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The Electronic Nature of Paramagnetic Oxygen Species Combined with Metal Ions at Surface and in Solution

Morio SETAKA and Takao KWAN

Faculty of Pharmaceutical Sciences, The University of Tokyo, Bunkyo-ku, Tokyo

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ESR spectra of adsorbed oxygen species were investigated on cadmium, cerium and uranium oxides supported on alumina. The principal g values, g_x, g_y and g_z of the oxygen species were computed and compared with those on the other metal oxides. It was pointed out that the principal g values observed on cerium and uranium oxides are interpretable by a peroxy-like model rather than an O_2^- radical. ESR spectra due to radicals formed on mixing solutions of VO^{2+} or UO_2^{2+} (containing Ti^{3+}) with H_2O_2 were also investigated by a rapid-mixing flow technique. The g value of the radicals was very close to the isotropic one of the peroxy-like species adsorbed on the corresponding metal oxide. The electronic nature of the interaction of oxygen species with metal ions at surface and with those in solution was comparatively discussed.

ESR spectra of adsorbed oxygen species on various metal oxides[1–11] have been reported by many workers. These spectra were asymmetric and characterized generally with three different principal g values near 2.0, which varied from one metal oxide to the other. The observed shifts in the principal g values have been discussed in terms of an adsorbed O_2^- model; effect of the electric charge of the constituent metal ion of the oxides on the O_2^- radical was taken into consideration.[3,6] According to Kasai[12] who had studied ESR spectra of γ-irradiated zeolites in the presence of oxygen, the principal g values of the O_2^- radical were strongly dependent on the electric charge associated with the zeolite cation (Na^+ or Ba^{2+}).

The shift of the principal g values has been recognized also by us[8] with respect to the O_2^- radical adsorbed on ZnO, TiO_2 and ZrO_2. It was felt worthwhile, therefore, to extend this sort of study to metal oxides having different electric charges of the constituent metal ion. Thus, in the present paper, special interest will be placed on the ESR of oxygen species adsorbed on metal oxides of higher valencies *e.g.* CeO_2 and UO_3.

Literature shows that a mixture of metal ion and H_2O_2 produces an ESR signal near the g value of 2.0. We have already reported[13] that a mixture of $VOSO_4$ and H_2O_2 yields an ESR signal near $g=2.0$ characterized with eight hyperfine lines due to vanadium nucleus ($I=7/2$) and that the signal is attributable to a *complex* hydroperoxy radical. The observed resemblance in the g values between the complex peroxy-like species in solutions[13] and the oxygen species adsorbed on the surface of V_2O_5[9] is worthy of note. Since the nature of the hydroperoxy or peroxy-like species often observable in solutions of metal ion and H_2O_2 is still unknown, it would be pertinent to investigate ESR spectra of such solutions with particular interest in the valencies of metal ions and to compare the g value of generated radicals with that of adsorbed oxygen species on the corresponding metal oxide. Thus in the present work, solutions containing metal ions such as Ti^{3+}, VO^{2+} and UO_2^{2+} mixed with H_2O_2 were also subjected to ESR studies by using a rapid-mixing flow technique.

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Experimental

Preliminary investigations indicated that the metal oxide such as CeO_2 or UO_3 gives only a weak ESR signal due to adsorbed oxygen species. Moreover the oxides became rather metallic, when outgassed at or above 500°C, leading to a decrease in the sensitivity of the cavity. Therefore, in the present work, we used Al_2O_3 as the support, and the supported Ce or U oxide sample (denoted as the Ce or U sample) was studied after appropriate pretreatment. The valency state of the cerium or uranium ion in the sample should therefore be regarded as indefinite. CdO was also investigated as an example of metal oxide having a lower valency.

A sample of Al_2O_3 powder (standardized, E. Merck AG) was impregnated with an aqueous solution of cadmium nitrate (guaranteed, Koso Chemical Co.), ceric ammonium nitrate (guaranteed, Wako Pure Chemical Co.) and uranyl nitrate (standardized, E. Merck AG), respectively. The samples were then dried at 100°C and calcined in a stream of oxygen (760 Torr) for four hours at 500°C except for the Cd sample which was pretreated below 400°C. The amount of added salts was so controlled that the metal ions were 5 wt% of the Al_2O_3. The calcined samples were white (Cd sample), pale yellow (Ce sample) and reddish brown (U sample).

