ESR studies of $O_2^-$ adsorbed on silica gel: Photoformation and rotational dynamics

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An ESR investigation is reported of oxygen radicals formed by UV radiation of silica gel surfaces in the presence of $O_2$. The species $O_2^-$ and $O_3^-$ are identified. The $O_2^-$ radical shows a temperature dependent signal shape between — 196 and 25 °C which is interpreted in terms of Brownian rotational surface diffusion about an axis perpendicular to the O–O bond and to the surface. Correlation times for surface diffusion are estimated from comparison of observed and computer simulated spectra, and an activation energy for surface diffusion of $2.4 \pm 0.8$ kJ mol$^{-1}$ calculated. Comparison with previously reported spectra for W/SiO$_2$ and Ti/SiO$_2$ surfaces indicates that the mobile $O_2^-$ species formed in all three systems must be located on the SiO$_2$ support, and that the mobility is due to the absence of strong interaction with transition metal sites.

INTRODUCTION

The superoxide ion $O_2^-$ can be formed on many different solid surfaces. The radical anion is generated by electron transfer from the solid, either spontaneous or under irradiation, to adsorbed $O_2$, and the species is noted for its relative stability on most surfaces. Several recent reports have described ESR evidence for surface mobility of adsorbed $O_2^-$. Clarkson and Kooser observed temperature variations in the saturation transfer ESR line shape for $O_2^-$ on Vycor-supported silver surfaces which were interpreted in terms of Brownian diffusion. The normal ESR line shape for $O_2^-$ generated by adsorbing $O_2$ on a silica gel supported tungsten surface was found by Howe, Kazusaka, and Youn to vary with temperature, and a similar explanation was suggested. A detailed study of oxygen radicals produced on Vycor supported titanium surfaces by Shirotani, Moro, and Freed revealed three different $O_2^-$ signals, one of which showed a temperature dependent line shape similar to that for $O_2^-$ on silica supported tungsten. These authors simulated the observed line shapes for the temperature dependent signal with a Brownian diffusion model and obtained correlation times and an activation energy for the surface rotational diffusion.

The similarity of the temperature-dependent $O_2^-$ signals reported for silica supported tungsten and Vycor supported titanium suggested to us that the adsorption sites for $O_2^-$ may be the silica (Vycor) support rather than W$^{+4}$ or Ti$^{+4}$. We therefore undertook an investigation of oxygen radicals formed on silica gel containing no added transition metal component. The results presented below show clearly that the mobile $O_2^-$ species characterized by Freed et al. is indeed associated with the support rather than the titanium.

EXPERIMENTAL

Silica gel was obtained from Davison Chemical (grade 950). It had a surface area of 750 m$^2$ g$^{-1}$ and consisted of 99.71% by weight SiO$_2$. The impurity content was, in wt. %, as follows: Fe$_2$O$_3$, 0.03%; Al$_2$O$_3$, 0.10%; TiO$_2$, 0.09%; CaO, 0.01%; Na$_2$O, 0.02%; ZnO, 0.1%, and all remaining trace elements 0.03%. Oxygen (Airco) and $^{17}$O enriched $O_2$ (Bio-Rad Laboratories) were used without further purification. The labeled oxygen had an enrichment of 60 at. % $^{17}$O. All sample preparations and ESR spectra were performed in the same high vacuum cell. The cell consisted of a greaseless stopcock connected to a Pyrex reactor section along with a quartz sidearm for the measurement of ESR spectra. Samples were prepared on a conventional all glass high vacuum system with a base pressure of $10^{-6}$ Torr. A mercury manometer was attached to a secondary glass manifold which allowed for quantitative adsorption of oxygen.

Superoxide adsorbed on silica gel was prepared by dehydroxylating the silica gel in vacuo at a heating rate of 100 °C/h. The final dehydroxylated temperature depended on the particular experiment; temperatures of either 400 or 800 °C were used. The sample was kept at the final dehydroxylation temperature overnight. After cooling to room temperature the silica was exposed to 5 Torr of $O_2$, then tapped into the sidearm and irradiated. Irradiation employed an Osram 200 W super pressure mercury lamp. All experiments used an irradiation period of 1 h, and sample heating was minimized by directing a stream of compressed air at the quartz sidearm during irradiation. From a thermal blank experiment it was determined that sample heating contributes to less than 1% of the photoformed signals.

