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Paramagnetic Oxygen Species Adsorbed on Reduced SnO_2

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The nature of the oxygen species adsorbed on slightly reduced SnO_2 has been investigated using oxygen enriched with $^{17}O_2$. The oxygen adsorbs as O_2^- with $g_1 = 2.024$, $g_2 = 2.009$, $g_3 = 2.0036$ and a hyperfine splitting (A_{xx}) about g_3 of 80.5 gauss. A second paramagnetic species is characterized by $g_1 = 2.034$, $g_2 = 2.004$ and $g_3 = 1.994$; this species shows no interaction with $^{17}O_2$ and is attributed to the localization of an electron in some lattice defect by the adsorbed oxygen.

INTRODUCTION

The formation of paramagnetic signals when oxygen is adsorbed on slightly reduced SnO_2 has been reported previously (*1–3*). The interpretation of the observed signals is difficult because $^{16}O_2$ has no nuclear spin, and the principal values of the *g* tensor are not unambiguous parameters for defining the nature of the adsorbed oxygen species. Recently, Tench *et al.* (*4–6*) have used oxygen enriched in $^{17}O_2$ to identify oxygen species adsorbed on oxides; this method makes use of the hyperfine structure resulting from the nuclear spin of 5/2 for ^{17}O. In the present work, the adsorption of $^{16}O_2$ and $^{17}O_2$ on reduced SnO_2 has been used to characterize the nature of the adsorbed oxygen.

EXPERIMENTAL

The SnO_2 used in this work was prepared by hydrolysis of $SnCl_4$ at 0°C. The solution was neutralized by ammonia to a final pH value of 7, and the precipitate was washed until no Cl^- ions were detected. SnO_2 obtained by this method has a specific surface area of 200 m^2/g. The samples were then outgassed in silica tubes in vacuo at 400°C for 12 hr, and then oxygen was adsorbed in the pressure range of 1 to 10 nm^{-2} at -196°C. The $^{16}O_2$ used was 'Spec-Pure', and the $^{17}O_2$ was enriched to 58 at. % of ^{17}O. All measurements were carried out at -196°C on a Varian spectrometer V4501 operating at about 9.2 GHz. DPPH was used as a standard for *g* value calibrations, and the field increases from left to right in all spectra.

RESULTS AND DISCUSSION

The reduction of SnO_2 results in the formation of Sn^{3+} ions as has been shown by Imai *et al.* (*7*). The spin lattice relaxation time is long at -196°C, and the Sn^{3+} EPR signal is not observable at this temperature.

When oxygen $^{16}O_2$ is adsorbed at -196°C on the reduced sample, an ESR signal appears (Fig. 1). By studying the reactivity of the species responsible for this signal, it has been possible to show that actually the spectrum results from the superposition of two triplets I and II (Fig. 1).

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FIG. 1. The adsorption of $^{16}O_2$ on SnO_2.

Similar experiments were repeated with oxygen enriched with $^{17}O_2$, and the ESR spectra obtained show a marked hyperfine structure (Figs. 2 and 3). The spectrum can be analyzed following the procedure of Tench (*4*) into three components arising from the ($^{16}O^{16}O$), ($^{16}O^{17}O$) and ($^{17}O^{17}O$) species. Raising the sample to 25°C for 10 min and then cooling appears to increase the intensity of the spectra, and there is no evidence of any exchange process. These spectra are ascribed to the presence of O_2^- on the surface of SnO_2. Only the A_{xx} component of the hyperfine tensor is resolved; this shows a splitting of 80.5 ± 2 gauss about the g_3 value, and the unpaired electron appears to interact equally with both oxygen nuclei. This result is very similar to that measured for oxygen on ZnO (*5*) and a little higher than the values obtained on MgO (*4*) and TiO_2 (*6*). The variation is small, but it is possible that the filled 'd' orbitals of Zn^{2+} and Sn^{4+} reduce still further the possibility of delocalization of the unpaired electron.