A given amount of each sample was placed in individual quartz tubes (4 mm dia.). The Cd sample was evacuated for thirty minutes at 400°C and heated in a hydrogen atmosphere (50 Torr) for one hour at 300°C and then evacuated for another hour at the same temperature. When the sample was treated with hydrogen at temperatures higher than 300°C, cadmium sublimed and condensed in a metallic state on the wall of the sample tube. The Ce and U samples were evacuated for thirty minutes at 500°C and treated with 50 Torr of hydrogen for one hour and evacuated for another hour at the same temperature. The color was greyish white for the Cd sample and greyish brown for the Ce and U samples.

A capillary tube containing MgO powder dispersed thermally with Mn^{2+} ion was inserted into the center of the sample as a means of measuring relative ESR sensitivity. The g values were calculated on the basis of the g value ($g=2.0036$) of DPPH. Signal simulation of the sample was made with a computer (Hitachi, HITAC 5020) to confirm the obtained g-values. ESR measurements were carried out at room temperature with a JEOL P-10 spectrometer (X band, 100 kcps field modulation).

A rapid-mixing flow technique coupled with ESR was utilized to detect peroxy-like species formed on mixing solutions of Ti^{3+}, VO^{2+} or $UO_2{}^{2+}$ with H_2O_2. The experimental procedures were nearly the same as those reported earlier.[13)]

Results

1. Supported Oxides. So far we have observed ESR spectra of adsorbed oxygen species on a number of metal oxides with or without support.[8)] For TiO_2 and SnO_2 supported on Al_2O_3, ESR spectra due to adsorbed oxygen species were essentially the same as those reported for the unsupported oxides.[7,8)] On the metal oxide such as MoO_3, it was difficult to distinguish the signal of adsorbed oxygen species from that due to molybdenium ion. Thus we confined ourselves to investigating the Cd, Ce and U samples, which exhibited distinct ESR signals due to adsorbed oxygen species as will be shown later.

No ESR signal was detectable at least in the magnetic field investigated ($g=1.8$—2.2) with the Cd and U samples outgassed in a high vacuum at room temperature. Neither heat treatment in a high vacuum nor hydrogen pretreatment resulted in ESR signals. However, when 50 Torr of oxygen was introduced to the pretreated Cd and U samples at room temperature, followed by slight outgassing, ESR signals as shown in Figs. 1 and 2 were obtained. For the Ce sample, a very small signal consisting of six resonance lines was detected

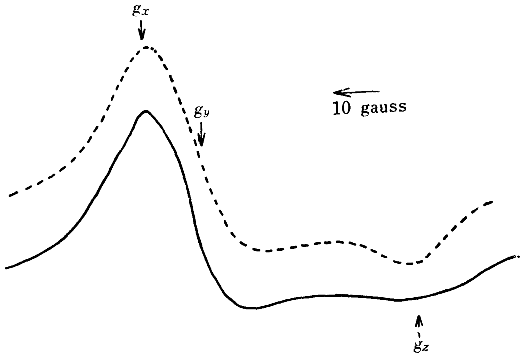

Fig. 1. ESR(X-band) spectrum of adsorbed oxygen species on a pretreated CdO-Al_2O_3 sample. Dotted curve: simulated

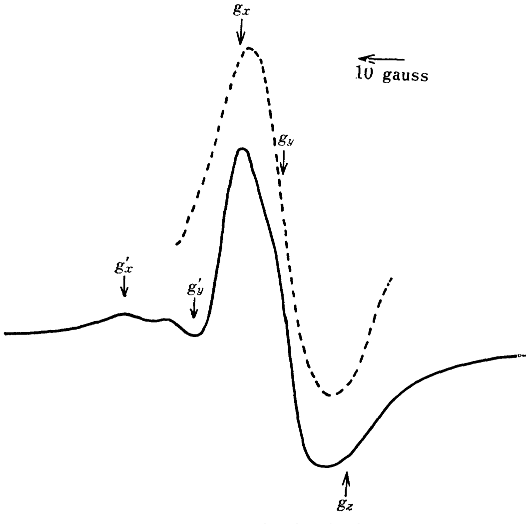

Fig. 2. ESR spectrum of adsorbed oxygen species on a pretreated UO_3-Al_2O_3 sample.
Dotted curve: simulated
g_x, g_y and g_z: g values for the major signal
g_x' and g_y': g values for the minor signal

for both untreated and pretreated samples. It was attributed to manganese impurities. The Ce sample showed, after a similar oxygen pretreatment, a large signal which overlapped the signal of manganese impurities. The manganese signal was so small compared with the major signal due to adsorbed oxygen species (1/300) that it could be neglected as shown in Fig. 3. The Al_2O_3 support itself gave no ESR signal even after pretreatment.

