orders of magnitude larger than the kinetic site density.

The Ward model predicts that the acid faujasite is the ultimate since the role of other cations is to provide an increasing number of acid-type hydroxyl groups. The model in my discussion, however, predicts that a cation with high ionic potential (to provide polarization) mixed with the H-faujasite (to provide the OH concentration) could be more acidic than the pure acid faujasite. Indications that this is the case for a rare earth–hydrogen faujasite have been claimed (*14*) but for stability reasons. Experiments with acid strength distribution measurements are needed to decide this issue.

Finally, the role of direct cation interaction, although minimized for carbonium activity by many authors, still may play an important role for other types of reactions, e.g., the radical dehydrogenation of cumene (*3*). Measurements of the field strengths through spectroscopic or ESR techniques will be required, in addition to experimental verification of the cation time-dependent field proposed by Tung (*6*).

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# Formation of Paramagnetic Surface Species during the Oxidation of Nonstoichiometric $TiO_2$(A), $SnO_2$, and ZnO

Iyengar, Codell, and Turkevich (*1*) recently published some ESR observations on the oxidation of nonstoichiometric rutile with oxides of nitrogen.

Similar measurements have been performed by us on $TiO_2$ (anatase), $SnO_2$, and ZnO and preceding a future and more detailed report we believe it relevant to summarize our results here, the more so, since they lead to a somewhat different explanation than that earlier given by Cornaz, van Hooff, Pluym, and Schuit (*2*) and van Hooff and van Helden (*3*).

$TiO_2$ (anatase) after outgassing at 500°C shows a similar signal as given by Iyengar *et al.* in their Fig. 1A. After admission (at room temperature) of $O_2$ and reevacuation (also at room temperature) this signal dis-

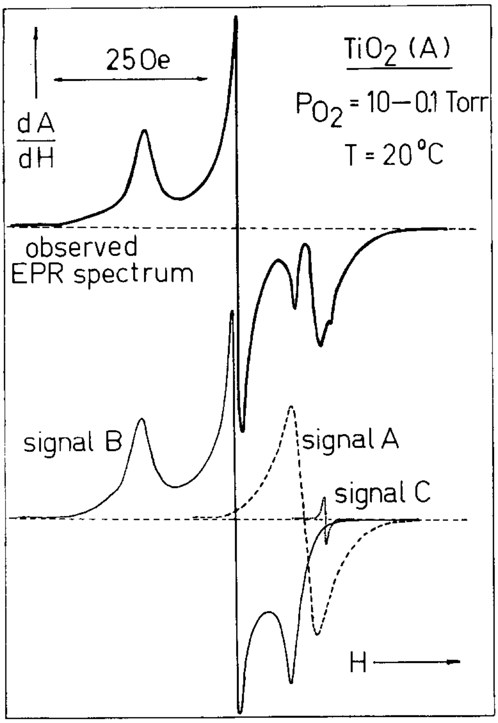

FIG. 1. Observed EPR Spectrum after admission of $O_2$ at outgassed $TiO_2$ (A) and the three EPR signals from which this spectrum can be built up.

appears and is replaced by a new signal observable at room temperature (see Fig. 1). The new signal is considered to consist of three separate signals, A, B, and C as shown in Fig. 1. The C signal is trivial because it originates from the quartz glass sample tube. Signal A is a 1*g*-value signal, signal B a 3*g*-value signal. The arguments to split the observed spectrum in A and B are as follows:

(i) A is easily saturated, B is not.
(ii) Admission of 1-butene, subsequent to the formation of the ESR spectrum mentioned above, causes the B signal to disappear rapidly, while the A signal decreases only slowly in intensity.
(iii) Only signal A is observed after contacting the "reduced" $TiO_2$ with either $N_2O$ or NO.

The formation of ESR-active surface species on nonstoichiometric $SnO_2$ and ZnO is very similar. However, the *g* values of the B signal are different, while the A signal hardly varies in its *g* value (see Table 1).

The analysis of the spectrum given is obviously different from our earlier suggestions and it is therefore necessary to compare the two proposals. Signal B is similar to our earlier signal *e* and moreover to the 3*g* signals given by Iyengar *et al.* (*4*), Kazanskii (*5*), and Lu Tun Sin *et al.* (*6*).

Signal A is related to our earlier signal d. The central line $d_2$ of d coincides with A and also with the central line of the $O_2^+$ signal of Iyengar *et al.* The disappearance of the satellites d, and $d_3$ in our new samples is somewhat mysterious. We have observed, however, that they can be reproduced by contacting the $TiO_2$ sample before evacuation with 4n ammonia.

TABLE 1

*g* VALUES OF THE DIFFERENT ESR SIGNALS

| | Signal A | Signal B | | |
|---|---|---|---|---|
| | $g$ | $g_1$ | $g_2$ | $g_3$ |
| $TiO_2$(A) | 2.003 | 2.019 | 2.010 | 2.004 |
| $SnO_2$ | 2.002 | 2.028 | 2.009 | 2.002 |
| ZnO | 2.003 | 2.051 | 2.009 | 2.002 |

The signal C earlier reported is now considered to be caused by line-broadening of B as a consequence of physical adsorption of $O_2$.

Consequent to the reevaluation of the ESR spectrum we consider it necessary to replace our former suggestions concerning the structure of the species by a new one. As in the earlier hypothesis the B signal is ascribed to the species $O_2^-$, but the A signal is now believed to belong to $O^-$ [see Kwan (*7*)]. Full details of the work will be reported in the near future.

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