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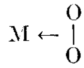
NOTES

An ESR Study of the Nature of the Surface Oxygen during the Oxidation of a Nonstoichiometric Rutile Surface with Oxides of Nitrogen

Electron spin resonance studies on the nature of the surface species on titanium dioxide powders have been reported by several investigators (*1–5*). Cornaz *et al.* (*2*) have identified at least three different surface coordination complexes involving molecular oxygen on anatase powders following vacuum outgassing at 500°C for 4 hr and subsequent oxygen treatment at room temperature. One of these complexes characterized by a triplet or a 3-g value signal centered around $g = 2.002$ in the spectrum was assigned to a complex of the type



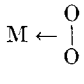
$$M \leftarrow \begin{matrix} O \\ | \\ O \end{matrix}$$

where an electron is donated by the adsorbing oxygen molecule to the metal. Iyengar *et al.* (*3, 5*) working with rutile powders noticed that vacuum outgassing of a sample at 500°C for 2 hr leads to loss of oxygen and formation of Ti^{3+} ions at the surface. Subsequent addition of oxygen to the sample maintained at room temperature (23°C) not only oxidized the surface Ti^{3+} to Ti^{4+} ions but also formed simultaneously the 3-g value signal attributed to O_2^+.

Oxygen deficiency at the surface of rutile can be restored through interaction with nitrogen dioxide. Reyerson and Honig (*6, 7*) in their investigation of the adsorption of $NO_2 \rightleftharpoons N_2O_4$ on rutile in the range —16° to 29°C have shown that the gas is chemisorbed dissociatively and an oxidation of the oxygen-deficient sites at the surface occurs. These authors not only observed a decrease in magnetic susceptibility and an increase in the weight of the sample after an adsorption and desorption cycle but were also able to show the presence of NO and N_2O_3 in the gas phase mass spectrometrically.

An electron spin resonance study of high-area rutile (~40 m^2/g) vacuum-outgassed at 500°C for 2 hr and subsequently allowed to interact at room temperature (23°C) with $NO_2 \rightleftharpoons N_2O_4$ (at 76 cm pressure) has been made. Simultaneously with the disappearance of the signal at $g_{av} = 1.95$ (attributed to the oxidation of Ti^{3+} to Ti^{4+}), a 3-g value signal identical to that assigned to O_2^+ in earlier studies appeared

The formation of one and the same signal (assigned to O_2^+) when rutile vacuum-outgassed at 500°C (2 hr) is treated at room temperature subsequently with either oxygen or nitrogen dioxide, coupled with the fact that nitrogen dioxide is known to add atomic oxygen to rutile surface by dissociative chemisorption, makes it possible to suggest that dissociatively chemisorbed rather than molecular oxygen is responsible for the formation of the species O_2^+ or



$$M \leftarrow \begin{matrix} O \\ | \\ O \end{matrix}$$

Further, a nonstoichiometric rutile surface (prepared by vacuum outgassing of the sample at high temperature) is known to react with molecular oxygen at room temperature (23°C) forming superoxide

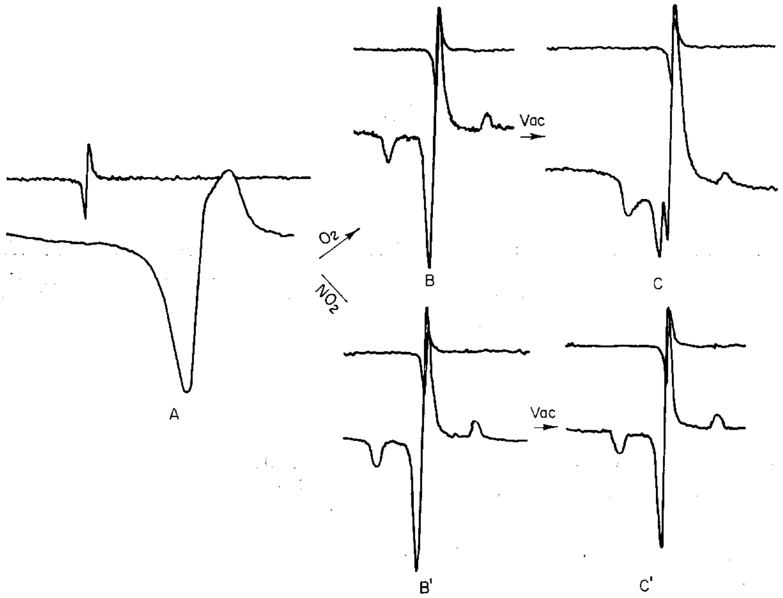


FIG. 1. ESR (X-band) spectra of rutile: A, sample outgassed at 500° for 2 hr; B, outgassed sample exposed to gaseous oxygen; C, sample reoutgassed for 30 min at room temperature; B′, outgassed sample exposed to nitrogen dioxide instead of oxygen; C′, reoutgassed for 30 min at room temperature. (All spectra recorded at liquid nitrogen temperature.)