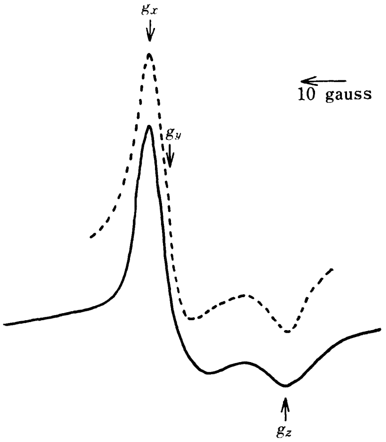

Fig. 3. ESR spectrum of adsorbed oxygen species on a pretreated CdO-Al_2O_3 sample.
Dotted curve: simulated

The ESR signals shown in Figs. 1, 2 and 3 were completely broadened by exposure to air. They were restored, however, by slight outgassing at room temperature. This phenomenon suggests that the signals are due to the surface paramagnetic species. When 50 Torr of NO was introduced onto the samples showing these signals, they disappeared in an irreversible manner. A chemical reaction probably had occurred between the paramagnetic species and NO. Although cerium and uranium ions of some lower valencies are indeed paramagnetic and hence may exhibit ESR signals, the observed *g* values are apparently different from those of the reported spectra.[14] Consequently, the ESR signals of Figs. 1, 2 and 3 should be regarded as due to adsorbed oxygen species.

In the case of the U sample, the major signal (g_x, g_y, g_z) appeared to overlap the minor one (g_x', g_y'). The two signals behaved quite similarly with respect to exposure to air or NO. It seems likely that there are two kinds of adsorped oxygen species on the surface.

It was rather difficult to obtain accurate ESR parameters directly from the maximum or the inflection point of the first derivative curve. The situation became more serious especially when the half width (ΔH) between the maximum slope of the derivative of the absorption line was large. Thus, signal simulation was carried out with a computer on the basis of the theoretical equation of the line shape given by Kneübuhl[15] for a polycrystalline sample having three principal *g* values.

The computed curves (dotted lines) are compared with the experimental curves (solid lines) in Figs. 1, 2 and 3. Agreement of both curves was rather poor with the U sample where two signals overlapped. The ESR spectrum of the O_2^- radical on ZrO_2[8] is reproduced in Fig. 4 where the signal simulation was similarly carried out and the *g* values were computed.

In Table 1, the principal *g* values reported for adsorbed oxygen species on various metal oxides

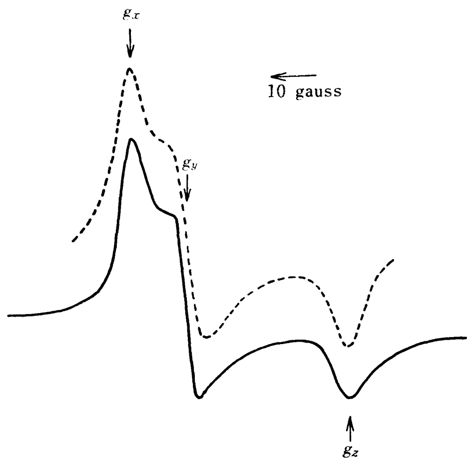

Fig. 4. ESR spectrum of adsorbed oxygen species on a pretreated ZrO_2 sample.

TABLE 1. THE PRINCIPAL *g* VALUES FOR PARAMAGNETIC OXYGEN SPECIES ADSORBED ON VARIOUS METAL OXIDES

Metal oxide	g_z	g_y	g_x	K[a]	Ref.
UV irrad. MgO	2.077	2.0073	2.0011	27	3
ZnO	2.051	2.0082	2.0020	41	3
TiO	2.024	2.009	2.003	92	6
SnO_2	2.028	2.009	2.002	78	7
V_2O_5-SiO_2	2.025	2.011	2.005	88	9
Vycor glass	2.030	2.014	2.002	72	5
ZrO_2	2.032	2.010	2.002	67	8
CdO-Al_2O_3	2.039	2.009	2.002	55	
CeO_2-Al_2O_3	2.030	2.014	2.011		
UO_3-Al_2O_3	2.035	2.025	2.018		
	—	2.012	2.003[b]		

a) $K \equiv 2/(g_z - g_e)$.
b) *g* Values for the minor signal of adsorbed oxygen radical.

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were listed in addition to those on the Cd, Ce and U samples determined in the present work.