All spectra were recorded on a Varian E-115 spectrometer employing 100 kHz field modulation. A double cavity (TM$_{010}$ mode) was utilized. g values were computed by reference to a Varian strong pitch sample. Spin concentrations were obtained by doubling integrating the first derivative absorption spectrum relative to the strong pitch sample. All spectra were recorded at $-196$ °C unless otherwise noted. Variable temperature (VT) spectra above $-196$ °C were obtained by use of a Varian VT probe, and below $-196$ °C with a Helitran liquid helium transfer cryostat.
Two computer programs were used in this investigation. Simulation of ESR spectra in the rigid limit were obtained with SIM 13. Simulations involving mobility were obtained with the program ORTHO1.

RESULTS

Photoformation of oxygen radicals

The EPR spectrum obtained on irradiation of silica gel outgassed at 400°C in O₂ at −196°C is shown in Fig. 1(a). This consists of two overlapping signals; the peak at g = 2.026 is assigned to O₂−, as discussed below, and the remaining features are due to a second oxygen radical. The two signals could be separated by subsequent exposure to H₂ or CO at room temperature. As shown in Fig. 1(b), such treatment removes almost completely the signal due to the second radical, leaving the O₂− signal with g-tensor components g_xx = 2.0261, g_yy = 2.0096, and g_zz = 2.0048. The maximum intensity of the O₂− signal generated in this manner corresponded to a spin concentration of ~6×10¹⁵ g⁻¹. Figure 2 shows computer simulated spectra; the observed composite spectrum in Fig. 1(a) could be satisfactorily simulated with the sum of two signals [Figs. 2(b) and 2(c)], using the parameters listed in Table I. The intensity ratio of 4:1 used in the simulation gives an approximate indication of the relative concentrations of the two paramagnetic species, recognizing that the exact ratio depends strongly on the linewidths used in the simulations.

Similar experiments with silica gel outgassed at 800°C produced a very different ratio of concentrations for the two oxygen radicals. As shown in Fig. 3(a), the spectrum obtained on irradiation in O₂ of silica gel outgassed at 800°C is dominated by the second signal, which has an intensity corresponding to 6×10¹⁶ spins g⁻¹. The O₂− signal is barely detected in Fig. 3(a) as a weak shoulder at g = 2.026. Subsequent exposure of the sample to H₂ at room temperature removed the second signal, leaving a residual O₂− concentration of ~2×10¹⁵ g⁻¹ [Fig. 3(b)].

![FIG. 1. Photoformation of oxygen radicals on SiO₂. (a) Spectrum recorded at −196°C after irradiation in O₂ of SiO₂ outgassed at 400°C; (b) after subsequent exposure to H₂ at room temperature.](image)

![FIG. 2. Computer simulation of spectrum in Fig. 1(a); superposition of O₂− (b) and O₂− (c) signals.](image)

![TABLE I. ESR parameters for selected O₂− radicals.](table)

<table>
<thead>
<tr>
<th>System</th>
<th>g_xx</th>
<th>g_yy</th>
<th>g_zz</th>
<th>A_x(¹⁷O)/G</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂− on SiO₂ (this work)</td>
<td>2.0048</td>
<td>2.0096</td>
<td>2.0261</td>
<td>77.5</td>
</tr>
<tr>
<td>O₂− on W/SiO₂ (Ref. 3)</td>
<td>2.003</td>
<td>2.009</td>
<td>2.027</td>
<td>74</td>
</tr>
<tr>
<td>O₂− on Ti/SiO₂* (Ref. 4)</td>
<td>2.0027</td>
<td>2.0088</td>
<td>2.0305</td>
<td>...</td>
</tr>
<tr>
<td>I</td>
<td>2.0035</td>
<td>2.0094</td>
<td>2.0237</td>
<td>...</td>
</tr>
<tr>
<td>II</td>
<td>2.0035</td>
<td>2.0092</td>
<td>2.0260</td>
<td>74.9, 80.3</td>
</tr>
<tr>
<td>O₂− on γ-irradiated SiO₂ (Ref. 9)</td>
<td>2.0031</td>
<td>2.0095</td>
<td>2.025</td>
<td>...</td>
</tr>
</tbody>
</table>

*Parameters quoted at −196°C
Figure 4 shows the two signals obtained with $^{17}$O enriched O$_2$. The O$_2^-$ signal was obtained in this case by irradiation of silica gel outgassed at 400 °C in $^{17}$O enriched O$_2$ followed by exposure to H$_2$ to remove the second signal, and the second signal by irradiation in $^{17}$O enriched O$_2$ of silica gel outgassed at 800 °C. Both signals contain $^{17}$O hyperfine splitting; the analysis is discussed below.

