

The interaction of H₂O₂ with exchanged titanium oxide systems (TS-1, TiO₂, [Ti]-APO-5, Ti-ZSM-5)[†]

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The interaction of hydrogen peroxide with a range of polycrystalline titanium oxide systems, including TiO₂, TS-1, [Ti]-APO-5 and ion-exchanged Ti-ZSM-5, has been investigated using c.w. X-band EPR spectroscopy. Decomposition of the peroxide occurs immediately upon contact with all of the metal oxides investigated, resulting in the formation of a series of paramagnetic oxygen centred radicals. In the TiO₂/H₂O₂ system, intense signals assigned to adsorbed O₂⁻ anions were observed. Traces of physisorbed water was found to retard the motional characteristics of the adsorbed O₂⁻ anion, as manifested in the variable-temperature EPR spectra. In addition, covalently bound superoxo species were also identified on the TiO₂/H₂O₂ surface. In the TS-1/H₂O₂ system, two different bound peroxy radicals were observed and identified firstly as (1) Ti(OSi)₄/O₂⁻/H₂O or Ti(OSi)₄/OO[•]/H₂O and secondly (2) as HOTi(OSi)₃/OO[•]/H₂O. In both cases, the adsorbed radical interacts with an adjacent water molecule, while the two models differ by the presence or absence of a titanol function. An EPR signal of the weakly adsorbed hyperperoxy radicals (HO₂[•]) was also observed in H₂O₂-treated TS-1. In the [Ti]-APO-5/H₂O₂ and Ti-ZSM5/H₂O₂ systems bound peroxy radicals are observed in both cases, but broader EPR resonances are observed in the latter case over ZSM5 due to the heterogeneity of extraframework Ti⁴⁺ adsorption sites for stabilisation of the radical anions.

Introduction

Reactive oxygen species adsorbed on oxide surfaces are important intermediates in both total and selective catalytic oxidation reactions.^{1–3} For many years the formation, characterisation and reactivity of these intermediates have been studied in depth by a plethora of experimental techniques. In the particular case of radical intermediates, the EPR (Electron Paramagnetic Resonance) technique has provided extensive data on the nature of these surface stabilised oxygen centre radicals. Che and Tench published a thorough review 20 years ago, on the characterisation and reactivity of mononuclear² and molecular³ oxygen species on oxide surfaces. They summarised the most general, widely used methods of activating oxygen on metal oxides into three main areas.

(i) Adsorption of gaseous oxygen onto a reduced or slightly reduced oxide surfaces, such as TiO₂, which is generally reduced by mild thermovacuum conditions.

(ii) Adsorption of gaseous oxygen on UV or γ irradiated stoichiometric oxides such as MgO, containing surface trapped electrons.

(iii) Adsorption of gaseous oxygen onto oxides containing pre-adsorbed reactive molecules, such as H₂, CO, organics, etc.). In this case the oxygen radicals are produced by secondary reactions.

In summary, the oxygen radicals produced in these ways (e.g., O⁻, O₂⁻, O₃⁻) were studied in enormous detail and can be regarded as being very well characterised.^{2,3}

The role of free radical intermediates, particularly oxygen based radicals, in the heterogeneous decomposition of organic

substrates over metal oxides and zeolite systems has recently attracted renewed interest. In particular, the catalytic oxidation by H₂O₂ over TiO₂ or V₂O₅ has been investigated with a view to understanding the role of the active peroxy or peroxy-acid species in the decomposition mechanism.⁴ Despite the extensive literature, a well defined description of the basic phenomena occurring at the interface of the H₂O₂-oxide system is far from complete. For example, in the field of advanced oxidation processes for aqueous phase pollution control, the role of oxygen centred radicals (in particular the OH[•] radical) has been demonstrated as crucial to the catalytic destruction of water-borne pollutants. Hydrogen peroxide has emerged as a prime industrial oxidant for such processes, due to the formation of OH[•] radicals in the presence of suitable catalysts. In addition, partial oxidation of organic substrates (such as alcohols, olefins, aromatic molecules) has also received significant attention in recent years with the discovery of novel zeolite catalysts such as TS-1. Again the presence of H₂O₂ is pivotal in these reactions.

Despite the known formation of oxygen based radicals in these systems,^{5,6} only a very small number of publications have appeared on the characterisation and reactivity of oxygen-centred radicals over H₂O₂-treated oxide catalysts. Some groups have investigated the nature of the radicals formed by hydrogen peroxide decomposition over metal oxides. In particular, Geobaldo *et al.*,⁷ have reported the observation of an EPR spectrum on H₂O₂-treated TS-1, which was formally assigned to an O₂⁻ anion, analogous to the O₂⁻ species typically observed at the gas/solid interface.^{2,3} A similar EPR spectrum of an ionic O₂⁻ species was also reported by Tuel *et al.*,⁸ on CO reduced TS-1; the reduced Ti³⁺ ions were oxidised in the presence of O₂. Similar radicals were also reported on H₂O₂-treated metal oxides such as MgO⁹ and zeolites.¹⁰ However the nature of these radical species, even one as simple

[†] Electronic supplementary information (ESI) available: XRD patterns and further EPR spectra. See <http://www.rsc.org/suppdata/cp/b3/b306398b/>

as O_2^- , depends very much on how it was generated at the surface. A number of recent studies have also appeared on the characterisation of these oxygen centred radicals in the $\text{H}_2\text{O}_2/\text{TS-1}$ system^{11–16} in relation to their stability with water and reactivity with selected substrates.

Therefore, in the present investigation the radicals produced at the liquid/solid interface in a number of different exchanged titanium systems, including $\text{H}_2\text{O}_2/\text{TS-1}$, $\text{H}_2\text{O}_2/\text{TiO}_2$ (rutile), $\text{H}_2\text{O}_2/[\text{Ti}]\text{-APO-5}$ (a framework incorporated Ti cation) and $\text{H}_2\text{O}_2/\text{Ti-ZSM-5}$ (an ion-exchanged Ti cation) will be examined in detail. There were several reasons for initiating this study, including (i) to examine the role of H_2O_2 (suggested to form during the *photocatalytic* cycle over TiO_2 oxides) in the ‘dark-reactions’ that can occur on the TiO_2 surface,¹⁷ (ii) to identify possible radical intermediates that may be present in advanced oxidation processes involving $\text{H}_2\text{O}_2/\text{TiO}_2$ and $\text{H}_2\text{O}_2/\text{TS-1}$ systems, (iii) to study the reactions of H_2O_2 with TiO_2 since traces of TiO_x nanophases like rutile and anatase are often present in synthesised TS-1 and can have unwanted effects such as the decomposition of H_2O_2 , and finally (iv) to explore the role of the titanium environment on the nature of the radicals formed. While H_2O_2 is an excellent source of oxygen (and oxygen based radicals), the unavoidable contact of the metal oxide with an aqueous phase (30 and 60 wt% H_2O_2) has limited the application of this reaction as a source of O_2^- radicals for detailed spectroscopic study. However, it must be argued that these are precisely the conditions under which reactive oxygen centres (such as O^- , O_2^- , OH^\bullet , HO_2^\bullet , ROO^\bullet , etc.) are formed during the actual catalytic reactions using hydrogen peroxide and therefore deserves a more thorough and detailed spectroscopic study.

Experimental

The rutile TiO_2 used in this work was supplied by Huntsman Tioxide. TS-1 was synthesised according to the method of Taramasso *et al.*,¹⁸ framework substituted [Ti]-APO-5 was synthesised according to the method of Kevan and co-workers,¹⁹ using titanium isopropoxide and ion-exchanged Ti-ZSM-5 was synthesised using the CVD method described by Klaas *et al.*,²⁰ The crystallinity of calcined TS-1 and [Ti]-APO-5 was determined by XRD prior to use (the XRD patterns are given as ESI†). The samples (TiO_2 , TS-1, [Ti]-APO-5 and Ti-ZSM-5) were stirred with 30 or 60 wt% H_2O_2 (ex Aldrich) for 1 h at room temperature. An intense yellow coloured sample developed in all cases at the end of the reaction period. The resulting powdered suspensions were filtered off and gently dried in air at room temperature for about 12 h. The samples were then gently ground using a mortar and pestle and placed in an EPR quartz tube with a suitable high vacuum stop-cock for connection to a conventional vacuum manifold system. The samples prior to evacuation still contain an appreciable amount of water and are referred to as hydrated samples. The samples were then degassed (10^{-5} Torr) for 1 h at room temperature, and referred to as dehydrated samples.

