ESR Studies of Oxygen, Sulfur Oxide, and Sulfur Radicals Adsorbed on NaX Zeolite

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The states of O_2 and SO_2 adsorbed on NaX zeolite were investigated by means of ESR. No oxygen anion radicals were formed thermally on NaX up to 773 K. The adsorption of O_2 on γ-irradiated NaX in a vacuum, however, resulted in an ESR spectrum due to O_2^-. Several kinds of O_2^- species and O_3^- were found to be formed on NaX by γ-irradiation in the presence of O_2. These oxygen anion radicals showed different reactivities with N_2O, ethylene and propylene, and transferred electrons to SO_2 to form SO_2^-. The SO_2^- radical was also produced on NaX by raising the temperature from 298 to 573 K after the introduction of SO_2. This reacted with O_2 to form a radical, like SO_4^-, but upon evacuating the O_2, the reaction was reversed to give the original SO_2^-. When the temperature of NaX was further raised to 773 K in the presence of SO_2, a spectrum assigned to a polyatomic sulfur radical appeared indicating that SO_2 decomposition occurred at high temperature. This polymer radical was stable in an O_2 atmosphere at room temperature.

It has been verified using ESR that O_2^- and other oxygen anion radicals are formed on partially reduced oxides of molybdenum, titanium, zinc, vanadium and chromium containing trapped electrons.[1—5] It has also been found that SO_2^- is formed on these surfaces by introducing SO_2 at room temperature.[4—7] The reaction of SO_2^- with O_2 was also investigated. On magnesium oxide, this reaction produced SO_3^-.[8] SO_4^- was formed in the case of vanadium oxide.[7] A diamagnetic ion was mainly produced by a reaction on partially reduced titanium oxide.[6] These investigations are helpful for determining the intermediates in the oxidation of SO_2 on solid surfaces.

On the other hand, it is known that the O_2^- radical is produced on various cation exchanged Y-type zeolites when subjected to γ-irradiation.[9—12] Ono *et al.* have found thermal formation of SO_2^- on Y-type zeolites and have reported that SO_2^- on decationated Y zeolite reacts with O_2 to give O_2^-.[13] This finding appears rather unusual in view of the higher electron affinity of SO_2 as compared with that of O_2. On X-type zeolites, however, the adsorbed state of SO_2 has not yet been studied, and oxygen was examined only for cerium- and lanthanum-exchanged zeolites.[14] In this paper, the formation of these radicals on NaX and their reactivities are reported in some detail to obtain insight into the electron-donating power of zeolite.

Experimental

The NaX zeolite used was Linde type 13X which has a unit cell composition of $Na_{88}[(AlO_2)_{88}(SiO_2)_{104}]$. This sample was soaked in an aqueous solution of sodium acetate, supplied by the Wako Pure Chemical Ind., Ltd., to remove impurity cations and to avoid decationation.[15] Then the sample was washed thoroughly with ion-exchanged water and dried at 383 K. About 0.1 g of the sample was placed in a quartz sample tube with a breakable seal and heated under vacuum up to 823 K at a rate of 150 K/h. After degassing for 6 h at 823 K, the sample was cooled to room temperature and was exposed to the respective gases at 5—20 Torr at room temperature.

Unless otherwise noted, the ESR measurements were made at 77 K using a JES-3BS-X spectrometer with 100 kHz field modulation and a TE_{012} mode cavity. After evacuating the NaX sample at 823 K, a negligibly weak singlet signal was observed at $g=2.002$. γ-Irradiation was carried out at room temperature using a ^{60}Co γ-ray source with a total dosage of 12 Mrads. The irradiated sample was transferred into one end of the sample tube and the measuring end of the tube was heated with a flame to remove color centers generated in the wall during γ-irradiation. The gases used were of high purity and were obtained from the Takachiho Chemical Co.