**Temperature dependence of O$_2^-$ signal**

The line shape of the O$_2^-$ signal was found to vary markedly with temperature between $-196$ °C and room temperature, as illustrated in Fig. 5 (the O$_2^-$ signal was generated by irradiation in O$_2$ and subsequent exposure to H$_2$ to remove the second signal). The changes observed (an increase in linewidth with increasing temperature and a shift of the low-field g-tensor component to higher field) were completely reversible over this temperature range. No variation in line shape was detected at temperatures below $-196$ °C (down to $-261$ °C). Above room temperature the O$_2^-$ signal broadened further, but these changes were accompanied by an irreversible intensity loss. Similar effects were observed in the O$_2^-$ signal generated from $^{17}$O-enriched O$_2$ in
addition the magnitude of the $^{17}$O hyperfine splitting decreased significantly with increasing temperature, as shown in Fig. 6. The line shape of the second oxygen radical signal did not vary with temperature between $-196$ and $25\,^\circ\text{C}$.

**Computer simulation of temperature dependent signals**

The line shapes of the temperature dependent $\text{O}_2^-$ signal (Fig. 5) were computer simulated using the program ORTHO, which calculates the line shape by solving the stochastic Liouville equation for the case of rotational Brownian diffusion about one or more molecular axes. Input parameters required for the simulation are the principal components of the $g$ tensor, the spin-lattice, and spin–spin relaxation times, and three rotational correlation times corresponding to rotational diffusion about the principal axes of the $g$ tensor. The $g$-tensor components were taken from the spectrum measured at $-196\,^\circ\text{C}$, since the line shape did not change below this temperature: $g_{xx} = 2.0261$, $g_{yy} = 2.0099$, and $g_{zz} = 2.0042$. Values of $T_1 = 1.4 \times 10^{-5}$ s and $T_2 = 1.9 \times 10^{-7}$ s at $-196\,^\circ\text{C}$ were obtained by the method of progressive saturation, assuming an ideally inhomogeneously broadened line. These agree approximately with the values reported for $\text{O}_2^-$ on Vycor supported silver ($T_1 = 1.2 \times 10^{-5}$ s and $T_2 = 1.3 \times 10^{-8}$ s at $-196\,^\circ\text{C}$). Figure 7 shows a set of simulated spectra obtained using the above parameters, $\tau_x$ and $\tau_y$, values of $1 \times 10^{-7}$ s and varying values of $\tau_z$ (the correlation times for rotational diffusion about the $x$, $y$, and $z$ axes). As discussed below, the $y$ axis is that perpendicular to the O–O axis and to the surface. Decreasing the correlation time for rotation about the $y$ axis causes a progressive averaging of the $x$ and $z$ $g$-tensor components; in the fast motion limit a line shape characteristic of an axial $g$ tensor is obtained with $g_{||} = g_{yy}$ and $g_{\perp} = \frac{1}{2}(g_{xx} + g_{zz})$.

The changes illustrated in Fig. 7, in particular the averaging of the high and low-field $g$-tensor components, do reproduce some features of the observed temperature-dependent signals in Fig. 5. The simulated rigid-limit spectrum agrees moderately well with that observed at $-196\,^\circ\text{C}$, but the line shapes at higher temperatures differ markedly from those calculated in Fig. 7. The agreement between simulated and observed spectra could not be improved by varying the correlation times for rotation about the $x$ and $z$ axes; the observed increase in linewidth with increasing temperature could be reproduced however by allowing $T_3$ to vary. Figure 8 shows a set of calculated spectra in which the rotational correlation times are fixed and $T_3$ varied between the value measured experimentally at $-196\,^\circ\text{C}$ ($1.9 \times 10^{-7}$ s) and $8 \times 10^{-9}$ s.