All EPR spectra were recorded on a Bruker ESP-300e series spectrometer operating at X-band frequencies and 100 KHz field modulation in a standard rectangular ER 4102 ST Bruker resonator. The g values were accurately determined using a Bruker ER 035M NMR gaussmeter calibrated using the perylene radical cation in concentrated H_2SO_4 . The EPR simulations were performed using the SIM14S program (ex QCPE). Double integration of the EPR signals, with reference to two different sets of standards (a series of CuSO_4 and TEMPO standards of different concentrations), were used to determine the radical concentration in each sample. In all cases the estimated spin concentration for the fresh H_2O_2 -treated oxide samples was found to be 4×10^{17} ($\pm 1 \times 10^{17}$) spins g^{-1} . For brevity some additional and supporting EPR spectra on the

H_2O_2 -oxide system are given in the ESI† and will be referred to throughout the text.

Results

EPR spectra of H_2O_2 -treated TiO_2

When TiO_2 (rutile phase with a surface area of *ca.* $87 \text{ m}^2 \text{ g}^{-1}$) is stirred with aqueous H_2O_2 (30 or 60 wt% H_2O_2) for 2 h at room temperature and is subsequently dried in air at the same temperature, a yellow coloured powder is produced. The low-temperature EPR spectrum of the unevacuated TiO_2 sample after contact with 60 wt% H_2O_2 , along with the computer simulated spectrum, is shown in Fig. 1. A similar spectrum was obtained with 30 wt% $\text{H}_2\text{O}_2/\text{TiO}_2$ except for some small differences in the g_{zz} region (as discussed below). In both cases, a typical orthorhombic EPR spectrum was observed and characterised by the spin-Hamiltonian parameters of $g_{zz} = 2.025$, $g_{yy} = 2.0094$, and $g_{xx} = 2.0030$ for 30 wt% $\text{H}_2\text{O}_2/\text{TiO}_2$ and $^1g_{zz} = 2.025$, $^2g_{zz} = 2.0215$, $g_{yy} = 2.0094$, and $g_{xx} = 2.0030$ for 60 wt% $\text{H}_2\text{O}_2/\text{TiO}_2$ (Table 1). In the latter case, two different g_{zz} components were clearly resolved indicating the presence of two different environments (or sites) for radical stabilisation. In the 30 wt% $\text{H}_2\text{O}_2/\text{TiO}_2$ system, only a single g_{zz} component was seen.

The orthorhombic EPR spectrum in Fig. 1 is characteristic of a superoxide (O_2^-) type-radical anion. The formal assignment of the signal to an O_2^- type species can be easily made based on the characteristic g tensor elements for the radical anion stabilised on metal oxides.^{3,21–24} Furthermore because the g_{zz} component is sensitive to the crystal field environment, the g_{zz} values of 2.025 and 2.0215 observed in Fig. 1 are consistent with those expected for O_2^- stabilised at a Ti^{4+} site.³ Under higher amplification traces of a signal assigned to an $\text{O}^- \cdots \text{O}^-$ radical pair can also be found in the wings of the spectra after contact with H_2O_2 (not shown in Fig. 1) and have been discussed elsewhere.²⁵

The samples of 30 and 60 wt% H_2O_2 -treated TiO_2 were then evacuated at room temperature to remove air from the cell. The intense yellow colour of the powder diminished slightly upon evacuation, indicating the poor stability of the species responsible for the coloration. The variable-temperature EPR spectra of the 60 wt% H_2O_2 -treated samples, after evacuation, are shown in Fig. 2. The heterogeneity of the two O_2^- species is manifested by their slightly different thermal characteristics, since the first species characterised by $g_{zz} = 2.025$ appears to undergo preferential broadening at higher

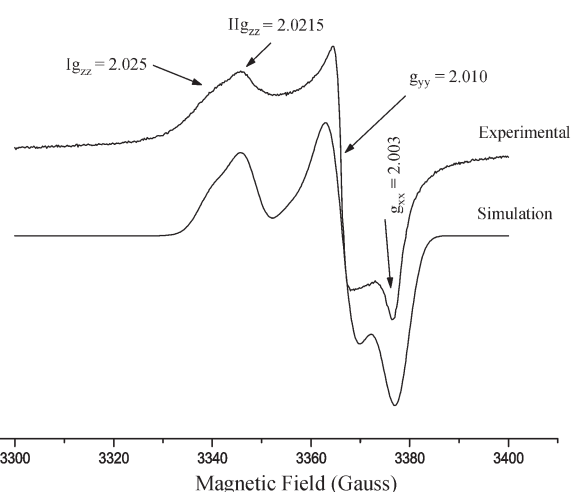


Fig. 1 Experimental and simulated EPR spectra of fresh (unevacuated) 60 wt% $\text{H}_2\text{O}_2/\text{TiO}_2$.

Table 1 Spin-Hamiltonian parameters for H₂O₂-treated TiO₂, TS-1, [Ti]-APO-5 and Ti-ZSM-5

Sample	Treatment	g_{zz}	g_{yy}	g_{xx}
TiO ₂	30 wt% H ₂ O ₂	I 2.025	2.009	2.003
	60 wt% H ₂ O ₂	I 2.025	2.009	2.003
		II 2.021	2.009	2.003
TS-1	30 & 60 wt% H ₂ O ₂	I 2.026	2.012	2.003
		II 2.024	2.012	2.003
TS-1	Reduced under CO, then exposed to O ₂	I 2.020	2.010	2.003
[Ti]-APO-5	30 & 60 wt% H ₂ O ₂	I 2.023	2.010	2.003
		II 2.021	2.010	2.003
		III 2.018	2.010	2.003
[Ti]-APO-5	Reduced under CO, then exposed to O ₂	I 2.023	2.010	2.003
		II 2.020	2.010	2.003
Ti-ZSM-5	30 & 60 wt% H ₂ O ₂	I 2.024	2.010	2.003

temperatures compared to the second species characterised by $g_{zz} = 2.0215$. A closer analysis of the spectra reveals that the g values do not undergo any averaging (*i.e.*, no change in peak or field position) as a function of temperature, while only small changes are observed in the linewidths. While a tightly bound surface anion will display limited motional behaviour at variable temperatures, and therefore constant g values, it is possible that other interacting surface adsorbates (such as water) may indirectly influence, and therefore restrict or retard, the mobility of the radical. For example, if traces of water are present at the surface, it is possible that they interact (through weak hydrogen bonds) with the O₂⁻ anions, and prevent the predicted averaging of the g tensors for a surface superoxide anion.

It is difficult however to comprehensively test this hypothesis by evacuation of the sample at elevated temperatures (*i.e.*, to ensure complete removal of all physisorbed water), since the signal is destroyed irreversibly at temperatures greater than 333 K. Nevertheless, the sample was gently degassed for several hours at 313 K, and the resulting EPR spectrum did indeed display a characteristic narrower series of lines at lower temperature. Furthermore, surface bound O₂⁻ anions can be generated by exposure of thermally reduced TiO₂ powders to molecular oxygen, as described in detail elsewhere.^{3,26} In that case, the O₂⁻ anions are present on a fully dehydrated surface (*i.e.*, effectively no hydrogen bonding in the absence of physisorbed or chemisorbed water) so that a pronounced averaging of the g tensors as a function of temperature is clearly seen (an example of this can be seen in the ESI,† and in the inset figure of Fig. 2). This result suggests the role of other surface adsorbates (such as physisorbed H₂O or surface OH groups) in preventing any extensive local rotational mobility of the anion on TiO₂/H₂O₂ at elevated temperatures.

It should be clearly recalled that changes in the shape of the EPR spectra recorded at different temperatures reflect the mobility of the radical under study. While sophisticated models of radical mobility are now well developed (*e.g.*, for nitroxide spin labels), a rough qualitative estimate of motional behaviour can be obtained by analysis of the partial averaging of the g tensor components at different temperature. For a side-on bonded O₂⁻ anion (Scheme 1), the radical can easily rotate about the y axis (among other types of rotational behaviour). When this occurs the g_{zz} and g_{xx} components average each other, while the g_{yy} (*i.e.*, the axis of rotation) remains constant (see ESI†). If this mobility about the y axis is hindered, for example by hydrogen bonding with surrounding OH