2. Solutions. The rapid-mixing flow technique was applied to $UO_2(NO_3)_2$-H_2O_2 similarly as in the case of $VOSO_4$-H_2O_2 system.[13] Since UO_2^{2+} does not act as electron donor, a very small amount of Ti^{3+} we added to the mixing solution in advance. In other words, we expected that UO_2^{2+} would capture peroxy-like species produced by Ti^{3+}–H_2O_2. As a result, the Ti^{3+}–UO_2^{2+}–H_2O_2 system yielded a signal of the g value of 2.023 entirely different from that due to Ti^{3+}–H_2O_2. It is suggested that the $g=2.023$ signal is atrributed to a peroxy-like species combined with UO_2^{2+}.

ESR spectra of a mixture of Fe^{2+}–H_2O_2 or Ti^{3+}–H_2O_2 with organic additives have been the subject of many investigations. Nevertheless, the signal near $g=2.9$ observable for Ti^{3+}–H_2O_2 has not been well identified[16–18] while the nature of organic radicals produced was extensively worked out for both systems. We were able to show an ESR signal near $g=2.0$ for a $VOSO_4$-H_2O_2 system in sulfuric iacid by utilizing a rapid-mixing flow technique.[13] The g value of the signal was found to be 2.0016, and the signal was characterized with eight hyperfine resonance lines due to vanadium nucleus ($I=7/2$). On the basis of these findings, we have proposed that the signal is due to a HO_2 radical complexed with VO^{3+}. Ti^{3+} or Ce^{4+} is reported to give an ESR signal having g values of 2.01195, 2.1335 or 2.016[19] when mixed with H_2O_2 while no such signal is reported for Fe^{2+}–H_2O_2.[20] In the second column of Table 2, the reported g values of the signal observed for various metal ion–H_2O_2 systems are listed together with that of the Ti^{3+}–UO_2^{2+}–H_2O_2 system. In Table 2 are shown the isotropic g values for the oxygen radical adsorbed on the corresponding metal oxides for comparions. It is rather surprising to see that the g values of the peroxy-like species produced from a mixture of metal ions and H_2O_2 is nearly the same as that of the radical adsorbed on the corresponding metal oxide.

Discussion

It can be seen from Table 1 that g_z is, in general, larger than the g value of a free spin ($g_e=2.0023$), while g_x remains nearly constant around g_e. The principal g values of the O_2^- ion trapped in the lattice of alkali halide have been formulated by Kanzig and Cohen.[21] This approach was applied here to the study of the adsorbed O_2^- radical. The ground-state electronic configuration of O_2^- is $(\sigma_g\ 2P)^2(\pi_u\ 2P)^4(\pi_g{}^*\ 2P)^3$. When O_2^- is adsorbed and exposed to the asymmetric surface field of the metal oxide, the originally degenerated $\pi_g{}^*$ orbitals are expected to split into two orbitals, $\pi_g{}^*$ $(2P_x)$ and $\pi_g{}^*$ $(2P_y)$, as shown schematically in Fig. 5. The three principal g values are then given by

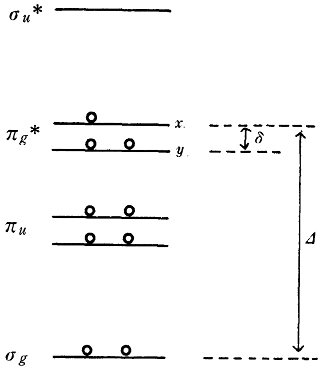

Fig. 5. Electronic energy levels of O_2^- after Kasai (Ref. 12).

$$g_x = \frac{g_e\delta}{(\delta^2+\lambda^2)^{1/2}} + \frac{\lambda}{\Delta}\left[\frac{\delta+\lambda}{(\delta^2+\lambda^2)^{1/2}} - 1\right]$$
$$\simeq g_e - \frac{\lambda^2}{\delta^2} + \frac{\lambda^2}{\Delta\delta} \tag{1}$$

TABLE 2. THE ISOTROPIC g VALUES FOR PARAMAGNETIC OXYGEN SPECIES COMBINED TO METAL IONS AT SURFACE AND IN SOLUTION

Metal ion-H_2O_2	g_{iso}	Metal oxide-O_2	g_{iso}	Ref.
Ti^{3+}-H_2O_2	2.01195 2.01335	TiO_2-O_2	2.011 (O^-) 2.012 (O_2^-)	15, 16, 17
VO^{2+}-H_2O_2	2.0116	V_2O_5-O_2	2.0137	13
Ce^{4+}-H_2O_2	2.016	CeO_2-O_2	2.018	18
UO_2^{2+}-H_2O_2 containing Ti^{3+}	2.023	UO_3-O_2	2.026	