**DISCUSSION**

**Identification of oxygen radicals**

The radical having $g$-tensor components $g_{xx} = 2.0261$, $g_{yy} = 2.0096$, and $g_{zz} = 2.0048$ is readily identified as $\text{O}_2^-$ from analysis of the $g$ and hyperfine tensors. The $g$-tensor components can be fitted to the theoretical values for $\text{O}_2^-$ derived by Kanzig and Cohen, taking the $z$ axis as the O–O bond and the $y$ axis as that perpendicular to the O–O bond and to the surface. The observed values are close to those reported for $\text{O}_2^-$ on W/SiO$_2$, one of the $\text{O}_2^-$ species on Ti/SiO$_2$, and for $\text{O}_2^-$ formed on $\gamma$-irradiated silica gel [Ref.
9 (Table 1)). The superimposed 6 and 11 line hyperfine patterns centered on \( g_{xx} \) observed with \(^{17}\)O enriched \( \text{O}_2 \) are completely consistent with an \( \text{O}_2^- \) radical containing equivalent oxygen atoms; the 11 line pattern is due to \(^{17}\text{O}^{16}\text{O}^-\) and the 6 line pattern to \(^{17}\text{O}^{17}\text{O}^-\). The absence of measurable splitting in the \( yy \) and \( zz \) components agrees with the small values for the \( A_{yy} \) and \( A_{zz} \) hyperfine tensor components found for \( \text{O}_2^- \) on the other surfaces.\(^1\) Decomposition of the hyperfine tensor in the usual manner leads to a calculated total spin density on the \( \text{O}_2^- \) of 0.99. A similar \(^{17}\text{O} \) hyperfine pattern (two equivalent oxygen atoms) is reported for \( \text{O}_2^- \) on \( \gamma \)-irradiated silica gel\(^1\) and \( W/\text{SiO}_2 \),\(^3\) although Freed et al.\(^4\) found that the oxygen atoms for \( \text{O}_2^- \) on \( \text{Ti}/\text{SiO}_2 \) are significantly inequivalent at 36 K.

The second oxygen radical which is the major species formed on silica gel surfaces outgassed at high temperature is more difficult to identify. The possibility of a second \( \text{O}_2^- \) species can be immediately dismissed, since the second signal has an axial \( g \) tensor with a \( g_\| \) value much less than that of any known \( \text{O}_2^- \) radicals. Likewise, the \( g \)-tensor components of the second radical are not close to those of any known \( \text{O}^- \) radical, and we could not form the second radical by adsorbing \( \text{N}_2\text{O} \) onto silica gel under irradiation (\( \text{N}_2\text{O} \) is the precursor most commonly employed for generating \( \text{O}^- \) on surfaces\(^1\)). A third possibility is the ozoneide radical \( \text{O}_2^- \). Irradiation of porous Vycor glass in \( \text{O}_2 \) was reported by Kubokawa et al.\(^15\) to give an ESR spectrum similar to that in Fig. 1(a) which was attributed to a mixture of \( \text{O}_2^- \) and \( \text{O}_2^- \).

The structure of the ozoneide radical on surfaces has been discussed in detail by Che and Tench.\(^1\) These authors distinguish between two types of surface \( \text{O}_2^- \) species: a so-called normal or classical ozoneide ion, which has ESR parameters similar to those of \( \text{O}_2^- \) in bulk crystals and consistent with a bent \( \text{AB}_2 \) radical, and an anomalous ozoneide radical whose structure is uncertain. Table II lists \( g \)-tensor components for both types of \( \text{O}_2^- \) species. The second oxygen radical observed in this work clearly belongs to the second category of \( \text{O}_2^- \), in that it has an axial \( g \) tensor with anisotropy much less than that expected for normal \( \text{O}_2^- \). The \(^{17}\text{O} \) hyperfine pattern [Fig. 4(b)] can be separated into a set of 6 lines and a set of 11 lines, with a splitting of \( \sim 72 \) G, although not all of the outer lines are detected. This hyperfine pattern indicating delocalization of the unpaired electron over two equivalent oxygen atoms (the 6- and 11-line patterns arising from singly and doubly labeled species, respectively) is closely similar to that reported for the anomalous \( \text{O}_2^- \) radical on silica supported vanadium\(^16\) (6- and 11-line patterns with a splitting of 78 G). Shelimov et al.\(^16\) suggested the anomalous \( \text{O}_2^- \) has a T-shaped structure

\[
\begin{align*}
V^{+5}&\text{O}^-| \\
&|\text{O}
\end{align*}
\]

although theoretical calculations do not support this model.\(^17\) and Che and Tench\(^1\) suggest that the exchanged coupled complex [\( \text{O}_2^-/\text{O}_2^- \)] should be considered as an alternative possibility. The present experiments with silica gel do not resolve this question further.