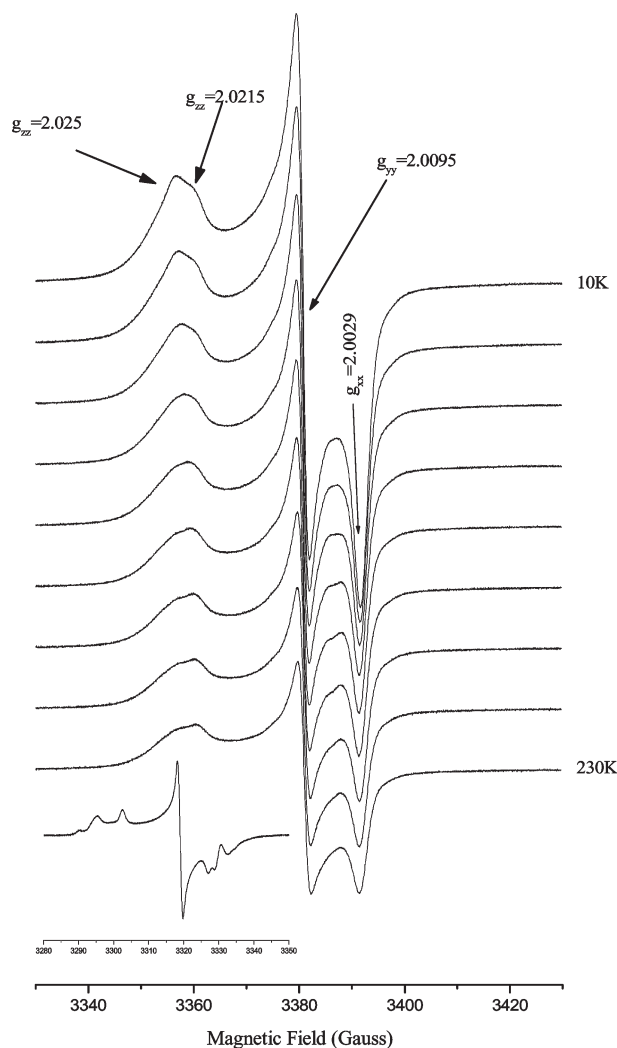
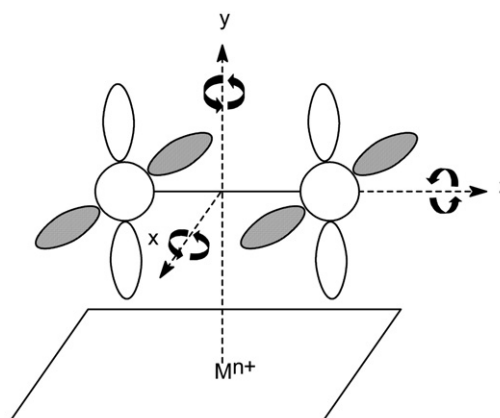


Fig. 2 Variable-temperature EPR spectra of 60 wt% H₂O₂/TiO₂. The spectra were recorded at 10, 20, 40, 60, 80, 110, 140, 170, 200 and 230 K. The typical EPR spectrum of a photogenerated O₂⁻ radical on TiO₂ is shown in the inset.

groups, then a restricted degree of mobility at increasing temperatures, and therefore restricted g tensor averaging, could be envisaged. Furthermore, a weak polarisation of the radicals through interaction with water or OH groups in the vicinity of the radicals, may cause slight distortions to the environment of the unpaired electron and result in a perturbation to the normal linewidths and this causes the lines to broaden at low



Scheme 1 Illustration of the principal coordinate axes of the adsorbed superoxide (O₂⁻) anion.

temperatures. Clearly neither influencing factors affect the EPR spectra of O_2^- formed photochemically on a completely water/OH group free TiO_2 surface.

Finally, the EPR spectra of both 30 and 60 wt% strength H_2O_2 -treated TiO_2 sample decayed after 2–3 days when exposed to air in parallel with the loss in sample coloration.

EPR spectra of H_2O_2 -treated TS-1

A sample of TS-1 was also treated with 30 and 60 wt% H_2O_2 as described above and after careful drying in air at 298 K, the EPR spectra were measured at different temperatures. The resulting spectra (shown in Fig. 3) were recorded at various temperatures between 100 and 298 K for the fresh (unevacuated) sample treated with 30 wt% H_2O_2 . A similar series of spectra, although with less resolution in the g_{zz} region, was observed for the 60 wt% treated $\text{H}_2\text{O}_2/\text{TS-1}$ sample. Once again, these EPR spectra are typical of an O_2^- type anion, with g values of $^1g_{zz} = 2.026$, $^2g_{zz} = 2.024$, $g_{yy} = 2.012$ and $g_{xx} = 2.003$. Similar to the case of 60 wt% H_2O_2 -treated TiO_2 (Fig. 2), two peaks also appear in the g_{zz} region of the spectra, highlighting the presence of two families (or sites) of O_2^- anions. In addition to the dominant signals arising from the O_2^- anions in $\text{H}_2\text{O}_2/\text{TS-1}$, a number of very weak

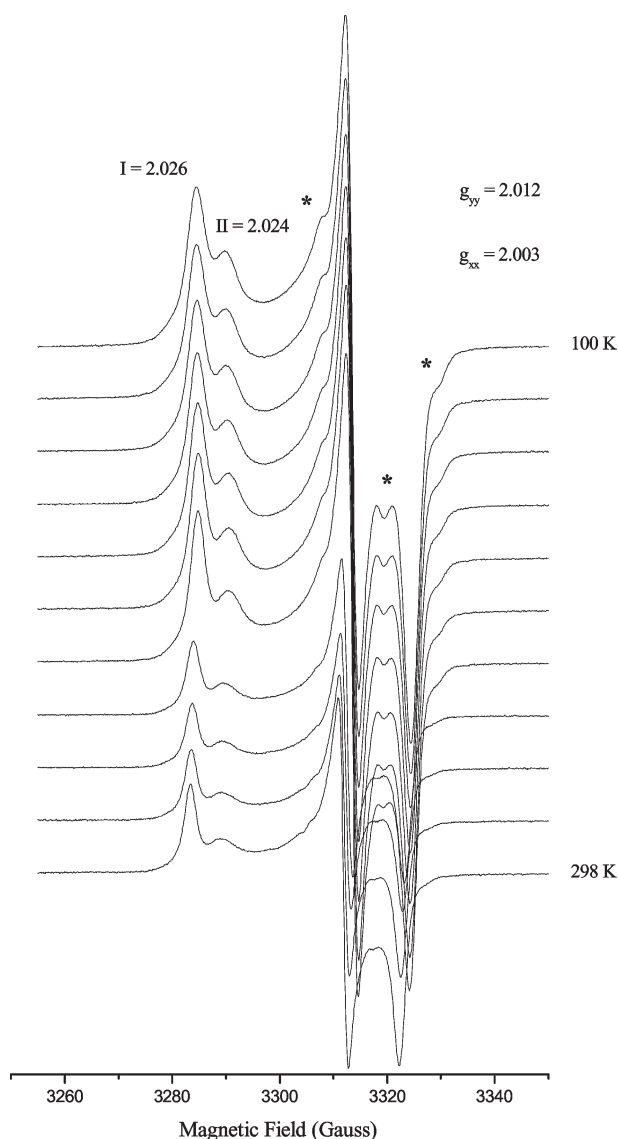


Fig. 3 Variable-temperature EPR spectra of fresh (unevacuated) 30 wt% $\text{H}_2\text{O}_2/\text{TS-1}$. The spectra were recorded at 100, 120, 140, 160, 180, 200, 220, 240, 260, 280 and 298 K.

resonances can also be seen in the EPR spectra of these unevacuated samples; for clarity the peaks are marked with an asterisk (*) symbol in Fig. 3. The origin and significance of these additional peaks will be discussed later.

It should be clearly reiterated that the above experiments on the fresh, unevacuated samples, were carried out in order to investigate the possibility that unstable radicals may be formed *initially* at the liquid/solid interface, but are so unstable that even mild evacuation conditions are sufficient to destroy the signal. Therefore the samples were subsequently evacuated at room temperature and the spectra recorded again. This step was performed because, similar to the case described above for $\text{H}_2\text{O}_2/\text{TiO}_2$, evacuation of the fresh sample resulted in a significant loss in coloration (from yellow to off-white) and possible loss of free radical concentration.

The EPR spectra for the evacuated 30 wt% treated $\text{H}_2\text{O}_2/\text{TS-1}$ sample are shown in Fig. 4. While the measured g values remained constant, the resolution/linewidths of the peaks have changed. This change is primarily induced by the preferential decrease in the intensity of the first radical (species I) characterised by the g_{zz} component at 2.026 and its increased linewidth at lower temperature. Prolonged evacuation of the sample at the slightly elevated temperature of 310 K leads to the eventual and complete destruction of this component. An analogous series of observations was found for the evacuated 60 wt% treated $\text{H}_2\text{O}_2/\text{TS-1}$ sample due to the preferential destruction of a single g_{zz} component. A similar series of spectra were also observed by Bonoldi *et al.*¹¹

Whilst some of the observed g_{zz} values are consistent with an O_2^- anion stabilised on a Ti^{4+} adsorption site, the g_{zz} value at

