EPR study of the H_2O_2 interaction with TiO_2; evidence for a novel $S = 1$ surface radical pair

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H_2O_2 reacts with rutile TiO_2 powder forming not only surface O_2^- anions but also two newly identified surface $S = 1$ triplet radical anion pairs composed of two interacting $O^-\cdots O^-$ centers characterised by the EPR spin Hamiltonian parameters of $g_{iso} = 2.0104$ and $D = 13.7$ mT for triplet 1 and $g_{iso} = 2.0064$ and $D = 12.7$ mT for triplet 2.

The role of free radical intermediates in the heterogeneous decomposition of organic substrates over metal oxides and zeolitic systems has been investigated for many years. In particular, the catalytic oxidation by H_2O_2 over TiO_2 or V_2O_5 has been studied in depth with a view to understanding the role of the active peroxo or peroxoacid species in the decomposition mechanism.[1] Despite the extensive literature available in this field, a well defined description of the basic phenomena occurring at the interface of the H_2O_2–oxide system is far from complete. Some of us have previously explored the reactivity of the H_2O_2–oxide system by EPR spectroscopy and a rich abundance of trapped radical species were identified.[2–5] It was found that for H_2O_2–MgO, a variety of oxygen based and protonated oxygen radicals including O^-, O_2^- and $OH^\bullet$ were formed.[3] Here, we present preliminary results on the nature of the various radical centers, which are generated by interaction of H_2O_2 with rutile TiO_2. Evidence will be presented for the direct observation of a novel $S = 1$ triplet radical pair on the TiO_2 surface.

The TiO_2 powder (Rutile, ICI Tioxide) was stirred for 2 h at room temp. with an aqueous solution of H_2O_2 (27.5 mass%, Aldrich). The resulting slurry was then filtered and gently dried in air at 308–313 K for *ca.* 1 h. The EPR spectrum of the fresh sample (100 K) is shown in Fig. 1(*a*). This spectrum is clearly dominated by the presence of an intense orthorhombic signal with $g_1 = 2.0036$, $g_2 = 2.0095$, $g_3 = 2.0243$ and assigned to the superoxide O_2^- anion. This anion is usually stabilised at a positive cationic site such that the electrostatic interaction splits the $2\pi^*$ antibonding orbitals by an amount (Δ) depending on the local cationic crystal field. The magnitude of the g_{zz} component (g_3 in this case) will give a measure of the cationic crystal field since $g_{zz} = g_e + 2\lambda/\Delta$ where λ is the spin–orbit coupling constant of oxygen.[6] A g_3 value of 2.0263 clearly indicates that the O_2^- anion is stabilised at a Ti^{4+} cation in agreement with the g values reported in the literature for O_2^- adsorbed on TiO_2.[6]

Evacuation of the sample (30 min at 298 K, to 10^{-5} Torr) leads to the EPR spectrum shown in Fig. 1(*b*). Two very distinguishing features can be noted. First, the intensity of the O_2^- signal has increased by a factor of about 40. This can be explained by the detection of predominantly surface O_2^- anions with a much smaller abundance of bulk/subsurface superoxide. Only the bulk O_2^- anions are visible in Fig. 1(*a*) since the surface O_2^- anions undergo dipolar broadening with O_2 at low temperatures and so are not visible in the non-evacuated sample.

The second notable feature of Fig. 1(*b*) is the appearance of a new signal characterised by two low field and high field lines. The paramagnetic center(s) responsible for this signal are clearly stabilised on the rutile surface, since the signal is absent in the presence of O_2 due to the dipolar broadening. We propose that these new features correspond to the $\Delta M_s = 1$ transition of an $S = 1$ surface triplet arising from two interacting $S = 1/2$ species. This assignment is based on the following:

(*i*) the presence of a low field $\Delta M_s = 2$ transition at the expected magnetic field position of 165 mT [Fig. 1(*c*)];

(*ii*) it is not related in any way to the O_2^- anions (*e.g.* as a superhyperfine interaction), since their respective saturation profiles are different and also the intensity of the new surface center varies slightly from one experiment to the next independent of the superoxide concentration.

