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LETTERS TO THE EDITORS

The Nature of the Paramagnetic Species Observed in Ammonia-Precipitated TiO_2 Powders

We have read with interest the recent studies of Dr. Van Hooff* on the nature of adsorbed species responsible for the various signals observed on oxygen-treated titanium dioxide (rutile or anatase). Of the various signals attributed to adsorbed oxygen, particular interest attaches to the triplet or 3-g value signal corresponding to $g = 1.980$, 2.002, and 2.024 (herein after referred to as triplet A), and attributed to coordinated oxygen at the surface (*1*) or the formation of an O_2^+ species (*2*). While it is possible that the high dielectric constant of rutile TiO_2 can reduce the ionization potential of an oxygen molecule and render the formation of O_2^+ possible (*3*), the absence of line-broadening for this triplet on addition of excess oxygen, has cast some doubt on this assignment. Recently it has been suggested that the triplet is caused by a solid state (bulk) defect in rutile rather than by a surface species formed during either the oxygen or NO_2 treatment (*4*).

In view of the above, we have reexamined the origin of triplet A and some of our preliminary experiments and conclusions are presented here. It appears that sufficient evidence exists for a revision of the previous assignment of this triplet.

Since high-area TiO_2 used in many of the current investigations is prepared by the hydrolysis of $TiCl_4$ with aqueous ammonia, it was thought that paramagnetic centers in the bulk as well as the surface of TiO_2 could arise from the presence of either chloride or ammonia as an impurity. Indeed, experiments on (a) a rutile sample prepared by the addition of NaOH to $TiCl_4$, (b) a high-area anatase prepared by flame hydrolysis, and (c) a high-purity anatase prepared by the addition of NaOH to a sulfuric acid solution of titanium, showed that the triplet A was not produced. However, when the high-purity anatase was soaked in a dilute solution of ammonia, washed, and dried in oxygen at 500° for 2 hr, the ESR spectrum of the resulting sample showed two triplets including triplet A. These experiments indicate in a direct way that the impurity centers responsible for triplet A arise not from chloride but from ammonia.

Triplet A could result from the interaction of an unpaired electron with a ^{14}N nucleus located at the impurity site. While this interaction is expected to yield three lines of equal intensity, with powders the lines corresponding to $m_I = \pm 1$ can be broadened compared to the line with $m_I = 0$. If the centers are rigidly bound to the lattice, both g and hyperfine anisotropy can be present and one can expect from three to nine lines in the spectrum, depending on the nature of the crystal field at the site, and on the extent of the splitting in the different directions. Thus, for an axially symmetric field ($g_\parallel$ and $g_\perp$) with hyperfine interactions, an apparent 3-g value signal has been observed for nitrobenzene anion radicals in the solid state (*5*) or adsorbed on catalytic aluminas (*6*), high-area MgO (*7*), or ZnO (*8*).

Recently, a complex signal with very nearly the same shape and splitting as is observed for triplet A has been reported following adsorption of NO both on MgO (*9*) and on ZnO (*10*). The signal has been

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* Van Hooff, J. H. C., *J. Catalysis*, **11**, 277–279 (1968).

attributed to NO_2^{2-} species. Further, our present studies also indicate that following adsorption of ^{14}NO on high-purity anatase, a triplet with g values 1.980, 2.006, and 2.022, very similar to those observed for triplet A, is obtained.

The evidence is conclusive enough to show that triplet A arises from a species containing nitrogen and oxygen formed from ammonia during the high-temperature drying or oxygen treatment.

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Nature of Catalytically Active Sites in Fluorided Alumina

Of late, in a number of papers the nature of catalytic activity of fluorided alumina has been discussed. The activity of fluorided alumina has been discussed. The activity of fluorided alumina in reactions involving hydrocarbons is explained by the acidic properties of the initial alumina (*1–3*) and by increased aprotonic sites (*4*) or development of strong protonic acidic sites (*5*, *6*). In a recent report, Holm and Clark (*7*) mention that the catalytic activity of fluorided alumina in cracking *n*-octane, isomerization of xylene, and polymerization of propylene increases noticeably when the fluorine content is increased up to 4–6%. Hall found that maximum activity occurs in cracking reactions of 2,3-dimethylbutane and isomerization of cyclopropane when the fluorine content in the samples is 2.7% and 1.2%, respectively. However, the quantities of ammonia chemisorbed on the fluorided alumina in both these works had very close values at 500°C and were maximum for samples containing 1.2–2.7% of fluorine. Gerberich *et al.* (*4*) have established a relation between activity and quantity of adsorbed ammonia, supposing that ammonia is adsorbed at 500°C on strong acidic sites. The absence of such a relation for the reactions studied in ref. (*7*) and the determination of heat of adsorption of ammonia (*3*) enabled Holm and Clark to suppose that the catalytic activity of fluorided alumina is due to the presence of acidic sites of medium strength on the surface. In discussing their results, they cite our work (*8*). When the acidity was determined by high-temperature adsorption of organic bases, then a difference in acidity between initial and fluorided alumina was observed; however in titrating *n*-butylamine, using Hammett indicator, it was found that the concentration of acidic sites of medium strength increases with fluorine content in a catalyst prepared by the interaction of