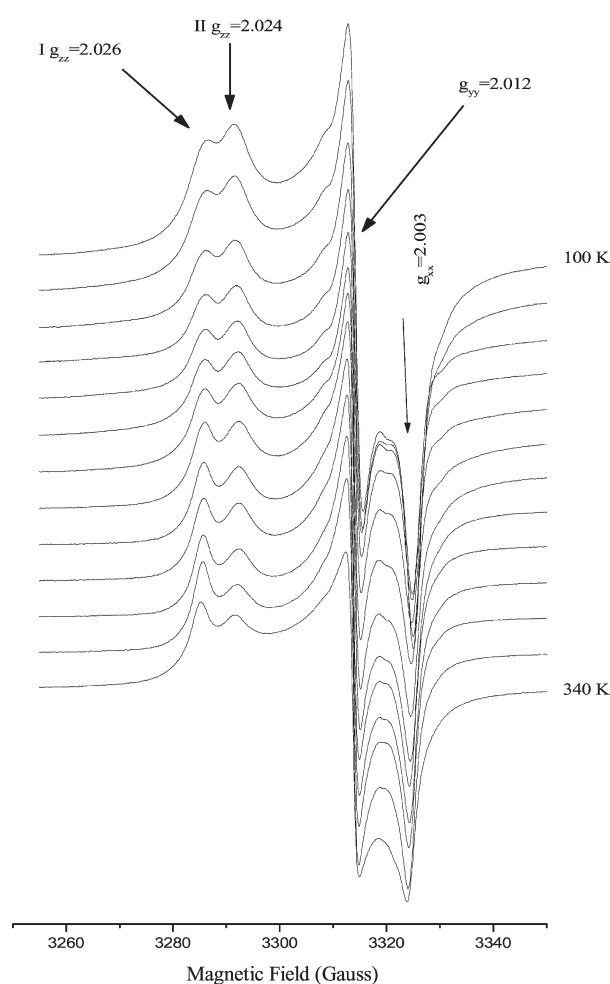


Fig. 4 Variable-temperature EPR spectra of evacuated 30 wt% $\text{H}_2\text{O}_2/\text{TS-1}$. The spectra were recorded at 100, 120, 140, 160, 180, 200, 220, 240, 260, 280, 300, 320, 340 K.

2.026 is rather high for an ionic superoxide species adsorbed at a Ti^{4+} site. It is reported for example that g_{zz} values of 2.024–2.031 are typical for O_2^- anions adsorbed at Si^{4+} sites,³ compared to 2.024–2.018 for O_2^- anions adsorbed at Ti^{4+} . To explore this idea further, an experiment was carried out in order to chemically reduce the Ti^{4+} cations to Ti^{3+} in the absence of aqueous hydrogen peroxide. Carbon monoxide was used as the reductant, and the presence of reduced Ti^{3+} cations could be clearly seen in the spectrum, characterised by a broad asymmetric peak at $g = 1.948$, typical of the d^1 paramagnetic system (spectrum shown in the ESI†). After addition of molecular oxygen, the Ti^{3+} signal disappeared and was immediately replaced by a characteristic spectrum of the O_2^- anion ($g_{zz} = 2.020$, $g_{yy} = 2.010$, $g_{xx} = 2.002$). In this case, the anion is formed by direct electron transfer from the Ti^{3+} cation to O_2 , in the absence of water at the gas/solid interface. By comparison, exposure of pure silicate to aqueous H_2O_2 does not produce any observable EPR signal. These results clearly indicate that the O_2^- anions, resulting from H_2O_2 decomposition on TS-1, are not formed at the Si^{4+} sites. An alternative explanation for the high g_{zz} values in Figs. 3 and 4 is based on the coordination mode and environment of the O_2^- anion at the Ti^{4+} sites, as discussed in detail later.

Although two paramagnetic centres can easily be distinguished in Figs. 3 and 4 (based on the two separate g_{zz} components), the origin of the minor signals marked with the * symbol deserves further attention at this point. A computer simulation of the EPR spectrum, corresponding to the fresh (non evacuated) sample at 100 K, was performed and the result is shown in Fig. 5. The spin-Hamiltonian parameters used in the simulation are listed in Table 2. As expected, the most dominant signals contributing to the spectrum arise from the two O_2^- type species (labelled species **I** and **II** in Table 2), with a 56% and 31% relative intensity, respectively. However, the simulation also identified a third paramagnetic species (labelled species **III**), with g values of $g_1 = 2.025$, $g_2 = 2.010$ and $g_3 = 2.003$. Most importantly it revealed that species **III** experiences a hyperfine interaction with a nucleus of nuclear spin $I = 1/2$ based on the simulated hyperfine values of $A_1 \approx 13$ G, $A_2 = 10$ G and $A_3 = 10$ G. This third species must therefore arise from a protonated oxygen centred radical.

The identity of species **III** can be easily understood by reference to the well known spin-Hamiltonian parameters of protonated oxygen radicals. Although the hydroxy radical (OH^*)

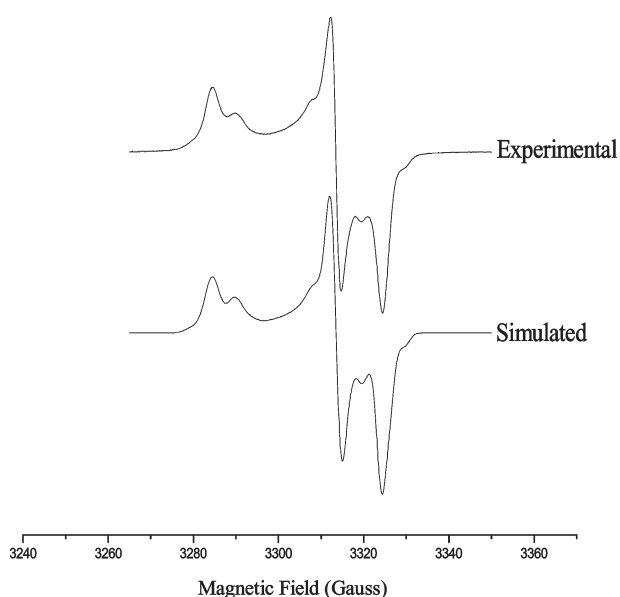


Fig. 5 Experimental and simulated EPR spectra of fresh (unvacuated) 60 wt% $\text{H}_2\text{O}_2/\text{TS-1}$.

Table 2 Spin-Hamiltonian parameters and percentage abundances obtained from the computer simulation of the EPR spectrum of the non-evacuated H_2O_2 -treated TS-1 sample recorded at 100 K

Species	Abundance (%)	Abundance					
		g_{zz}	g_{yy}	g_{xx}	A_{zz}/G	A_{yy}/G	A_{xx}/G
I	56	2.026	2.010	2.003	–	–	–
II	31	2.024	2.010	2.003	–	–	–
III	13	2.025	2.010	2.003	13 ± 1	10	10

has been observed over H_2O_2 -treated MgO ,⁹ the reported g and A values of OH^* are sufficiently unique and different to those reported for species **III** (Table 2), that this hypothesis can be immediately eliminated. The hydroperoxy radical (HO_2^*) is also proposed to form after interaction of hydrogen peroxide with metal oxides,⁶ and has been identified on TiO_2 ,²⁶ but its unambiguous assignment is made difficult by the fact that the g values are very similar to those observed for the ionic superoxide anion (O_2^-).²⁷ However, the presence of the proton produces a characteristic hyperfine pattern in the EPR spectrum which can be used to fingerprint the anion. Arutyunyan *et al.*,²⁸ have reported the formation of radicals from H_2O_2 vapour decomposition over silica and assigned the observed EPR orthorhombic signal to the HO_2^* radical. The EPR values for the radical on silica were reported as $g_1 = 2.032$, $g_2 = 2.0098$ and $g_3 = 2.0063$, with an A_1 value of 7.5 G.²⁸ The hydroperoxy radical has also been extensively studied in irradiated ice and aqueous solutions of H_2O_2 , and the general spin-Hamiltonian parameters reported are $g_1 = 2.035$, $g_2 = 2.0065$ and $g_3 = 2.0023$ while the hyperfine constants have values of $A_1 = 12.5$ G, $A_2 = 12.5$ G and $A_3 = 14.2$ G. Based on the comparison with literature, it is reasonable to assign species **III** to the hydroperoxy radical (HO_2^*). The g_1 value of 2.025 is slightly lower than that reported by Arutyunyan *et al.*,²⁸ over silica, and suggests that on H_2O_2 -treated TS-1 the HO_2^* anion is weakly stabilised at a Ti^{4+} site rather than Si^{4+} . This is not an unreasonable assignment as the Ti^{4+} cations are responsible for the decomposition of the hydrogen peroxide. The HO_2^* anion is also neutral so that, unlike the other highly charged radicals, it may be difficult to strongly coordinate this species on the highly ionic surface. This would explain the relatively low observed abundance (13%) of the anion in the EPR spectra.

EPR spectra of H_2O_2 -treated [Ti]-APO-5

When framework incorporated [Ti]-APO-5 is stirred with aqueous H_2O_2 (30 or 60 wt% H_2O_2) for about 2 h at room temperature, and subsequently gently dried in air at the same temperature, a yellow coloured powder is produced (similar to that described above for TiO_2 and TS-1). The EPR spectra of the unevacuated 30 and 60 wt% H_2O_2 -treated [Ti]-APO-5 samples were poorly resolved, producing a broad and ill-defined g_{zz} peak at ≈ 2.023 (spectra shown in the ESI†).