Careful inspection of the new triplet signal reveals a ‘splitting’ of the two low field lines into an apparent doublet which is absent in the two high field lines. Assuming mutual orientation of the spin–spin and spin–nuclear axes with respect to the applied magnetic field, then simulation of the signal based on an $S = 1$ system with isotropic symmetry and $m_I = 1/2$ does not satisfactorily account for the line shape. In that case all $\Delta M_S = 1$ lines were split into doublets. The intensities of the

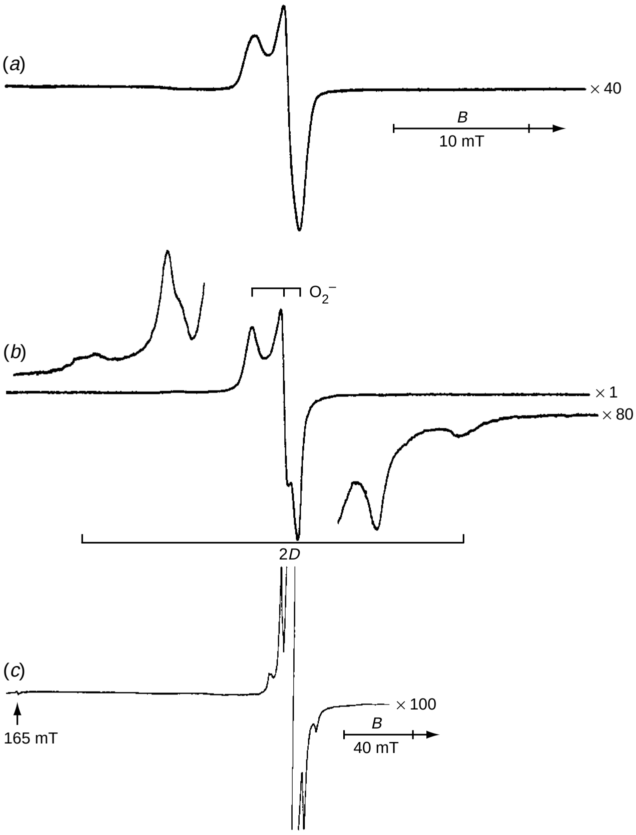

Fig. 1 EPR spectrum (100 K) of rutile TiO_2 after contact with an aqueous solution of H_2O_2. (*a*) Sample prior to evacuation, (*b*) sample after evacuation at 298 K for 30 min, (*c*) sample as in (*b*) but recorded over wide scan range to show the half field feature at 165 mT.

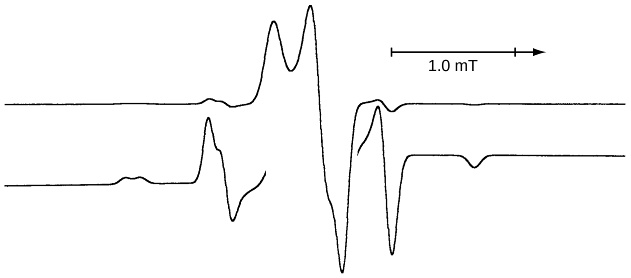

Fig. 2 Computer simulation of Fig. 1(*b*) revealing the O_2^- and the triplet $S = 1$ radical pair

apparent low field doublets also vary from one experiment to the next, suggesting the splitting arises from two separate signals rather than a hyperfine doublet. The best simulation obtained (Fig. 2) was based on two separate $S = 1$ centers having slightly different spin Hamiltonian parameters; *i.e.* triplet 1, $g_{\mathrm{iso}} = 2.0104$ and $D = 13.7$ mT and triplet 2, $g_{\mathrm{iso}} = 2.0064$ and $D = 12.7$ mT.

D is the zero field splitting term and for randomly oriented triplets the separation between the $\Delta M_S = 1$ outer vertical lines is just $2D$ [Fig. 1(*b*)] so D is easily extracted from the experimental spectrum.[7] The symmetry of the g tensor, although reported as isotropic, may be slightly axial since small changes in the g values did not produce drastic alterations to the simulation. Even though the individual $S = 1/2$ centers may have significantly lower symmetry (*e.g.* axial), in the coupled $S = 1$ state they appear to have a different symmetry, close to isotropic. Because the intensity of the $S = 1$ signal is so weak, precise analysis of the symmetry is not possible at present. Assuming D is due entirely to a dipole–dipole interaction between two $S = 1/2$ species, then the distance r separating the two species may be calculated using the equation $D = 3g^2\mu_B^2/2r^3 = -1.949 \times 10^{-4}g^2/r^3$ MHz.[8] This leads to a value of $r = 5.9$ and 6.0 Å riplet 1 and 2, respectively.

