The ESR Study of the Interaction of O_2 with Ag Dispersed on Silica Gel

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The state of adsorbed oxygen on metallic silver dispersed on silica gel has been studied by ESR. The spectra observed by the interaction of oxygen and the surface were found to be composed of spectra due to two different species. One of the species, which was formed separately by the contact with oxygen at −110 °C, was identified with O_2^- chemisorbed on metallic silver by a comparison of the observed g values and the other features with those previously reported. The other species has a doublet at $g=2.036$. This spectrum was reproduced by the interaction of N_2O with the silver surface. Further, the γ-irradiation of the silver samples in the presence of O_2 and N_2O markedly enhanced the intensity of this spectrum, showing a low-field hump. On the basis of the g values and the splitting of the high-field doublet, assuming that the doublet is due to the hyperfine interaction of an unpaired electron with the silver nucleus, the species was assigned to Ag^{2+} in the present system. It is postulated that this species is possibly formed by the dissociative and/or charge-transfer chemisorption of O_2 and N_2O, suggesting the presence of non-paramagnetic oxygen species, such as O^{2-}, as a counter ion of Ag^{2+}.

It is of importance to investigate the nature of adsorbed oxygen on silver because of its interesting behavior in the catalytic oxidation of ethylene. Recently Clarkson and Cilliro[1] have reported the ESR observation of O_2^- chemisorbed on a metallic silver surface supported by Vycor glass, together with the reactivity of the O_2^- with CO. However, the nature of the adsorbed states of oxygen has not yet been satisfactorily elucidated, since various forms of adsorbed oxygen have been suggested to be present on the silver surface.[2-5] The work of the present paper was initiated to investigate the catalytic activity of metallic silver in the oxidation of olefins by means of electron spin resonance spectroscopy (ESR).

In the present study we found ESR evidence for the presence of two kinds of oxygen species adsorbed on metallic silver dispersed on silica gel; we then incorporated our results with those of experiments with the γ-irradiation of the silica gel samples.

On the other hand, the ESR spectra of γ-irradiated silica gel and the effects of some additives have been reported previously.[6-9] However, no ESR study of the effects of metallic adsorbates on the irradiation has yet been reported despite the relevance to radiation chemistry.[10,11] In the present paper we will also report on the effects of γ-irradiation on the ESR spectra.

Experimental

Silica gel was prepared by the hydrolysis of ethyl orthosilicate, followed by drying at 110 °C and heating at 450 °C in air. Ethyl orthosilicate was distilled several times before the hydrolysis. Silver was impregnated on silica gel from the solution of silver nitrate, followed by drying and heating as above. The concentrations of silver were in the range of 0.5—6.0 wt%. The samples were reduced with hydrogen of 40 Torr at 100 °C and then at 300 °C for 2 hours in each case. High-purity gases of H_2, O_2 and N_2O from the Takachiho Chemical Co. were used without further purification.

γ-Irradiation was carried out by exposure to ^{60}Co at room temperature. The dose was 1—2 Mrads. The ESR measurements were made by means of a JEOL JES-3BS-X spectrometer with 100 kHz modulation. All the spectra were recorded at −110 °C.

Results and Discussion

Figure 1 (a) shows the spectrum (A) ($g=1.98$, $\Delta H=175\pm5$G) observed in the sample of the dispersed silver (2 wt%) on the silica gel after reduction. The intensity of this signal increased with the amount of silver. As has been suggested by Nicolau *et al.*,[12] who observed the spectra in the systems of Pt and Pd supported on charcoal, this signal (A) may be attributed to the unpaired electron produced by the strong interaction of the silver with the silica gel surface.

When the silver samples were exposed to oxygen of 5 Torr at 26 °C, new spectra were observed, as is shown in Fig. 1 (b). By heating the samples to 200 °C, the spectra were changed; particularly, the lower-field shoulder increased and became distinct (Fig. 1 (c)). Therefore, the signal is possibly composed of spectra due to two different species. This was further confirmed by the following experiments. When oxygen came into contact with the silver samples at −110 °C and the spectra were recorded at the same temperature, only the B signal was observed as a new signal (Fig. 2 (a)). The lower-field pattern in Fig. 1 (c) was reproduced when the silver samples were exposed to N_2O (110 Torr) at room temperature for about 60 hours, as is shown in Fig. 2 (b).