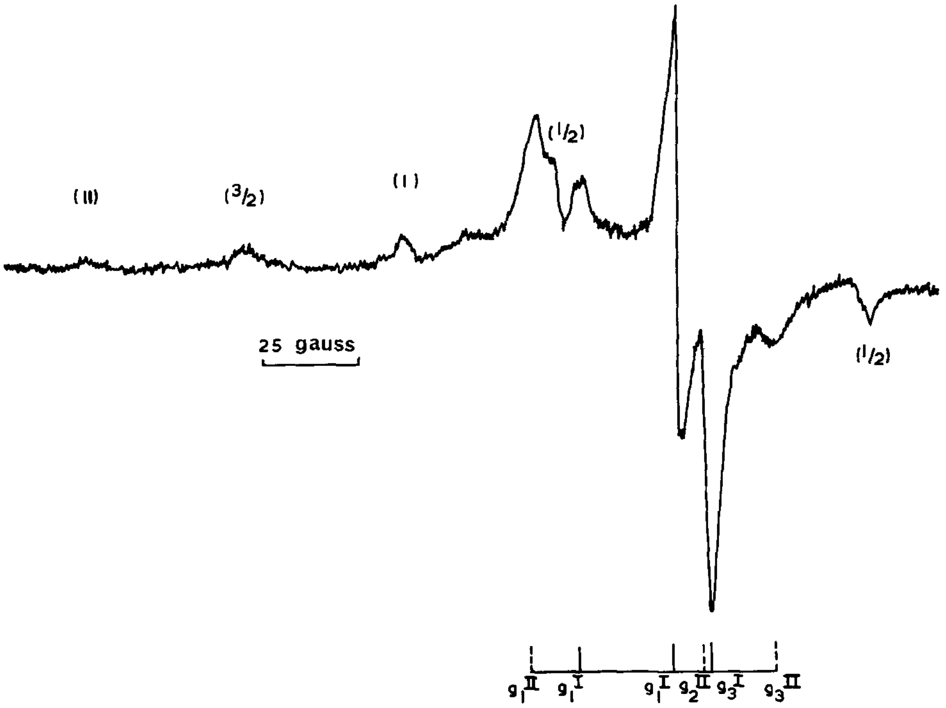

FIG. 2. Effect of the adsorption of $^{17}O_2$ on the central lines. The magnetic quantum numbers of the lines have been inserted in brackets.

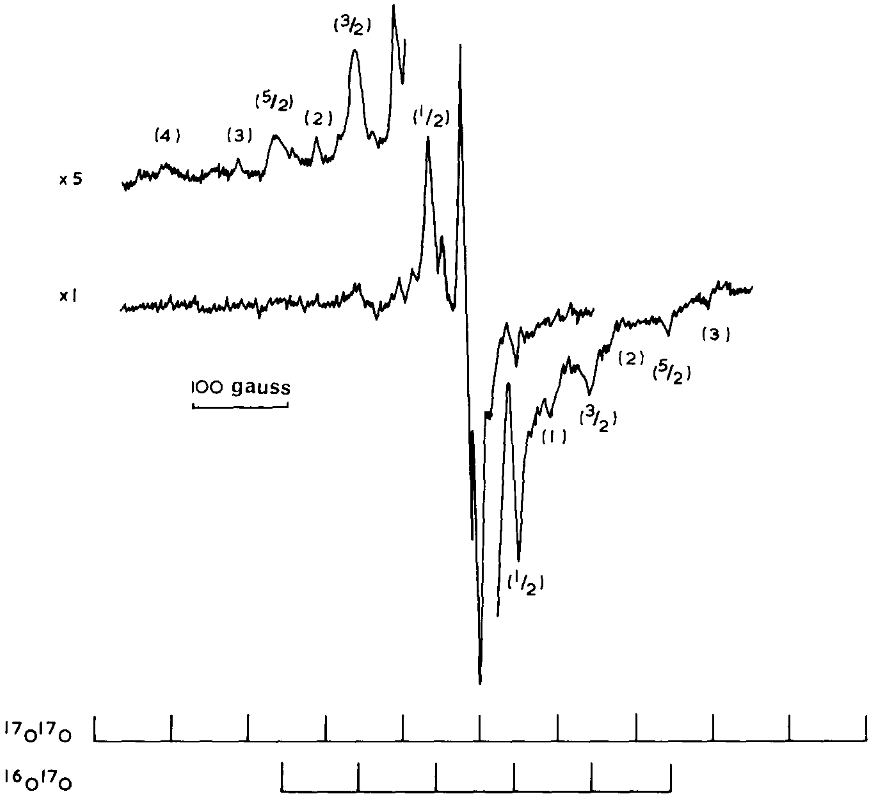

FIG. 3. The adsorption of 58 at. % of $^{17}O_2$ on SnO_2. The magnetic quantum numbers of the lines have been inserted in brackets.

A comparison of Figs. 1 and 2 shows that the g_3 component becomes more intense with respect to the g_2 component on adding $^{17}O_2$. This behavior is the reverse of what is expected since the g_3 line is split by a hyperfine interaction which will reduce its intensity whereas, the g_2 line has no resolved hyperfine structure. A detailed examination of the spectra leads to the conclusion that two species are present; one is O_2^- characterized by $g_1 = 2.024$, $g_2 = 2.009$, $g_3 = 2.0036$ and $A_{xx} = 80.5$ gauss and a second by $g_1 = 2.034$, $g_2 = 2.004$ and $g_3 = 1.994$. This latter species appears when oxygen is adsorbed on the surface but does not show any hyperfine interaction with the ^{17}O nucleus. It is probable that it should be ascribed to an electron localized by the presence of adsorbed oxygen but still within the lattice. Alternatively, it may arise from some oxygen containing species which undergoes a fast exchange with oxygen ions from the lattice even at −196°C; this, however, is unlikely, and it is thought to be a lattice defect.

The interpretation of these results leads to a different model of the adsorbed species on the surface than has been previously suggested (*1–3*). The use of $^{17}O_2$ has confirmed that O_2^- exists on the surface in good agreement with the other oxides; however, there is no evidence to support the presence of O_2^+ on the surface. It is unlikely that the other triplet signal arises directly from an adsorbed form of oxygen, but its behavior is similar to the results obtained for anatase (*6*), and in both cases, it is probably associated with a defect in the lattice.

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