Results and Discussion

Oxygen Radicals on NaX. An NaX sample was treated with O_2 at various temperatures between 298 and 773 K. No ESR spectrum, except a background, was observed. However, the ESR spectrum shown in Fig. 1(a) was observed when the sample was irradiated

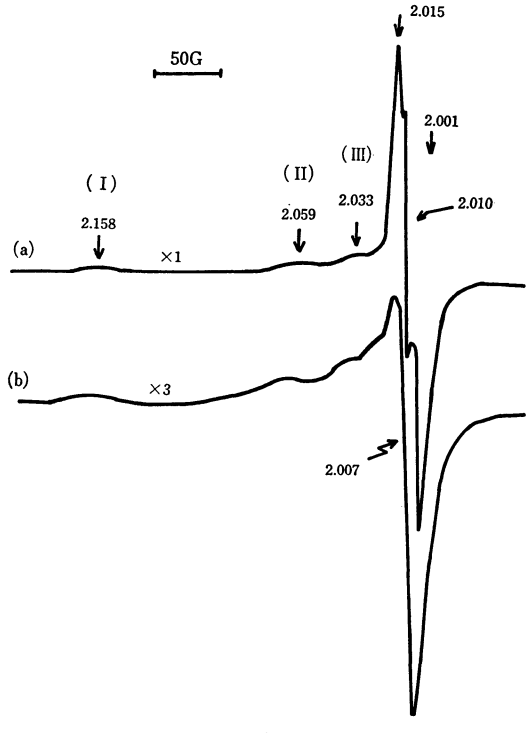

Fig. 1. ESR spectra of (a) NaX γ-irradiated in the presence of O_2 and (b) the same sample followed by N_2O addition.

in the presence of O_2. The high-field side of this signal (g_z=2.015, g_y=2.010, and g_x=2.001) is assigned to O_3^- from a comparison with ESR spectra due to various kinds of oxygen radicals.[1,11,16-22] The shape of this spectrum did not change upon evacuation at room temperature, but the intensities of all lines (the I, II, III, and O_3^- signals) were reduced to from 3/4 to 2/3 of the original values.

When N_2O was introduced into this sample after evacuation at room temperature, the spectrum due to O_3^- disappeared and a typical O_2^- spectrum[1,11,14,19] was clearly observed, as is shown in Fig. 1(b). This indicates that O_3^- is unstable compared with O_2^- and is affected by N_2O which is an efficient electron acceptor.[22] Several low-field lines correspond to O_2^- having different g_z values (g_z(I)=2.158, g_z(II)=2.059, and g_z(III)=2.033 in Fig. 1(b)) because of various crystal-field environments.[11] The lines corresponding to different g_x and g_y are superposed on each other to some extent. The spectrum in Fig. 1(b) was also obtained by heating the NaX sample at 373 K; the O_3^- signal disappeared above 373 K, while those for O_2^-(I), (II), and (III) remained up to 423, 523, and 473 K, respectively, upon heating.

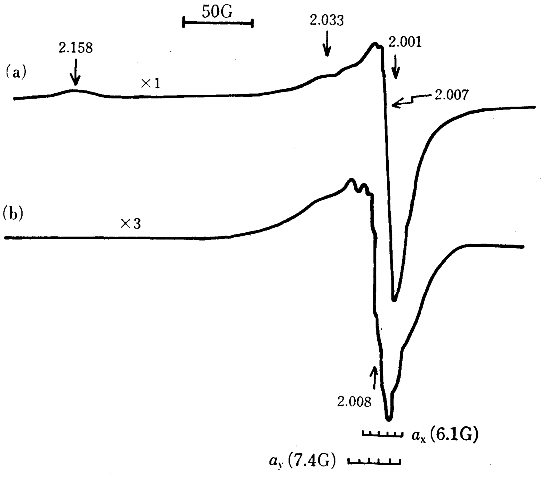

Fig. 2. ESR spectra obtained from NaX γ-irradiated in the presence of O_2 and exposed to (a) ethylene and (b) 1-butene or propylene.

