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NOTE

The ESR of the Oxygen Adsorbed on Supported Vanadium Pentoxide

The ESR spectra of radicals formed by oxygen adsorption on ZnO, TiO_2, SnO_2, and MgO are reported in refs. (*1–8*). They are usually ascribed to adsorbed O_2^- ion radicals and the crystal-field approximation is used for their treatment. The character of the g-factor anisotropy indicates that the O_2^- are located near surface metal ions (*5, 8*). The best support of this conclusion would be the observation of hyperfine splitting (hfs) caused by metal ions of oxide. None of the spectra reported, however, have it, due to the absence of the nuclear momentum of metal ions in oxides studied. In the present work the attempt was made to observe hfs for the system of oxygen adsorbed on supported vanadium pentoxide that contains 100% ^{51}V isotope with $S=7/2$ and $I=5.15$.

The V_2O_5/SiO_2 samples were prepared in a similar way as in ref. (*9*) by impregnating silica gel (surface area 520 m^2/g) with excess NH_4VO_3 solution, followed by drying at 70–80°C and calcining at 500°C. The vanadium content was about 2%. The samples were then placed in quartz ampules for ESR measurements and heated in oxygen for 15 min at 500°C. Then they were evacuated for 1 hr, reduced with hydrogen for 5 min, and finally evacuated for 1 hr at the same temperature. This procedure leads to the partial reduction of V_2O_5 with formation of tetrahedrally coordinated V^{4+} ions. Their ESR spectra could be observed, however, only at 20°K due to the fast spin lattice relaxation at higher temperatures (*9*).

The oxygen was adsorbed at room temperature and a pressure of 10 mm Hg. The excess was pumped off before ESR measurements that were carried out at 77°K using a JEOL JES 3BS-Q instrument.

The Q- and X-band ESR spectra that appeared after oxygen adsorption are shown in Figs. 1 and 2, respectively. Both of them have well-expressed hyperfine splitting in addition to the g-factor anisotropy. The Q-band spectrum consists of 23 lines divided in three groups with the following parameters (Fig. 1).

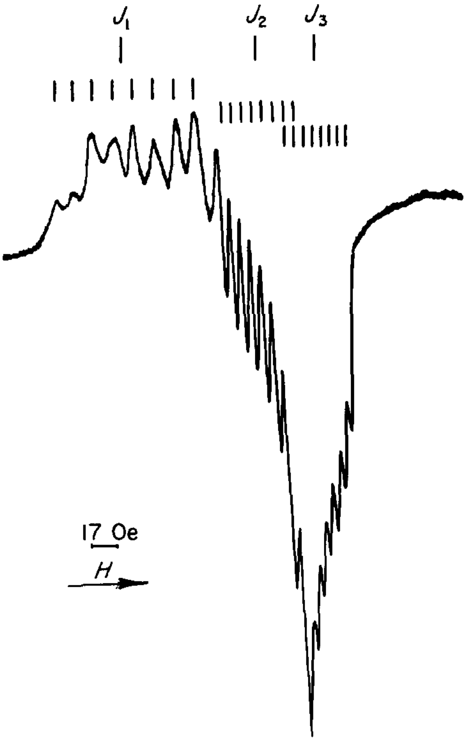

FIG. 1. Q-Band spectrum of oxygen on V_2O_5/SiO_2.

FIG. 2. X-Band spectrum of oxygen on V_2O_5/SiO_2.

$$g_1 = 2.025, \quad g_2 = 2.011, \quad g_3 = 2.005$$

$$A_1 = 13.2 \times 10^{-4}\ \text{cm}^{-1}; \quad A_2 = 6.4 \times 10^{-4}\ \text{cm}^{-1}; \quad A_3 = 5.6 \times 10^{-4}\ \text{cm}^{-1}$$

The X-band spectrum is more complicated due to the overlapping of the lines belonging to different groups.

So far as the g-values of the ESR spectra obtained after oxygen adsorption are close to those reported for $O_2^{-\cdot}$ adsorbed on TiO_2 and SnO_2 (*5, 7*) they can be ascribed to adsorbed oxygen radicals. On the other hand the anisotropic hyperfine splitting in eight lines can be interpreted as due to interaction with ^{51}V nucleus. This may be considered as a strong support for the conclusion that adsorption centers are the surface metal ions of the oxide, apparently tetrahedrally coordinated V^{4+} ions.

The hfs indicates also that the bonding of adsorbed oxygen to the adsorption centers may be at least partially covalent. However the spin density on V^{4+} ions is relatively low, resulting in the splitting being about ten times less than that for tetravalent vanadium compounds. The detailed interpretation of the ESR spectra requires quantitative calculations.

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