The yellow coloured sample of 60 wt% H_2O_2 -treated [Ti]-APO-5 was subsequently evacuated to a residual pressure of 10^{-4} Torr. The resulting EPR spectra for this evacuated sample, recorded at different temperatures between 10 and 298 K are shown in Fig. 6 (a typical spectrum of the unevacuated sample is also shown in the inset of Fig. 6). The most marked change in the spectra compared to the unevacuated case pertains to the approximate ten-fold increase in signal intensity. Clearly the presence of oxygen in the air causes more extensive spin-spin broadening of the lines in the [Ti]-APO-5 samples compared to the TiO_2 or TS-1 systems, although unusually it appears to affect the g_{zz} components to a greater extent than the g_{xx} or g_{yy} components. This could quite possibly be due to a heterogeneity of adsorption sites in the pre-evacuated

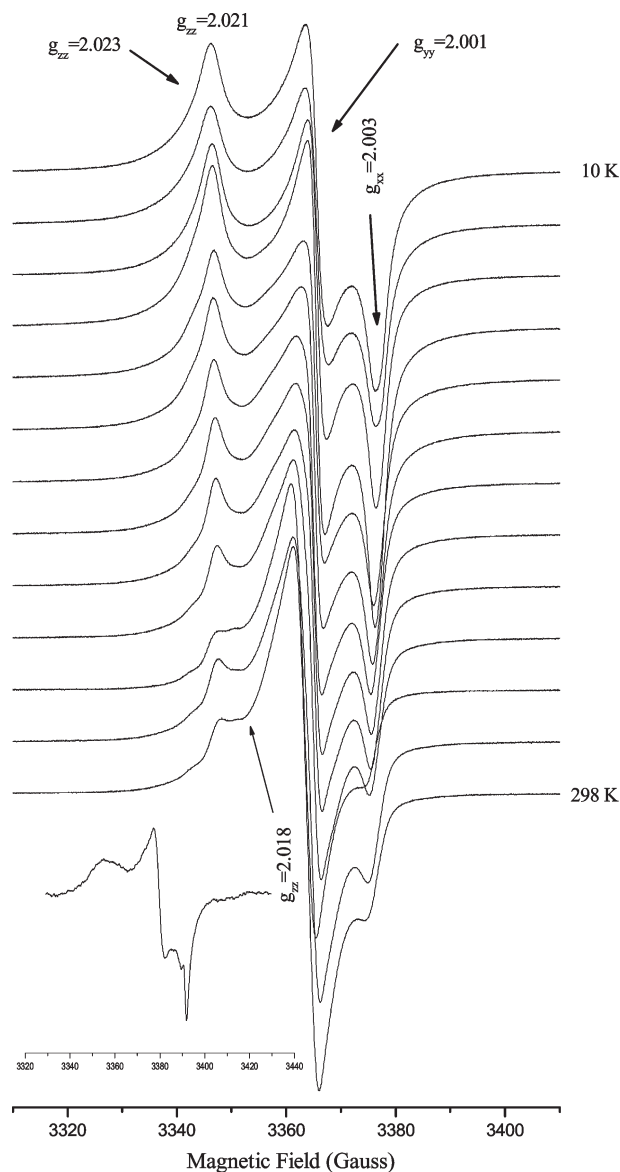


Fig. 6 Variable-temperature EPR spectra of evacuated 60 wt% H_2O_2 /[Ti]-APO-5. The spectra were recorded at 10, 30, 60, 90, 120, 135, 150, 165, 180, 210, 240, 270 and 298 K. The typical EPR spectrum of an unevacuated 60 wt% H_2O_2 /[Ti]-APO-5 sample is shown in the inset.

sample which influences the g_{zz} component to the greatest extent. Secondly, the resolution of the spectra increased significantly so that a heterogeneity of g_{zz} components can be seen ($g_{zz} = 2.023$, 2.021 and 2.018; Fig. 6). The radical responsible for the g_{zz} component at 2.021 is by far the most dominant.

A sample of [Ti]-APO-5 was also chemically reduced at elevated temperatures under a CO atmosphere in order to reduce Ti^{4+} to Ti^{3+} . The resulting EPR spectrum (shown in the ESI†) displays a broad asymmetric resonance at high field ($g \approx 1.995$), easily assigned to a Ti^{3+} species. After addition of oxygen to the reduced system, the EPR spectrum due to O_2^- is immediately seen (Fig. 7), and two distinct g_{zz} components can be easily identified ($^1g_{zz} = 2.023$ and $^2g_{zz} = 2.020$), evidencing the presence of two types of O_2^- anions. At the lowest temperatures investigated, three well defined peaks are observed typical of an orthorhombic O_2^- type radical. At higher temperatures (e.g. 280 K), the g_{zz} and g_{xx} components have smaller intensities, which is representative of a radical undergoing motional averaging. Interestingly, the observed averaging of the g tensors in the purely ionic case (i.e. the $\text{O}_2^- \cdots \text{Ti}^{4+}$ stabilised system formed at the gas/solid interface)

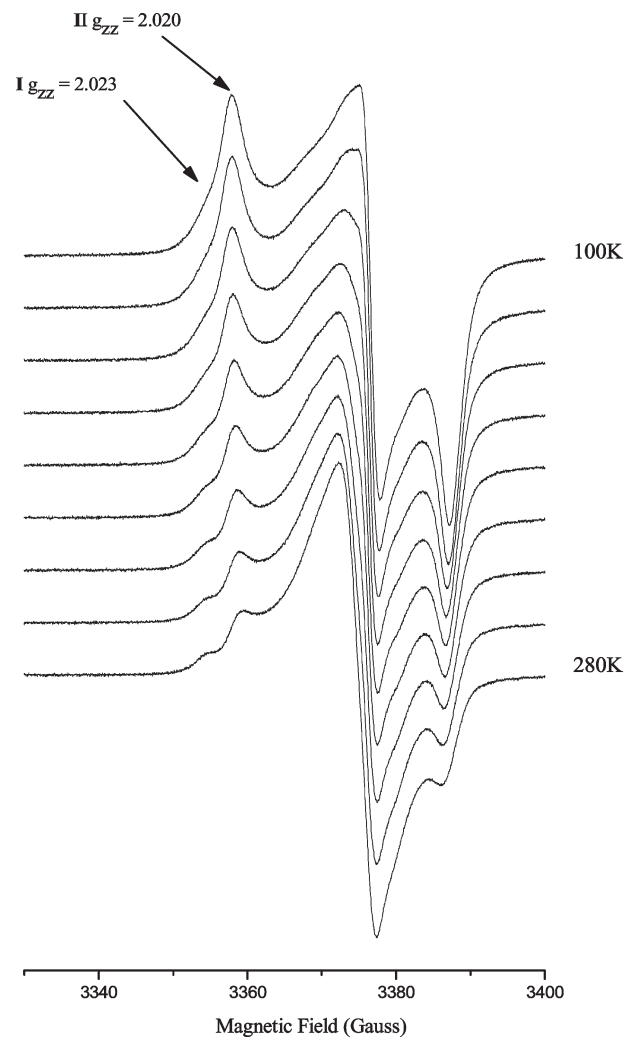


Fig. 7 Variable-temperature EPR spectra of [Ti]-APO-5 reduced under a CO atmosphere, and subsequently exposed to molecular oxygen. The spectra were recorded at 100, 120, 140, 160, 180, 200, 220, 240, 260 and 280 K.

is very similar to the effects observed for the O_2^- type radicals formed at the liquid/solid interface in the [Ti]-APO-5/ H_2O_2 system.

EPR spectra of Ti-ZSM-5

When Ti ion-exchanged ZSM-5 is stirred with aqueous H_2O_2 (30 or 60 wt% H_2O_2) for 2 h at room temperature, and is subsequently dried in air at the same temperature, a yellow coloured powder is produced. The resulting EPR spectra for the fresh (unvacuated) 60 wt% H_2O_2 -treated Ti-ZSM-5 sample are shown in Fig. 8. A similar series of spectra were observed for the 30 wt% treated sample, although the signals were less intense. A well defined orthorhombic signal, typical of an O_2^- type species, can be clearly seen with g values of $g_{zz} = 2.024$, $g_{yy} = 2.010$ and $g_{xx} = 2.003$. Only one dominant g_{zz} component is resolved, indicating the presence of only one type of O_2^- centre. The EPR spectra of the H_2O_2 -treated Ti-ZSM-5 sample decayed after 2–3 days when exposed to air in parallel with the loss in sample coloration. No EPR signal was observed for H_2O_2 -treated ZSM-5 in the absence of titanium.