Ethylene, propylene, and 1-butene were introduced in order to investigate the reactivities of the oxygen radicals. When the irradiated sample was exposed to ethylene at room temperature, the signals due to O_3^- and O_2^-(II) disappeared and the spectrum shown in Fig. 2(a) was obtained. This fact indicates that the O_3^- and O_2^-(II) can react with ethylene. For propylene and 1-butene addition, all the oxygen radicals except O_2^-(III) reacted and their ESR signals disappeared (Fig. 2(b)). A line shape characteristic of O_2^-(III) was clearly observed after this reaction, that is, g_z=2.033, g_y=2.008, and g_x=2.002. This spectrum appeares to show superhyperfine lines due to ^{27}Al (I=5/2), although they are not clearly resolved. The splittings ($|a_x|$=6.1 G, $|a_y|$=7.4 G) coincide well with those for O_2^- adsorbed on other zeolites.[10,12]

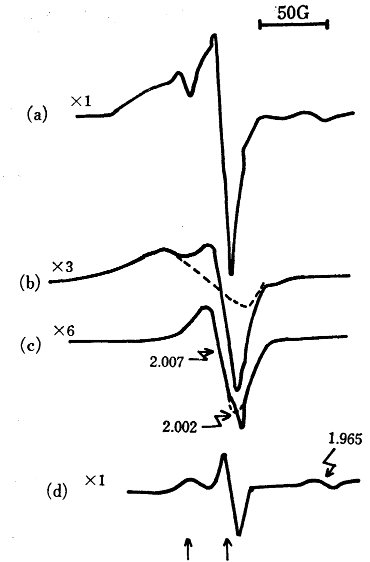

Fig. 3. ESR spectra of γ-irradiated NaX (a) under vacuum, (b) after N_2O addition, and (c) after heated at 423 K. (d) ESR spectrum obtained by subtracting (b) from (a).

Upon further addition of oxygen (150 Torr) to the sample, the spectrum due to O_2^-(III) was observed only because of the broadening of other lines. All the spectra recovered upon evacuation of the oxygen. This broadening effect indicates that O_2^-(III) exists in the sodalite unit or hexagonal prism, while O_3^-, O_2^-(I) and O_2^-(II) occur in the supercage.[11,15]

The ESR spectrum shown in Fig. 3(a) was obtained after NaX had been irradiated in a vacuum. The introduction of N_2O gradually changed this spectrum. Fig. 3(b) shows the result observed after exposure to N_2O for 24 h. This spectrum is converted to that shown in Fig. 3(c) upon heating the sample to 423 K after evacuation of the N_2O. The dotted line in Fig. 3(b) was obtained by subtracting spectrum (c) from spectrum (b). Similarly, Fig. 3(d) shows the difference between spectra (a) and (b). These spectra indicate that spectrum (a) is composed of a broad singlet signal (g=2.010, the dotted line in Fig. 3(b)), isotropic signals (g=2.007, 2.002, and 1.965, in Figs. 3(c) and (d)), and an anisotropic signal ($g_{/\!/}$=2.024, $g_\perp$=2.005, in Fig. 3(d)). A comparison of the g values and the line shapes of these signals with those obtained by γ-irradiation of other samples[10,11,16,23] leads to the conclusion that the isotropic signals (g=2.007 and 2.010) and the anisotropic signal can be attributed to V centers, while the other signals (g=2.002 and 1.965) are due to F centers.

When O_2 was introduced into the NaX which had been subjected to γ-irradiation under vacuum, the signals due to the V and F centers disappeared and a new signal (g_z=2.027, g_y=2.008, and g_x=2.001, in Fig. 4), which can be assigned to O_2^-, was obtained.[11,16] It is known that the trapped electron at an anion vacancy reacts with O_2 to form O_2^-.[11,24] The spin concentration of the O_2^- formed on irradiated NaX was several times larger than those of the V and F centers of the original NaX sample, as estimated from ESR signals. This result suggests the presence of other kinds of trapped

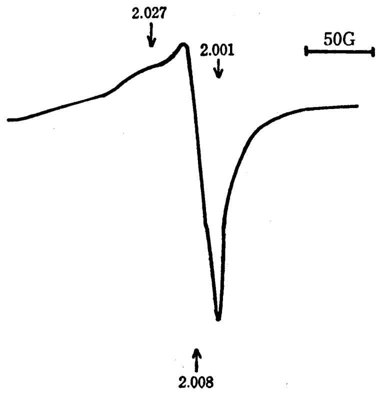

Fig. 4. ESR spectrum obtained from NaX γ-irradiated and exposed to O_2.