From these results, it was concluded that the spectra in Figs. 1 (b) and (c) consist of three signals, A, B, and

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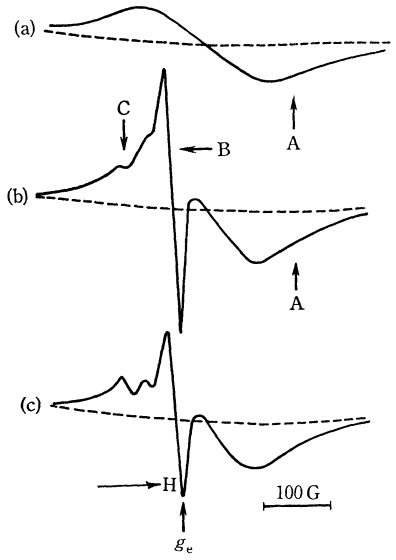

Fig. 1. Electron spin resonance spectra obtained after a) reduction of Ag dispersed silica gel, b) exposure of the Ag–SiO_2 to oxygen (5 Torr) at 26 °C, and c) heating at 200 °C in the presence of oxygen. All spectra were recorded at −110 °C. The broken line shows the signal from silica gel treated under the same conditions as the Ag–SiO_2 samples. g_e indicates the resonance field of free electron.

C. By evacuation at room temperature, the B signal decreased in its intensity, but after heating at 200 °C in the presence of oxygen the B signal became independent of the evacuation. The contact of O_2 and N_2O with the silica gel did not give any spectra of the surface species under the same conditions as those described for the silver samples.

The g tensors for oxygen species adsorbed on various surfaces have been reported.[13-14] According to the recent report by Clarkson and Cilliro,[1] the spectrum observed in the system of O_2–Ag supported on Vycor glass has been identified with that of O_2^-. The g values estimated from the B spectrum, which was obtained by subtracting the A and C signals from the observed spectra, were $g_{xx}=2.002\pm0.001$, $g_{yy}=2.010\pm0.001$, and $g_{zz}=2.040\pm0.005$. These g values, though they have some experimental error, are only reasonable for O_2^- as the oxygen species, and they are comparable to those reported by Setaka and Kwan.[14] Therefore, the B spectrum can be identified with that of O_2^-.

In order to obtain a definite assignment of these spectra, the γ-irradiations of silica gel and the silver samples were carried out. In the irradiations of the silver samples, the signals due to the paramagnetic centers formed by the irradiation, as is shown in Fig. 3, were observed in addition to the broad signal, A. The spectra were composed of a sharp and intense single line near $g=2.001$ and a number of lines due to other centers.

These spectra were essentially the same as those reported by Kazanskii *et al.*,[7] though the resolution and the relative intensity of each component were different. As may clearly be seen in Fig. 3, the spectra obtained by reducing the field modulation showed a number of lines which could not simply be identified, as has been done by Kazanskii *et al.*, with the center that couples with four equivalent protons on the surface. In the irradiation of silica gel itself, unlike the case with silver samples, the lines due to the surface centers were relatively intense compared to the sharp line. It has been suggested[7] that the sharp line can be assigned to the spectrum of the trapped electron in the bulk. Therefore, the fact that the relative intensity of the sharp line to the surface centers was larger in the irradiated silver samples than in the irradiated silica gel may suggest that the formation of the surface centers by the irradiation is hindered by the surface silver metal.

When the silver samples were irradiated in the presence of O_2 (5 Torr), in addition to the signals in Fig. 3 the B and C signals were observed with an increased intensity compared with those observed before the

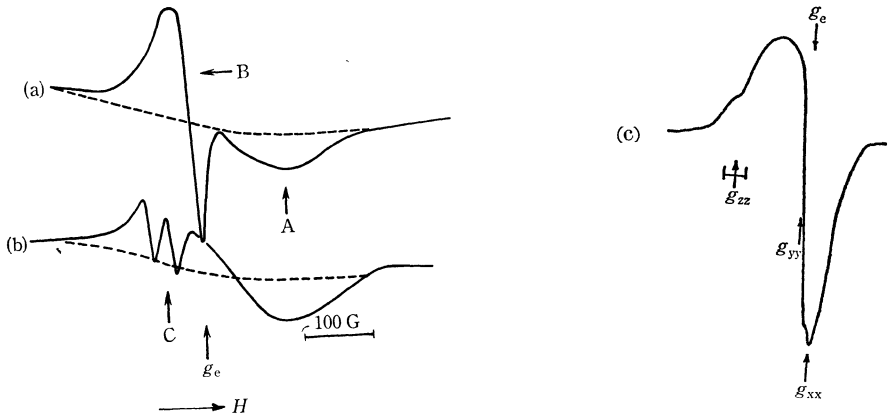

Fig. 2. Electron spin resonance spectra obtained after exposure of the Ag–SiO_2 samples to a) oxygen (5 Torr) at −110 °C, and b) nitrous oxide (110 Torr) at 26 °C for 60 hours. The spectra were recorded at −110 °C.
c) The spectrum obtained by subtracting the spectrum A from (a) in order to estimate the g- values of the spectrum B.