In addition, the g components did not change or average as a function of temperature. This implies the absence of rotational motion in the radicals at the temperatures investigated. However, the linewidth of the spectra did increase at the lower

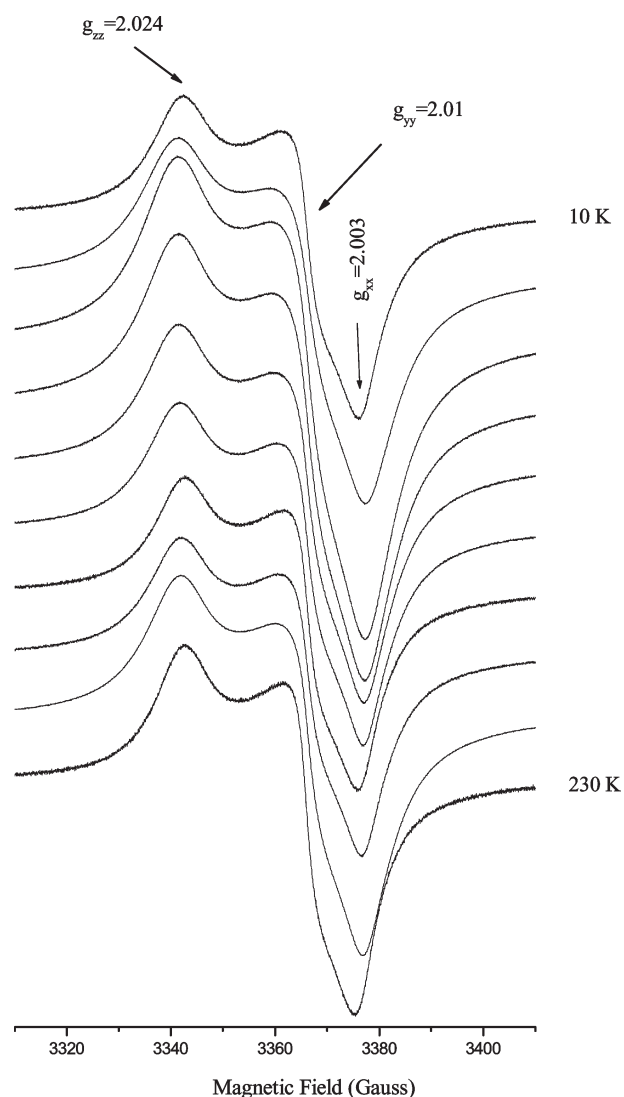


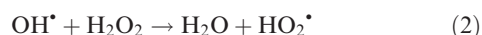
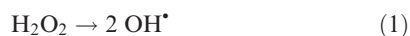
Fig. 8 Variable-temperature EPR spectra of fresh (unvacuated) 60 wt% $\text{H}_2\text{O}_2/\text{Ti-ZSM-5}$. The spectra were recorded at 10, 20, 40, 60, 80, 110, 140, 170, 200 and 230 K.

temperatures. This unusual behaviour was not observed in the evacuated sample (spectra shown in the ESI†), and therefore it may be concluded (as discussed above) that this broadening effect most likely arises from traces of water still present in the fresh non-evacuated sample.

Discussion

General mechanism of H_2O_2 decomposition at the liquid solid interface

It has been proposed⁹ that the general mechanism leading to the formation of adsorbed O_2^- species at the H_2O_2 -MgO interface is as follows;

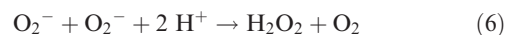
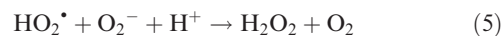


where the hydroperoxyl radical (HO_2^{\bullet}) is a weak acid and the protonated form of the ionic ion that forms subsequently and which is electrostatically bound to the oxide surface;



This general reaction sequence will also occur on other oxide supports, particularly those incorporating transition metal ions such as titanium, in a Haber-Weiss type mechanism.

However the process of radical stabilisation at the solid/liquid interface is more complex. While reactions (1)–(3) account for the formation of O_2^- anions, other competing reactions will occur in solution leading to the destruction of the O_2^- anions;²⁹



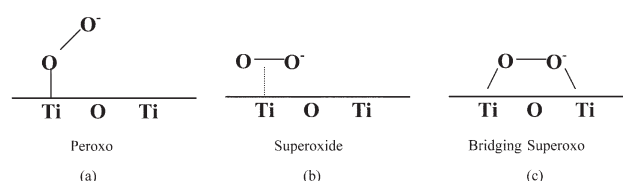
While the formation mechanism for O_2^- is accounted for in eqn. (3), the process by which it becomes stabilised on the oxide support producing intense EPR spectra is not evident. In a recent paper we demonstrated that the lifetime of the photogenerated O_2^- anions on a hydrated titania surface (anatase) was too short for detection by EPR at ambient temperature.³⁰ While this anion is easily stabilised on a fully dehydrated surface, it can only be observed as a short lived intermediate at 100 K on a hydrated anatase surface but by comparison it can persist for several hours on a hydrated rutile surface.³⁰ Clearly, the presence of a fully hydrated surface (*i.e.* containing both physisorbed and chemisorbed water), particularly at the solid/liquid interface (coupled with the recombination and disproportionation reactions (4)–(6)), will not allow easy adsorption of the O_2^- anion from solution. This must be considered when discussing the nature of the adsorbed O_2^- species observed by EPR in the H_2O_2 -oxide system.

One must also consider the unusual aspect observed in some of the EPR spectra of the H_2O_2 -oxide system, whereby the complete lack of g tensor averaging at increasing temperatures. The unusual changes observed in the linewidths of the g components was evidenced above as arising from the presence of (hydrogen bonded) water molecules on the partially hydrated or wet surface after contact with the aqueous H_2O_2 . For normal ionic superoxide (O_2^-) species formed at the gas-solid interface, the anions are typically electrostatically adsorbed in either “end-on” or “side-on” (see Scheme 1 earlier) positions.³ As a result, the motional behaviour of the anions produces a characteristic averaging of the g tensors that reflects the mode of bonding to the surface, as opposed to the radical freely migrating in solution or liquid water. While the presence of adsorbed water may account for the lack in surface motional behaviour, one must also consider the possibility of unusual coordination modes preventing facile rotation of the anion.

Formation of oxygen radicals on H_2O_2 -treated TiO_2

Although the observed EPR profile of the radicals formed in the H_2O_2 -treated TiO_2 system is typical of an O_2^- type anion, the motional behaviour is unusual. In principle, the paramagnetic anion could be adsorbed onto the TiO_2 surface in a number of different ways (Scheme 2).

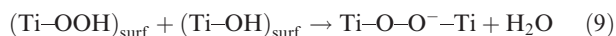
In the first case (a), for a unidentate peroxy radical which is bound covalently *via* σ bonding to the cation, then rotation about the Ti–O bond would be expected to occur at increasing temperatures. Such a rotation would lead to a characteristic averaging of the g tensor components, similar to those expected of a peroxy type radical. Schlick and Kevan³¹ have



Scheme 2 Illustration of possible coordination modes of dinuclear oxygen radicals on TiO_2 .

described and explained the distinctive transformation of the rhombic EPR signal to an axial signal at higher temperatures for peroxy polyethylene radicals on urea–polyethylene complexes, while D’Anna and Giannello³² noted the characteristic motional averaging of peroxy silicon radicals on H₂O₂-treated NaY zeolite. In the second case (b) of adsorbed superoxide species, the motional averaging of the anion has been extremely well documented^{2,3,31,33–35} and can be easily observed by EPR (see Fig. 2 and ESI† for example).

In the third case (c), a paramagnetic superoxo complex (*i.e.*, covalently bound) may explain the observed EPR signal and the expected chemistry of the system. The yellow coloration of TiO₂ after treatment with H₂O₂ is believed to arise from the presence of surface titanium peroxo complexes. Indeed, titanium peroxide complexes in solution are known to produce an intense yellow colour.^{36,37} Boonstra *et al.*,³⁸ noted the appearance of a yellow coloration after exposure of TiO₂ to H₂O₂ vapours, whereas illumination of the sample in the presence of dioxygen (*i.e.*, formation of the ionic O₂[−]··Ti⁴⁺ system) did not produce the same coloration. The yellow colour was attributed to the presence of pertitanic acid moieties on the oxide surface (Ti–OOH). At acidic pH, H₂O₂ exists in the form H₃O₂⁺ and can interact with basic sites on the oxide surface. The initial step of the interaction can therefore be described by eqn. (7) followed by deprotonation (eqn. (8)) and dehydration of the titanium hydroperoxy function by a neighbouring titanol function (eqn. (9)), to produce a surface superoxo type species;

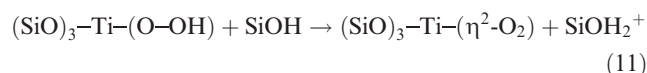
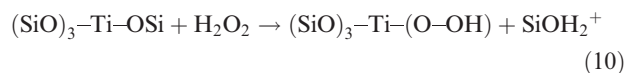


This assignment is also consistent with the surface paramagnetic superoxo species. Lever *et al.*,³⁹ noted that for early transition metal ions, the net electronic charge for dioxygen adducts is found more on the oxygen atoms, due to back donation of electron density from the metal 3d orbital to the π* antibonding orbitals of the oxygen adduct. Therefore for titanium with low electron affinity, the back donation is efficient, producing a higher density on the oxygen atoms. Klissurski *et al.*,⁴⁰ have also reported that H₂O₂-treated anatase TiO₂ contains an IR absorption at 1160 cm^{−1}, which was attributed to a stretching mode of the peroxide group, O₂^{2−}. However, Lever *et al.*,³⁹ suggest that O–O stretching frequencies in the range 1075–1195 cm^{−1} are more indicative of superoxo-like dioxygen adducts, whereas peroxide adducts have stretching frequencies in the range 790–932 cm^{−1}.