Table 1. g values of oxygen anion radicals produced on NaX

		g_1	g_2	g_3
γ-Irradiation in the presence of O_2	O_2^-	2.158	2.007—2.008	2.001
	O_2^-	2.059	2.007	2.002
	O_2^-	2.033	2.008	2.003
	O_3^-	2.015	2.010	2.001
Exposure to O_2 after γ-irradiation	O_2^-	2.027	2.008	2.001

electrons which are not ESR active. Table 1 summarizes the g values of the oxygen anion radicals formed on NaX after γ-irradiation. Details of the absorption sites of these O_2^- species will be discussed in a subsequent paper.

Reaction of Oxygen Radicals with SO_2. The introduction of SO_2, which has a higher electron affinity than does O_2,⁶⁾ to NaX irradiated in the presence of O_2 removes the signals due to O_3^-, O_2^-(I) and O_2^-(II), resulting in the spectrum shown in Fig. 5(a). The spectrum is composed of the O_2^-(III) signal and a new signal with principal g values of $g_{/\!/}=2.008$ and $g_\perp=2.001$. This result was confirmed by the ESR spectra obtained at room temperature, since the signal due to O_2^-(III) was broadened at this temperature and a new signal was clearly observed (Fig. 5(b)). This new signal can be attributed to SO_2^-, since the g components and the shape coincide well with those for the radical.⁴,⁶,⁷⁾ The formation of SO_2^- on NaX which was not γ-irradiated was negligibly small at room temperature. Therefore, the SO_2^- formation is considered to be caused by charge transfer from O_2^- to SO_2 (1), or electron capture from an F center (2), thus

$$O_2^- + SO_2 \longrightarrow SO_2^- + O_2 \qquad (1)$$

or

$$SO_2 + e^- \longrightarrow SO_2^-. \qquad (2)$$

It was found that the introduction of SO_2 into NaX irradiated under vacuum also produced an SO_2^- signal which had the same g components as that for NaX irradiated in the presence of O_2. This SO_2^- radical is formed by the capture of an electron from an F center and the amount of the radical formed is about 50% of that of the O_2^- produced on NaX upon γ-irradiation in the presence of O_2. This shows that the number of F centers produced on NaX by γ-irradiation in an O_2 atmosphere is small, since most of the electrons would be trapped by O_2 to form O_2^-. Moreover, reaction (1) appears to occur easily since the electron affinity of SO_2 is higher than that of O_2. From these points of view, it can be concluded that the transfer of an electron from O_2^- to SO_2 occurs predominantly on NaX γ-irradiated in the presence of O_2. The spin concentration of the SO_2^- produced on this NaX was found to be about 50% of that of the O_2^- which disappeared upon the introduction of SO_2. This indicates that the reaction of SO_2 with O_2^- leads partly to the formation of diamagnetic compounds.⁶⁾

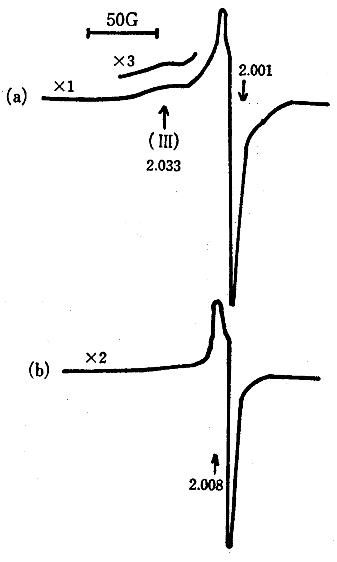

Fig. 5. ESR spectra obtained from NaX γ-irradiated in the presence of O_2 and exposed to SO_2, recorded at (a) 77 K and (b) room temperature.