### Mechanism of photoformation

There is growing evidence for the existence of oxide ions in sites of low coordination on dehydroxylated metal oxide surfaces which can show unusual electron donor properties, in particular electron transfer to oxygen to form \( \text{O}_2^- \).\(^1\) Porous Vycor glass\(^18\) shows similar excitation and emission photoluminescence spectra to MgO,\(^19\) which have been assigned to charge-transfer transitions in low coordination surface sites. The photoluminescence of porous Vycor glass is quenched on exposure to \( \text{O}_2 \); Anpo et al.\(^19\) attribute this to the photoformation of \( \text{O}_2^- \).

### Table II. ESR parameters for selected \( \text{O}_2^- \) radicals.

<table>
<thead>
<tr>
<th>System*</th>
<th>( g_{xx} )</th>
<th>( g_{yy} )</th>
<th>( g_{zz} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal ( \text{O}_2^- )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>on MgO (Ref. 10)</td>
<td>2.002</td>
<td>2.0148</td>
<td>2.0121</td>
</tr>
<tr>
<td>(Ref. 11)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>on TiO(_2) (Ref. 12)</td>
<td>2.003</td>
<td>2.014</td>
<td>2.009</td>
</tr>
<tr>
<td>Anomalous ( \text{O}_2^- )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>on SiO(_2) (Ref. 13)</td>
<td>2.003</td>
<td>2.00345</td>
<td>2.008</td>
</tr>
<tr>
<td>on Vycor (Ref. 15)</td>
<td>2.0033</td>
<td>2.0033</td>
<td>2.0088</td>
</tr>
<tr>
<td>on Ti/SiO(_2) (Ref. 14)</td>
<td>2.001</td>
<td>2.001</td>
<td>2.0038</td>
</tr>
<tr>
<td>on TiO(_2) (Ref. 12)</td>
<td>2.001</td>
<td>2.001</td>
<td>2.008</td>
</tr>
<tr>
<td>on V/SiO(_2) (Ref. 16)</td>
<td>1.998</td>
<td>2.002</td>
<td>2.007</td>
</tr>
<tr>
<td>on SiO(_2) (this work)</td>
<td>2.003</td>
<td>2.003</td>
<td>2.0088</td>
</tr>
</tbody>
</table>

*See the text for distinction between normal and anomalous radicals.
Our observations of oxygen radical formation on irradiated silica gel are consistent with low coordination oxide ions being the surface sites responsible. On silica gel outgassed at 400 °C a relatively low concentration of such surface sites is present, and O$_2^-$ is the major oxygen radical formed ($6 \times 10^{16}$ g$^{-1}$); the formation of O$_2^-$ is envisaged to occur in the following way:

\[
O_{2C}^I + h\nu \rightarrow O_{2C}^- + e^-, \\
e^- + O_2 \rightarrow O_2^-.
\]

No EPR signal due to the trapped hole species O$_{2C}^-$ is detected, although this species ought to be paramagnetic. The formation of O$_2^-$ in small amounts can be attributed to the reaction on O$_2$ with the trapped hole

\[
O_{2C}^- + O_2 \rightarrow O_3^-.
\]

The subsequent removal of the O$_2^-$ signal on treatment with H$_2$ or CO is due to displacement of the relatively weakly bound O$_2$, e.g.,

\[
O_3^- + H_2 \rightarrow OH^- + O_2
\]

irradiation of silica gel in the presence of CO or H$_2$ has been shown to inhibit O$_3^-$ formation.\textsuperscript{13}

On silica gel outgassed at 800 °C the concentration of low coordination surface oxide ions will be much higher; the intensity of the photoluminescence attributed to these species on porous Vycor glass increases markedly with increasing outgassing temperature.\textsuperscript{18} There is a corresponding increase in the total concentration of oxygen radicals produced on irradiation in O$_2$, to $\sim 6 \times 10^{16}$ g$^{-1}$, and O$_2^-$ is the dominant species. The reaction between O$_2$ and O$_{2C}$ (trapped holes) to form O$_3^-$ is evidently more favorable on extensively outgassed surfaces than that with trapped electrons to form O$_2^-$ (although we cannot dismiss the possibility suggested by Iwamoto and Lunsford\textsuperscript{20} for MgO that O$_3^-$ is formed by photodissociation of O$_2^-$.)

