrent decrease of signal-D suggests that the defect states are partially repopulated, probably by a transfer of excess photopromoted electrons from the conduction band [reaction (6)], which evidently predominates over the effect of oxygen readsorption that tends to cause upward bending of the bands and hence an increase in signal-D.

In the case of high-pressure oxygen, photoillumination results in photoadsorption, as judged from the increase of signal-D (Fig. 2) and from the greater intensity of signal-O, observable after reducing the ambient oxygen pressure. The fact that signal-D increased, in contrast to its behavior during photodesorption, can be accounted for if ionization of the defect states occurred according to reactions (4) and (5). When the light is turned off, signal-D decreases further, presumably by the same mechanism as discussed for the low oxygen pressure case.

The dependence of the behavior of signal-D on the wavelength of illumination suggests that the defect state is in the band gap where it may directly participate in photoexcitation processes. For example, the results are consistent with a defect state which is ionized [reaction (4)] by wavelengths shorter than 500 mμ and which is populated [reaction (6)] by an electron excited from the valence band by wavelengths longer than 525 mμ. Accordingly, the defect state is about 2.4 eV below the bottom of the conduction band.

In summary, the present study on TiO_2, together with that on ZnO (*4*) has demonstrated some general properties of the interaction of oxygen with inorganic semiconductors during photoillumination. We have shown that photoillumination of TiO_2 results in electronic processes which affect oxygen sorption, and that high oxygen pressure favors photoadsorption and low oxygen pressure favors photodesorption of presorbed oxygen. In addition, a defect center in the band gap has been shown to participate in the photoexcitation processes when resonance signals of sorbed species are not observable, for example, in the present study of high oxygen pressures. We have restricted our attention to the photobehavior of signal-D and signal-O; however, to better understand the photocatalytic nature of TiO_2, further work is desirable to evaluate the photobehavior of the ESR signals due to Ti^{3+} centers and O^- sorbed species.

REFERENCES

1. Fujita, Y., and Kwan, T., *Bull. Chem. Soc. Japan* **31**, 830 (1958).
2. Terenin, A., and Solonitzin, Y., *Disc. Faraday Soc.* **28**, 28 (1959).
3. Barry, T., and Stone, F., *Proc. Roy. Soc.* (*London*) **A225**, 124 (1960).
4. Setaka, M., Sancier, K. M., and Kwan, T., to be published.
5. Fujita, Y., *Shokubai* (*Tokyo*) **3**, 235 (1961).
6. Komuro, I., Fujita, Y., and Kwan, T., *Bull. Chem. Soc. Japan* **32**, 884 (1959).
7. Ikekawa, A., Kamiya, M., Fujita, Y., and Kwan, T., *Bull. Chem. Soc. Japan* **38**, 32 (1965).
8. Mashio, F., *Kogyo Kagaku Zasshi* **67**, 1136 (1964).
9. Kennedy, D. R., Ritchie, M., and Mackenzie, J., *Trans. Faraday Soc.* **54**, 119 (1958).
10. Iyengar, R. D., Codell, M., and Turkevich, J., *J. Catalysis* **9**, 305 (1967).
11. Fukuzawa, S., Sancier, K. M., and Kwan, T., paper presented before the Japan Chemical Society Meeting, April, 1967, Tokyo.
12. Cornaz, P. F., van Hooff, J. H. C., Pluijm, F. J., and Schuit, G. C. A., *Disc. Faraday Soc.* **41**, 290 (1966).
13. Iyengar, R. D., Codell, M., Karra, J. S., and Turkevich, J., *J. Am. Chem. Soc.* **88**, 5055 (1966).
14. Mashchenko, A. I., Kasanskii, V. B., Pariiskii, G. B., and Sharapov, V. M., *Kinetika i Kataliz* **8**, 853 (1967).
15. Setaka, M., Fukuzawa, S., Kirino, Y., Fujita, Y., and Kwan, T., *Shokubai* (*Tokyo*) **9**, 45 (1967).
16. Setaka, M., Fukuzawa, S., Kirino, Y., and Kwan, T., *Chem. Pharm. Bull.*, to be published.