Based on the above EPR data, an assignment on the nature of the triplet center may be proposed. The absence of any hyperfine structure on the fine structure disfavours the possibility of any protonated $S = 1/2$ centers such as pairwise interacting $OH^\bullet$ or $H_2O^\bullet$ radicals. These radicals are involved in the homogeneous and heterogeneous decomposition of H_2O_2 and have been observed by EPR. H_2O_2 decomposition on MgO produces trapped $OH^\bullet$ radicals[3] and the pairwise trapping of $HO_2^\bullet$ radicals in aqueous glasses of H_2O_2 produce radical pairs with characteristic triplet state spectra.[9] Photoadsorption of O_2 on hydrated TiO_2 has also been reported to lead to the formation of surface trapped $HO_2^\bullet$ radicals but there was no observation of any $S = 1$ triplet centers.[10] However both $OH^\bullet$ and $HO_2^\bullet$ have appreciable hyperfine couplings of $a_{\mathrm{iso}} \approx 2.7$ mT[3] and $a_{\mathrm{iso}} \approx 1.1$ mT[11] respectively which should be visible in Fig. 1(*b*) where the line width of the $\Delta M_S = 1$ transition is only 0.9 mT. Furthermore ENDOR experiments failed to reveal the presence of any ^{1}H ENDOR lines. This would then indicate that the individual $S = 1/2$ species of the triplet pair do not contain a proton suggesting O_2^- or O^- as alternative candidates. A large number of oxide systems containing surface stabilised superoxide anions have been studied in the past. Despite the high concentrations of O_2^- that may be formed, the pairing of two O_2^- anions to produce a net $S = 1$ spin state has never been reported. Surface stabilised O^- anions, with axial symmetry, have been reported on MgO but always as independent monomeric $S = 1/2$ centers.[12,13] However triplet state O^- radical ion pairs have been observed in bulk monocrystals of alkaline earth oxides with D terms ranging from 22.7 mT for MgO to 13.5 mT for SrO and spin–spin distances comparable to the lattice parameters of the oxides.[14] The observed D terms in the present case (13.7 and 12.7 mT) are similar to those observed for other $O^-\cdots O^-$ radicals in oxides.

The formation of the triplet pair O^- centers on the surface of rutile TiO_2 most likely occurs *via* the decomposition of the peroxide radical anion ($O_2^{2-} \rightarrow 2O^-$), the peroxide itself being formed directly or *via* the disproportionation of superoxide ($2O_2^- \rightarrow O_2 + O_2^2$).[4] Indeed a similar mechanism has been proposed in the decomposition of surface O_2^{2-} anions into active oxygen species, likely $2O^-$, over barium–lanthanum–oxygen mixed oxides, which have been postulated to be active in the oxidative coupling of methane.[15] We do not however speculate on any possible catalytic relevance of the $O^-\cdots O^-$ radical pair on TiO_2.

To summarise, a number of paramagnetic radicals have been observed following the heterogeneous decomposition of H_2O_2 over rutile TiO_2. Apart from the dominant presence of surface O_2^- anions, a triplet state ($S = 1$) surface radical pair has been identified. This paramagnetic center arises from a pair of surface $O^-\cdots O^-$ anions in mutual interaction on rutile TiO_2 producing a net $S = 1$ triplet state. The observation of this surface centre is interesting since, despite the complex nature of the H_2O_2 interaction and the heterogeneous morphology of polycrystalline rutile TiO_2, the reproducibility of the results evidences the preferential stabilisation of O^- anions at very specific surface sites consistently 5.9 or 6.0 Å apart. Similar surface triplet centers were not observed by us on anatase TiO_2 treated under similar conditions. This is to the best of our knowledge the first reported EPR spectrum of an $S = 1$ $O^-\cdots O^-$ radical anion pair stabilised on an oxide surface.

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