**Motional dynamics of adsorbed O$_2^-$**

The ESR line shape of both $^{16}$O$_2^-$ and $^{17}$O$_2^-$ on silica gel did not vary significantly with temperature below $-96^\circ$ C, and the spectrum below $-96^\circ$ C consists of the powder pattern characteristic of a radical with an orthorhombic g tensor which is immobile on the ESR time scale. Above $-96^\circ$ C however the reversible changes in line shape and $^{17}$O hyperfine coupling indicate the onset of mobility. Rotational motion about any one of the principal axes of the g tensor will cause an averaging of the other two g tensor and $^{17}$O hyperfine tensor components (assuming coincidence of the g and hyperfine tensor axes). With the axis convention described above, rotation about the y axis will cause an averaging of $g_{xx}$ and $g_{zz}$, and $A_{xx}$ and $A_{yy}$. In the fast motion limit, axial g and hyperfine tensors are expected with $g_\| = g_{yy}$, $g_\perp = \frac{1}{2}(g_{xx} + g_{zz})$, $A_\perp = A_{yy}$ and $A_\| = \frac{1}{2}(A_{xx} + A_{zz})$; i.e., $g_\| = 2.0096$, $g_\perp = 2.0154$, $A_\| = 0$, and $A_\perp = 39$ G.

The observed spectral changes above $-96^\circ$ C are consistent with such rotation about the y axis causing partial averaging of the g and hyperfine tensors. The shift to higher field of the $g_{zz}$ component between $-96^\circ$ and $+25^\circ$ C follows that predicted in the simulated spectra (Fig. 7) for variation in the correlation time for rotation about the y axis between $5 \times 10^{-8}$ and $3 \times 10^{-9}$ s. The broadening of the central region of the spectrum observed experimentally is not accounted for in terms of motional averaging, but can be attributed to an increase in the spin–spin relaxation time $T_2$, as shown in Fig. 8. The concentrations of O$_2^-$ formed on silica gel correspond to a minimum average distance between adjacent O$_2^-$ radicals of 3500 Å; thus line broadening due to a static dipolar interaction can be eliminated. We suggest instead that the decrease in $T_2$ is due to an increase in spin–spin interactions between adjacent O$_2^-$ radicals which undergo translational diffusion across the silica surface. Such translation across the surface is accompanied by reorientation about the y axis, producing the observed effects.

The correlation times for rotational reorientation could be estimated by comparing the observed separation of the $g_{xx}$ and $g_{zz}$ components with those in spectra simulated for various values of the correlation time $\tau$. The correlation times obtained ranged from $2 \times 10^{-8}$ s at $-196^\circ$ C to $2.6 \times 10^{-9}$ s at $25^\circ$ C, and an Arrhenius plot of $\ln \tau$ vs $T^{-1}$ yielded an apparent activation energy of $2.4 \pm 0.8$ kJ mol$^{-1}$.

**Comparison with other systems**

The characteristics of the O$_2^-$ species generated on UV-irradiated silica gel are closely similar to those of the temperature-dependent O$_2^-$ reported by Freed et al.\textsuperscript{14} These authors considered in detail several alternative models for the rotational motion of adsorbed O$_2^-$ and concluded that anisotropic Brownian diffusion best explained the observed line shapes above 57 K, although at lower temperatures a jump diffusion model was preferred. The decrease in $T_2$ with increasing temperature noted above was also found for O$_2^-$ on Ti/Vycor. The correlation times for Brownian diffusion were reported to vary between $5 \times 10^{-8}$ s at 78.7 K and $6.3 \times 10^{-9}$ s at 263 K, and the estimated activation energy for rotational diffusion of 2.0 kJ mol$^{-1}$ agrees well with that obtained above. One point of difference between these two studies is the hyperfine splitting observed with $^{17}$O enriched O$_2^-$, Freed et al.\textsuperscript{4} show evidence (as a splitting in the outer components of the singly labeled species) for slight inequivalence of the two oxygen atoms, which was confirmed by careful simulation of the observed spectrum. No such splitting was observed in our case, although the $^{17}$O$_2^-$ spectrum was recorded at a significantly higher temperature ($-196^\circ$ C) than that described in Ref. 4, and the temperature dependence of the $^{17}$O hyperfine pattern is not commented on by Freed et al.