ions (O_2^-) at the surface (*5*). The ESR signal for O_2^- species is not observed (Fig. 1,B) in the presence of excess molecular oxygen at the surface because of the exchange reaction

$$O_2^- + O_2 = O_2 + O_2^-$$

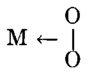
Removal of excess oxygen by outgassing for 30 min at room temperature (23°C) leads to observation of the signal due to O_2^- ions at the surface (Fig. 1,C). Corresponding studies made on rutile samples outgassed at 500°C for 2 hr and exposed at 23°C to nitrogen dioxide instead of oxygen interestingly showed no O_2^- ions at the surface (Fig. 1,C′).

The interaction of nitrous oxide (N_2O) with an oxygen-deficient rutile surface can be expected and is known (*8, 9*) to furnish oxygen directly to the surface. Thus,

$$N_2O \rightarrow N_2 + [O] \text{ (to the surface)}$$

Therefore ESR studies were also made with samples of rutile vacuum-outgassed at 500°C for 2 hr and subsequently allowed to interact at 350°C with N_2O at 76 cm pressure. The spectra, identical to those observed with samples treated with $NO_2 \rightleftharpoons N_2O_4$, showed the same 3-*g* value signal and no superoxide (O_2^-) ions. (cf. Fig. 1,C′.)

These observations suggest that the formation of O_2^+ or



$$M \leftarrow \begin{matrix} O \\ | \\ O \end{matrix}$$

on rutile involves a dissociative chemisorption of oxygen from oxygen molecules or oxides of nitrogen. On the other hand the formation of O_2^- ions at the surface requires molecular oxygen for the reaction $Ti^{3+} + O_2 \rightarrow Ti^{4+} + O_2^-(\text{ads})$ and therefore does not occur when oxides of nitrogen are employed.

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A Method for Studying Catalytic Hydrogenation of Aqueous Cinnamaldehyde over Platinum and Nickel Wire

Prevention of catalyst poisoning is a general problem in the hydrogenation of aldehydes in aqueous solution over nickel and platinum catalysts, apparently, because of the accompanying formation of polymeric products that are strongly adsorbed on the catalyst surface. To measure this type of catalyst poisoning and to learn how to regenerate used nickel and platinum catalysts in aqueous medium, the hydrogenation of cinnamaldehyde (β-phenylacrolein) was employed as a convenient test reaction. This aldehyde has an intense absorption band at 2900 Å that enables measurement of the concentration changes that occur during the catalytic hydrogenation of dilute aqueous solutions (10^{-4} to 10^{-5} *M*) at 25°C. Extremely low rates of hydrogenation can, therefore, be determined—even as low as those occurring over massive platinum or nickel wire. Use of a catalytic metal in the form of wire rather than in the form of a dispersion on a porous support enables rapid changes in catalyst treatment, and precludes diffusion limitations.

The high intensity of the 2900-Å band in cinnamaldehyde arises because of conjugation of the phenyl, vinyl, and carbonyl groups in this molecule. Hydrogenation of the carbonyl group to form cinnamyl alcohol would shift the above band to 2500 Å but this did not occur. The other probable hydrogenation products, 3-phenyl-1-propanol and 3-phenyl-1-propanol, have maximum absorptivities one-hundredth of that for cinnamaldehyde, so these products are not detected. However, since former studies of the catalytic hydrogenation of a conjugated aldehyde (acrolein) have shown that initial attack occurs at the carbon–carbon double bond during hydrogenation over nickel (*1*) and platinum (*2*), it is likely that cinnamaldehyde is hydrogenated to 3-phenyl-1-propanal in all the following experiments.

An all-glass flow apparatus was devised that would enable measurement of the extent of conversion of cinnamaldehyde (10^{-4} *M*) as the aqueous solution was passed over platinum wire at a constant rate (0.2 ml/sec) at 25°C. The solution was saturated with hydrogen at atmospheric pressure (the solubility of hydrogen is sufficient to give 10 moles of hydrogen per mole of cinnamaldehyde), then passed through the