Yesodharan and Gratzel⁴¹ proposed a superoxo structure, similar to that illustrated in Scheme 2(c), to explain the absence of dioxygen evolution during the decomposition of water over rhodium and ruthenium loaded titanium dioxide. This structure would account for the absence of significant *g* tensor averaging (*i.e.*, shift in the measured *g*_{zz} values) observed in the EPR spectra, since the rigidity of the η² bound complex prevents easy rotation of the anion. With C_{2v} symmetry, any rotation or jump about the C₂ axis should result in a characteristic averaging of the *g*_{zz} and *g*_{xx} components which was clearly not observed in the spectra. It should be recalled that the EPR spectra of the purely ionic O₂[−] species formed on UV irradiated TiO₂, did undergo the typical averaging of the *g* tensors expected for a side-on type superoxide species (as shown in the ESI†). Furthermore, the unusual line-broadening of the spectra observed upon decreasing the temperature, was demonstrated as arising principally from the weak interactions with physisorbed water. Removal of this water by gentle evacuation of the sample at 40 °C, restored the characteristic profile expected of a surface bound radical at low temperatures (*i.e.*, narrower lines).

Formation of oxygen radicals on H₂O₂-treated TS-1

It is well known that the addition of H₂O₂ to titanium silicates produces a titanium peroxo complex⁶ and it has been proposed^{42,43} that the initial mechanistic step of the oxidation sequence with H₂O₂ involves hydrolysis of the Ti–O–Si bond to yield a silanol function and a hydroperoxytitanium(IV) function (eqn. (10)), which subsequently leads to the formation of water and a Ti(IV)(η²-O₂) peroxo complex (eqn. (11));



These peroxo structures have been proposed to be the active oxidising sites for TS-1 mediated oxidations,⁴⁴ although arguments persist in the literature as to whether these complexes are the true oxidants or mere spectators in the catalytic event.⁴⁵ Huybrechts *et al.*,⁴⁴ proposed that the oxidising species for the oxyfunctionalisation of alkanes is the open “end-on” form of the η²-peroxo complex (TiOO*) whereas Clerici⁴⁶ suggests that the most likely candidate is the hydroperoxy function (TiOOH*), owing to the instability of the hydroperoxy function relative to the peroxo complex. There is no evidence to suggest that the side-bonded ionic superoxide species (Ti–O₂[−]) is involved in the catalysis. Nevertheless, it is clear that in acid solution, the Ti–O–O species suggested by Huybrechts *et al.*,⁴⁴ would exist in the form as a hydroperoxy function.¹⁶

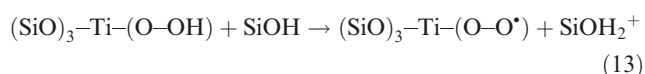
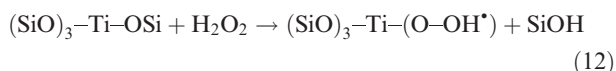
Experimental evidence has also demonstrated the presence of surface peroxo species (TiOO*) on H₂O₂-treated TS-1. Geobaldo *et al.*,⁷ convincingly demonstrated the formation of peroxo complexes on H₂O₂-treated TS-1 based on a characteristic UV absorption assigned to a charge transfer process O₂[−] → Ti⁴⁺. Based on the chemistry of Ti⁴⁺ compounds in solution, it is also well known that H₂O₂ acts as a bidentate ligand and can displace other ligands to form the very stable side bonded η²-O₂ peroxo species. In some cases the ‘end-on’ hydroperoxo complexes can also be formed. However, the stability of the peroxo complexes formed with H₂O₂ are much higher than the corresponding stability of the hydroperoxo complexes. The strong repulsion between formally unshared electrons in planar H₂O₂ are reduced by Ti⁴⁺ as they accept electron density from the filled antibonding orbital of H₂O₂ interacting with the empty metal d orbitals. Therefore, even the less stable hydroperoxo complexes may prefer the ‘side-on’ configuration to provide added stability. Nevertheless, the stability of even the peroxo complexes is limited to a temperature of 333 K and they rapidly decompose at temperatures of 373 K.⁴⁴ A resonant Raman study was also recently carried out on TS-1/H₂O₂/H₂O in order to clarify the nature of the bound oxo-species (*i.e.*, the “side-on” Ti–peroxo or the “end-on” Ti–hydroperoxo species).⁴⁷ The authors concluded that the species responsible for the band at 26000 cm^{−1} in TS-1/H₂O₂/H₂O was due to the “side-on” Ti–peroxo.

One may conclude from the above analysis of the literature that; (i) a variety of paramagnetic oxygen centred radicals can in principle be formed in H₂O₂/TS-1 including TiOO*, TiOOH* and Ti–O₂[−], (ii) the η²-O₂ peroxo complexes (and their associated yellow colour) are unstable above 333 K, (iii) they have been observed experimentally by UV-vis, and (iv) the peroxo complex likely forms *via* reaction of the hydroperoxo intermediate. All these facts may be reconciled with the above EPR data to aid in the interpretation of the two principal paramagnetic species (characterised by the *g*_{zz} components of 2.026 and 2.024). As demonstrated earlier, the third minor species in the spectrum has already been unambiguously identified as the hydroperoxy complex (HO₂*).

It should be recalled that both the yellow coloration of the sample (characteristic of peroxo type species) and the EPR

spectra were irreversibly and simultaneously destroyed by gentle heating, and more importantly the spectra displayed no significant averaging of the g tensors at increasing temperatures. The absence of any motional averaging of the g tensor for species **I** and **II** (*i.e.*, g_{zz} components of 2.026 and 2.024) is consistent with a model of either a tightly bound $\text{Ti}^{4+} \cdots \text{O}_2^-$ species and/or a covalently bound η^2 -peroxo complex, with little or limited rotation about the C_2 molecular axes even at higher temperatures. It is clear therefore, that species **I** and **II** could arise from two different radicals in the TS-1 material. It is most unlikely that these two signals originate from similar peroxo complexes adsorbed at *different* framework sites (*e.g.*, framework and extraframework titanium), since only one type of Ti^{4+} environment exists in TS-1. It is reported in the literature that Ti^{4+} in TS-1 is preferentially sited in existing silicalite defect sites, at sites T6, T7 and T11. However, all sites are in the main 10-ring cage, and therefore chemically equivalent.^{48,49} Without extensive radical mobility, stabilisation of radicals on Si^{4+} alone cannot occur. Bonoldi *et al.*,¹¹ have also reported similar EPR spectra to those shown above in Fig. 3 for $\text{H}_2\text{O}_2/\text{TS-1}$ samples where the absence of any extraframework titanium was conclusively demonstrated. This rules out the possibility for any assignment based on similar oxygen radicals stabilised at different framework and extraframework Ti^{4+} sites.

A possible assignment of the radicals may be advanced based on an understanding of the mechanism of the H_2O_2 interaction with TS-1. As discussed above in eqns. (1)–(3), hydrogen peroxide may decompose over the TS-1 material *via* formation of HO^\bullet radicals and subsequently hydroperoxy radicals ($^\bullet\text{OOH}$). The latter radicals may deprotonate to yield the corresponding O_2^- radical ($\text{HO}_2^\bullet \rightarrow \text{H}^+ + \text{O}_2^-$). Considering the fact that traces of the $^\bullet\text{OOH}$ radical were identified in the EPR spectrum, one may conclude that one of the radical species should be assigned to $\text{Ti}^{4+} \cdots \text{O}_2^-$. In addition H_2O_2 may react with the TS-1 material causing hydrolysis of the Ti–O–Si bond, producing the silanol function. However, a small fraction of these hydroperoxytitanium(IV) species may resist dehydration and remain in a paramagnetic state with a sufficiently long lifetime to be observed in the EPR spectrum. These hydroperoxo species are unstable and easily decompose (by gentle evacuation of the sample) to produce the paramagnetic $\text{Ti}(\text{IV})(\eta^2\text{-O}_2^-)$ peroxo complex;



The paramagnetic Ti–(O–O $^\bullet$) species would also produce an EPR spectrum typical of the superoxide anion. It is important to note that the difference between the two mechanisms leading to paramagnetic oxygen radicals (*i.e.*, eqns. (1)–(3) compared to eqns. (12) and (13)) emanates from the hydrolysis of the Ti–O–Si bond.