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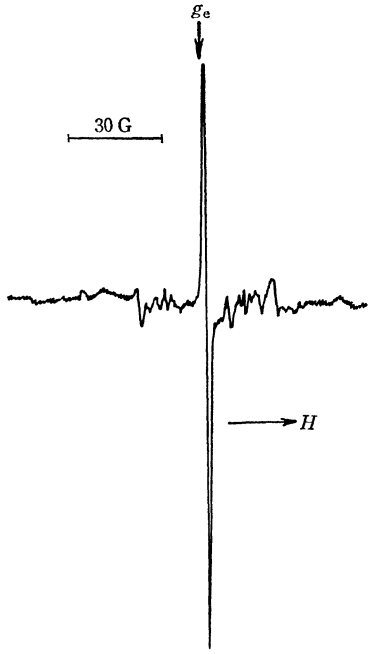

Fig. 3. Electron spin resonance spectrum obtained after γ-irradiation of the Ag–SiO_2 samples at 26 °C, and recorded at −110 °C.

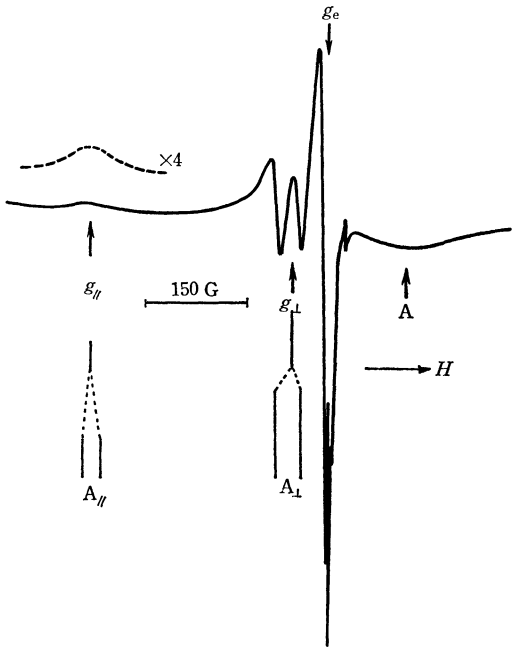

Fig. 4. Electron spin resonance spectrum obtained after γ-irradiation of the Ag–SiO_2 sample at 26 °C in the presence of O_2. The stick diagram indicates our assignment for the g and A of Ag^{2+}. The broken line at extremity corresponds to a signal amplification of 4.0. $g_\perp$ and $g_{//}$ corresponds to the resonance fields of the perpendicular and parallel components. $A_\perp$ and $A_{//}$ are the hfs of silver nucleus in perpendicular and parallel components. The value from reference (16) is used for $A_{//}$.

irradiation. The intensity of the sharp signal decreased in the presence of O_2. This is, possibly, a result of the interaction between the electron trapped in the center and oxygen, this interaction forming O_2^-.[7] The spectra are given in Fig. 4. The γ-irradiation of

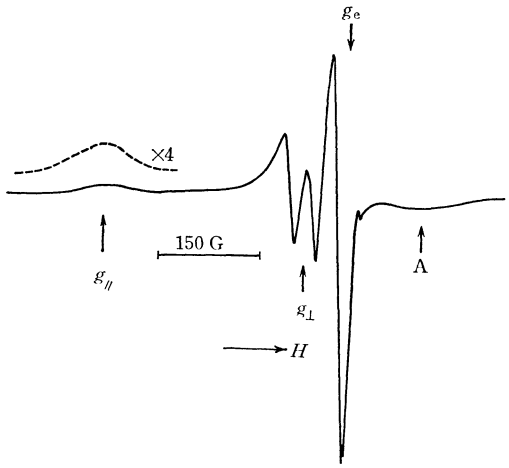

Fig. 5. Electron spin resonance spectrum obtained after γ-irradiation of the Ag–SiO_2 in the presence of nitrous oxide at 26 °C, and recorded at −110 °C.

the silver samples in the presence of N_2O (300 Torr) provided spectra almost identical with those obtained in the presence of O_2, as is shown in Fig. 5, though the intensity of B relative to C was slightly different.