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$$g_y = \frac{g_e\delta}{(\delta^2+\lambda^2)^{1/2}} - \frac{\lambda}{\Delta}\left[\frac{\delta-\lambda}{(\delta^2+\lambda^2)^{1/2}}+1\right]$$

$$\simeq g_e + \frac{2\lambda}{\Delta} - \frac{\lambda^2}{\delta^2} - \frac{\lambda^2}{\Delta\delta} \qquad (2)$$

$$g_z = g_e + \frac{2\lambda}{(\delta^2+\lambda^2)^{1/2}} \simeq g_e + \frac{2\lambda}{\delta} \qquad (3)$$

where, z is chosen along the internuclear axis of O_2^-, δ and Δ are the energy separations shown in Fig. 5. λ is the spin-orbit coupling constant for O_2^-. Approximate equations are useful when $\Delta > \delta \gg \lambda$.

As shown from the approximate equations, the principal g value, which deviates farthest from g_e, should be assigned to g_z, while g_x should be closest to and slightly below g_e. The obtained data except for the Ce and U samples are well explained by such an O_2^- radical model. The effect of a trapping site, which gives rise to the energy separation (δ) of the two $\pi_g{}^*$ orbitals, is well reflected in the deviations in g_z values. The value, $K=2/(g_z-g_e)\simeq\delta/\lambda$ was calculated as a possible measure of the interaction of O_2^- with a cation. The results are shown also in Table 1 together with some results of K given by the other workers.[3,6] The K value is expected to increase when the interaction energy between the O_2^- radical and the trapping site increases.

The sequence of this effect, according to Table 1, is given by

$TiO_2 > V_2O_5/SiO_2 > SnO_2 >$ Vycor glass $>$
$ZrO_2 > CdO > ZnO > MgO$

It should be recognized, however, in view of the uncertainty in the g values and also in the approximation used in the theory that the sequence is only qualitative. Nevertheless, it may be inferred from the above sequence that the O_2^- radical is bound more strongly on oxides with cations of higher valencies.

The important role of metal cations for the adsorption of oxygen has already been pointed out by Schvets *et al.*[9] as well as by Kasai.[12] In this connection, mention should be made of the fact that the g_x values (2.011, 2.018) obtained for the Ce and U samples are considerably larger than that of a free spin. The fact suggests that the positive electric charge of Ce and U ions is large enough to interact with the O_2^- radical so that the O_2^- radical model is no longer applicable to these oxides. Probably, a peroxy-like model would be adequate.

Let us review the ESR spectra of hydroperoxy radical trapped in organic or inorganic matrices, since the principal g values of the spectra are known to be similar to those of the O_2^- radical adsorbed on the metal oxides. For example, $g_1=2.0495$, $g_2=2.0081$, $g_3=2.0018$ and $g_1=2.0353$, $g_2=2.0086$, $g_3=2.0042$ have been reported for HO_2 radicals generated in a γ-irradiated single crystal of H_2O_2-$CO(NH_2)_2$ and in a γ-irradiated H_2O_2-water matrix at 77°K, respectively.[22,23] Such O_2^--like spectra could be anticipated, if the unpaired electron, in the π * orbital, is affected by the field of the proton,[24] and moreover if the unpaired electron is located on the unprotonated oxygen.

The ESR of the organic peroxy radicals has been summarized by Bersohn and Thomas.[25] Accordingly, the g values differs slightly but significantly from one organic peroxy radical to another. For example, the principal g values ($g_1=2.0267$, $g_2=2.0193$, $g_3=2.102$) have been reported by Lontz[26] to an organic peroxy radical, $CF_3CF(\text{-}OO\cdot)CONH_2$, generated on a γ-irradiated single crystal of $CF_3CF_2CONH_2$. It is interesting to note that the observed g values are not much different from those of the oxygen species adsorbed on the supported Ce and U samples.

It can be seen from Table 2 that any metal ion that gives rise to an ESR signal of the complexed radical in a mixed solution with H_2O_2 also produce an ESR signal due to adsorbed oxygen on its oxide surface and that the g shifts are parallel at surfaces and in solutions. The phenomena led us to presume that the electronic nature of paramagnetic oxygen species combined with metal ion at surface is similar to that in solution.

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