The O$_2^-$ signal observed from UV-irradiated silica gel is identical to that reported previously for O$_2^-$ on W/SiO$_2$.\textsuperscript{5} It should be noted that the g-tensor components were incorrectly assigned in the earlier work, leading to an incorrect identification of the axis about which rotational averaging occurs (the $^{17}$O hyperfine splitting for $^{17}$O$_2^-$ on W/SiO$_2$ was reported to be temperature invariant, but the hyperfine components had insufficient intensity above $-163^\circ$ C for the splitting to be accurately measured). Comparison of all three systems leads to the conclusion that the same mobile
TABLE III: Activation energies for surface diffusion.

<table>
<thead>
<tr>
<th>Adsorbed species</th>
<th>Surface</th>
<th>$E_a/(kJ\ mol^{-1})$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2^-$</td>
<td>SiO$_2$</td>
<td>2.4</td>
<td>this work</td>
</tr>
<tr>
<td>$O_2^-$</td>
<td>Ti/Vycor</td>
<td>2.0</td>
<td>4</td>
</tr>
<tr>
<td>$O_2^-$</td>
<td>Ag</td>
<td>24$^a$</td>
<td>2</td>
</tr>
<tr>
<td>$O_2^-$</td>
<td>Co(pc)/Al$_2$O$_3$</td>
<td>2.0</td>
<td>21</td>
</tr>
<tr>
<td>NO$_2^-$</td>
<td>Vycor</td>
<td>2.0</td>
<td>22</td>
</tr>
<tr>
<td>DBTN$^b$</td>
<td>SiO$_2$</td>
<td>7.6</td>
<td>23</td>
</tr>
<tr>
<td>$CO_2^-$</td>
<td>NaX$^c$</td>
<td>16.5</td>
<td>24</td>
</tr>
<tr>
<td>Cyclopentene radical cation</td>
<td>mordenite$^d$</td>
<td>5.6</td>
<td>25</td>
</tr>
<tr>
<td>Benzene radical cation</td>
<td>HY$^e$</td>
<td>9.2</td>
<td>26</td>
</tr>
</tbody>
</table>

$^a$ Calculated from data given in Ref. 2.
$^b$ pc = phthalocyaninato.
$^c$ DBTN = di-tertbutylnitroxide.
$^d$ Zeolites.

$O_2^-$ species is generated in each case, and that this species must therefore be associated with the SiO$_2$ (or Vycor) support and not the transition metal sites previously proposed.$^{3,4}$ The role of the transition metals (Ti or W) is evidently to assist in the electron transfer to $O_2$ responsible for $O_2^-$ formation. On W/SiO$_2$, UV irradiation is not required to produce $O_2^-$; spontaneous electron transfer from W cations is followed by migration onto the silica support. Freed et al. found that UV irradiation of Ti/Vycor was necessary to produce the mobile $O_2^-$ species, which was not formed on irradiation of Vycor alone. Band-gap irradiation of solid TiO$_2$ produces an adsorbed $O_2^-$ by reaction of $O_2$ with conduction band electrons which is not however mobile on the surface.$^1$ A similar mechanism for formation of $O_2^-$ can be proposed for the Ti/Vycor system, except that some $O_2^-$ migrates to the support (Freed et al. observed other $O_2^-$ species which showed no mobility and presumably remain located on titanium sites). On silica gel, the adsorption sites for $O_2^-$ are believed to be low coordination surface oxide ions, as discussed above.

The activation energy for rotational diffusion of $O_2^-$ on silica gel is comparable in magnitude with values reported for other adsorbed species, as shown in Table III. (The internal pore structures of zeolites are expected to restrict mobility to a greater extent, as is observed.) The high value of 24 $kJ\ mol^{-1}$ estimated for $O_2^-$ on Vycor supported Ag probably reflects a specific interaction of $O_2^-$ with Ag$^+$ cations; in this system the correlation times for surface diffusion are up to six orders of magnitude longer than on silica.

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