The irradiation of the silica gel in the presence of O_2 and N_2O was also examined. A signal with a broad linewidth was observed upon the irradiation in the presence of O_2. The signal was similar to the B signal and has been assigned to the surface peroxide on silica gel[7] by Kazanskii. The irradiation of the silica gel with N_2O did not give the broad line, unlike the results of the irradiation of the silver samples. Further, it was found that the intensity of the surface peroxide was decreased to about 55% by warming the samples from −110 °C to 25 °C, while that of the B signal was decreased to about 35%. Therefore, the spectra obtained in the irradiation of the silver samples with O_2 and N_2O are not likely to be the surface peroxide on the silica gel, though the simultaneous formation of the surface peroxide can not be excluded in the irradiation of the silver sample with O_2. Consequently, the formation of O_2^- on the surface of the silver samples is the result of the interaction of O_2 not with silica gel, but with the metallic silver dispersed on silica gel.

In the identification of the C signal, assuming that the low-field hump, which becomes distinct by γ-irradiation, shows the parallel component of C, and that the doublet at g=2.036 is due to the hyperfine splitting, the magnetic parameters of this signal were

Table 1. ESR parameters for Ag^{2+}

$A_\perp$ (G)	32±1	—	31.6
$A_{//}$ (G)	—	25±3	48.0
$g_\perp$	2.036	—	2.065
$g_{//}$	2.249	2.233	2.265
Reference	This work	16)	15)[a]

a) The values were obtained from the spectra of Ag^{2+} formed in frozen acid solution at 77 K.

estimated to be as listed in Table 1. This was further confirmed by the fact that the intensity ratios of the high-field doublet to the low-field hump were constant in different experimental run with a variety of dosages. Since these values are almost equivalent with those of Ag^{2+} which have been reported by McMillan and Smaller,[15] the C signal can be identified with that of Ag^{2+} in the present system, though the poor resolution of the spectrum made it difficult to measure the splitting in the parallel component. More recently, Starkie and Symons[16] have reported their observation of Ag^{2+} trapped on silica gel formed by the γ-irradiation of the silica gel samples, which were integrated with an alcoholic solution of silver nitrate. The spectra of Ag^{2+} were only obtained in samples which had been dried for a long time *in vacuo*, while the irradiation of the wet samples provided the spectra of atomic silver. The magnetic parameters reported are also listed in Table 1.

The observation of Ag^{2+} in the present system suggests that there is a particular state of adsorbed oxygen which stabilizes Ag^{2+} by abstracting electrons from Ag. In the case of N_2O adsorption without the irradiation, though Ag^{2+} was obtained, the spectrum of O_2^- was not observed. Therefore, Ag^{2+} may be formed by the interaction with the electron-accepting species such as O_2 and N_2O, forming non-paramagnetic oxygen species such as O^{2-} as a counter ion of Ag^{2+}.

The observation of the O_2^- spectrum in the irradiation of the N_2O-silver sample can be explained if one takes into consideration the possibility that the molecular oxygen is produced by the catalytic[17] or radiolytic decomposition of N_2O by the irradiation on the silver surface.

In addition, the reactivity with ethylene of these oxygen species adsorbed on the silver surface was examined. The results obtained preliminarily showed that, when ethylene (5 Torr) was added to the silver samples, showing the B and C spectra, at 200 °C for 4 hours, the C spectrum was gradually decreased and the B spectrum disappeared. From the present results, it is not sufficient to conclude the participation of those oxygen species in the epoxidation reaction of ethylene. However, it is evident that the species identified with O_2^-, and Ag^{2+}, which was possibly formed accompanied by non-paramagnetic oxygen species, can react with ethylene.

In the present experiments we have for the first time observed Ag^{2+}, which may be formed by the interaction of metallic silver with such electron-accepting species as O_2 and N_2O. As a counter ion of Ag^{2+}, we postulated the presence of non-paramagnetic species such as O^{2-} [2] which may be formed by the dissociative adsorption of O_2 and N_2O. The presence of O_2^- on the surface of metallic silver was confirmed.

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