The two signals previously observed in the EPR spectra of $\text{H}_2\text{O}_2/\text{TS-1}$ ¹¹ were examined in detail and both O_2^- anions adsorbed on Ti^{4+} sites and TiOO^\bullet species, generated by homolysis of the O–H bond in the hydroperoxide Ti–OOH $^\bullet$ function, were considered. After examination of the data, the authors appeared to favour the assignment for two O_2^- species interacting with an adjacent water molecule (*i.e.*, $\text{HO-Ti}(\text{OSi})_3/\text{O}_2^-/\text{H}_2\text{O}$ and $\text{Ti}(\text{OSi})_4/\text{O}_2^-/\text{H}_2\text{O}$) and differing by the presence or absence of a titanol function. However, it was also recently demonstrated by Dewkar *et al.*,⁵⁰ that an exceptionally stable titanium superoxide radical ion could be formed in the homogeneous phase simply by reaction of $\text{Ti}(\text{OR})_4$ (where R = *i*Pr, *n*Bu) with 50% H_2O_2 . In that case the EPR spectrum revealed a slightly asymmetric g_{zz} profile

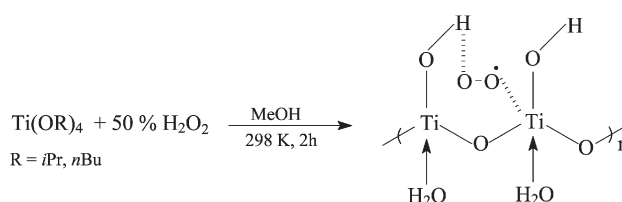
but most interestingly with a g_{zz} value of 2.0235. The structure of the proposed radical complex is shown in Scheme 3.

In this particular case, the paramagnetic entity was present in the homogeneous phase where there is no possibility for a heterogeneous environment for the titanium ions. Therefore it would appear that a low-coordinated TiOO^\bullet species (in this case $\text{Ti}(\text{O})_3$) will produce a superoxide-like EPR spectrum with low g_{zz} values. Based on this argument, the higher g_{zz} component could most likely be assigned to the higher coordinated TiOO^\bullet radical species. In other words the g_{zz} component in TS-1 at 2.026 can be assigned to $\text{Ti}(\text{OSi})_4/\text{O}_2^-/\text{H}_2\text{O}$ or $\text{Ti}(\text{OSi})_4/\text{OO}^\bullet/\text{H}_2\text{O}$ while the g_{zz} component at 2.024 can be assigned to the low-coordinate case $\text{HO-Ti}(\text{OSi})_3/\text{OO}^\bullet/\text{H}_2\text{O}$. Without recourse to ^{17}O labelled H_2O_2 , it is not possible to unambiguously differentiate between the side-on bonded O_2^- species or the end-on bonded OO^\bullet species.

Formation of oxygen radicals on H_2O_2 -treated [Ti]-APO-5 and Ti-ZSM-5

In the case described above for TS-1, it was demonstrated that two well defined g_{zz} components (*i.e.*, two different radical species) can be formed even when a single type of Ti environment exists in the sample. The radicals responsible for both components where rigidly held at the adsorption site, either by strong electrostatic forces and/or additionally by hydrogen bonding with residual surrounding water molecules. As a result the spectra were characterised by a lack of any significant g tensor averaging. In the present case of [Ti]-APO-5, the results are less straightforward to interpret. One of the most unusual aspects of the [Ti]-APO-5 samples investigated is the fact that the spectra of the evacuated 60 wt% H_2O_2 -treated sample display averaging of the g tensors at elevated temperatures, while the 30 wt% treated sample does not. It should be noted that in all the cases studied so far (TS-1 and TiO_2) in the presence of an aqueous H_2O_2 phase, the presence of water appears to have a significant influence on the line shape of the superoxide signal and certainly prevents any motional averaging of the g tensors. However in Fig. 6 this clearly does not happen. The observed changes to the g_{xx} and g_{zz} components are in fact analogous to those found in Fig. 7 (*i.e.*, the case where the superoxide radical was formed by CO reduction of the sample, in the absence of water). The only possible explanation for this is the possibility that the sample was evacuated extensively leading to the complete dehydration of the material. This can be contrasted with the evacuated 30 wt% treated [Ti]-APO-5 sample, which did *not* display any averaging at elevated temperatures and so presumably still contained traces of physisorbed water.

Considering the assignment of the radicals present in H_2O_2 /[Ti]-APO-5, one dominant species appears to exist in both the 30 and 60 wt% treated samples (at $g_{zz} = 2.021$) with minor species at 2.023 and 2.018. As demonstrated in the case of $\text{H}_2\text{O}_2/\text{TS-1}$, both mechanisms for H_2O_2 decomposition can occur producing $\text{Ti} \cdots \text{O}_2^-$ radicals and $\text{Ti} \cdots \text{OO}^\bullet$ radicals. The latter radical species appear to produce the g_{zz} component with the lower value. Therefore as a tentative assignment, it would appear that the most dominant species observed in [Ti]-APO-5 is due to the three-coordinate (3C) $\text{Ti} \cdots \text{OO}^\bullet$ type



Scheme 3

radical centre, and the decomposition mechanism responsible for the formation of this radical predominates in this particular zeolite. This completely contrasts the situation with TS-1 where there exists an almost equal concentration of both radical sites.

The interaction of hydrogen peroxide with a titanium ion-exchanged zeolite was investigated in order to examine the differences in the EPR spectra of the superoxide radicals associated with tetrahedral Ti framework sites as opposed to extraframework Ti sites. In the ion-exchanged Ti-ZSM-5 sample, all EPR spectra were broad with an ill-defined g_{zz} component at *ca.* 2.024. This is in stark contrast to the samples of framework incorporated titanium cations (either in TiO₂, TS-1 or [Ti]-APO-5) where at least two well defined g_{zz} components could be observed. The broad nature of this signal can easily be accounted for based on the likely heterogeneity of extraframework titanium cations stabilised at different ion-exchanged sites. If a distribution of such sites exists (which is commonly observed with other paramagnetic transition metal cations) then a distribution of Ti \cdots O₂⁻ environments will also exist. Clearly the absence of well defined tetrahedral Ti sites in the ion-exchanged sample produces a different EPR spectrum of the adsorbed O₂⁻ radical which is broad and is easily characterised by the slightly lower g_{zz} values. This suggests that EPR of adsorbed O₂⁻ could be used as a probe to differentiate between framework *versus* extraframework Ti⁴⁺ cations.

Conclusions

It is clear from the above results and discussion that a series of oxygen centred radicals, can be formed upon contact of aqueous hydrogen peroxide with the metal oxides TiO₂, TS-1, [Ti]-APO-5 and ion-exchanged Ti-ZSM-5. The presence of lattice incorporated titanium leads to the formation of EPR spectra with well defined g components, indicating the presence of specific Ti⁴⁺ sites or environments, in contrast to the ion-exchanged Ti⁴⁺ samples (Ti-ZSM-5) where a heterogeneity of adsorption sites appears to produce broader EPR spectra. The radicals formed at the H₂O₂-oxide interface exhibited unusual motional behaviour, since the line width of the EPR signal appeared temperature independent. This observation was assigned to the presence of surface H₂O, (weakly) hydrogen bonding with the O₂⁻ anions and therefore limiting the motional behaviour of the radical; *i.e.*, mimicking the EPR profile of a tightly bound surface anion.

In the case of H₂O₂/TS-1, two reactions occur simultaneously, one being the 'self degradation' of H₂O₂ (catalysed by TS-1) to form HOO \cdot , with subsequent deprotonation to yield the corresponding superoxide (O₂⁻ or OO \cdot) radical. This is confirmed by the observation of the HOO \cdot radical in the EPR spectra. The other mechanism that predominates in these oxides is the hydrolysis of the Ti-O bond to form either a four-coordinate Ti⁴⁺ \cdots OO \cdot species, or, a three-coordinate Ti⁴⁺ \cdots OO \cdot species, where the latter is formed by homolysis of the O-H bond in TiOOH. These two different coordinative Ti centres can be seen clearly in the all EPR spectra (apart from H₂O₂/Ti-ZSM-5), with the lower coordinated Ti species having the lower g value, and the higher coordinate Ti⁴⁺ having the higher g value. Both mechanisms form superoxide radicals, the difference being how they are bonded to the surface of the Ti⁴⁺.

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