Sulfur Oxide and Sulfur Radicals on NaX. Upon heating NaX from 298 to 573 K after the introduction of SO_2, the intensity of ESR spectrum attributed to SO_2^- was found to increase. This spectrum is exactly the same as that obtained for γ-irradiated NaX. When the temperature was further raised to 673 K, the SO_2^- signal was attenuated and a new anisotropic signal appeared at low field (Fig. 6(a), $g\approx2.030$). This signal became distinct after heating to 773 K (Fig. 6(b)). It is evident that a polyatomic sulfur biradical is present on the surface from a comparison of this spectrum ($g_z=2.048$, $g_y=2.030$, $g_x=2.002$) with those obtained

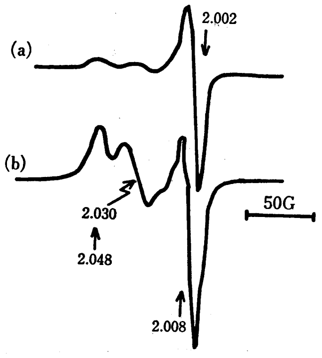

Fig. 6. ESR spectra obtained from NaX after heat treatment at 673 K (a) and 773 K (b) in the presence of SO_2.

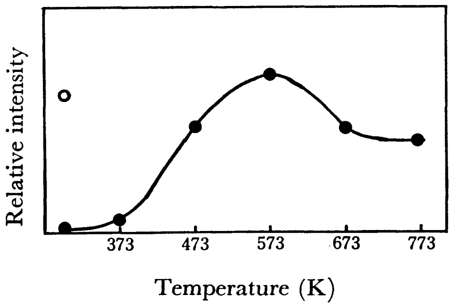

Fig. 7. Temperature dependence of SO_2^- formation on NaX (●). The radical formed on NaX γ-irradiated under vacuum at room temperature is also shown in the figure (○).

by the photolysis of solid COS,[25] sublimed sulfur[26] and sulfur-saturated zeolites 3A, 4A, and 5A.[27] The line corresponding to the smallest g value, $g=2.002$, overlaps with the spectrum of SO_2^-. Figure 7 shows the temperature dependence of the SO_2^- formation. The relative intensity for the radical produced on γ-irradiated NaX is also plotted in the figure.

It is known that both SO_2^- and O_2^- are formed on partially-reduced oxides soon after the introduction of SO_2 and O_2.[1-7] On the other hand, the amount of SO_2^- formed was small on NaX without heating in an SO_2 atmosphere and no O_2^- was formed without γ-irradiation. These results indicate that NaX is a rather weak electron donor compared with partially-reduced oxides. This fact can be attributed to the difference in the electron-donating centers on the respective surfaces: for the oxides, the center consists of low-valent metal cations, while $[AlO_{4/2}]^-$ is suggested as the center for the zeolites.[13]

When O_2 was introduced at room temperature onto NaX which was treated at 573 K in the presence of SO_2, the observed spectrum of SO_2^- after cooling to 77 K showed an appreciable change, as is shown in Fig. 8(a). In the spectrum recorded at room temperature (Fig. 8(b)), however, the SO_2^- signal with decreased intensity due to the reaction is distinguished from the new broadened signal at this temperature. The spectrum shown in Fig. 8(c) was obtained by subtracting this SO_2^- signal from the spectrum shown in Fig. 8(a). After evacuation at room temperature, the new signal almost disappeared and the intensity of the SO_2^- signal was restored.

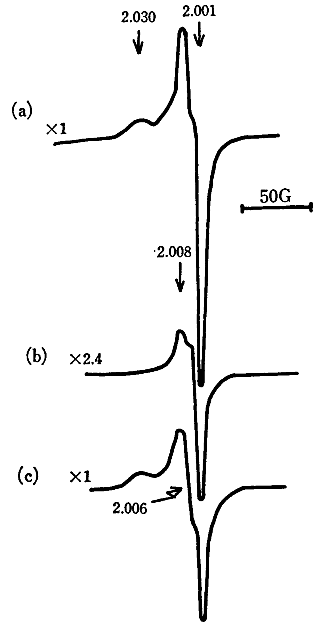

Fig. 8. ESR spectra after reaction of SO_2^- with O_2 recorded at (a) 77 K and (b) room temperature. (c) The spectrum obtained by subtracting the signal due to SO_2^- from (a).

The g_y value of the new signal was estimated to be 2.006, although the superposed SO_2^- signal decreased the accuracy of the measured value. Rao *et al.* have reported that SO_2^- adsorbed on vanadium oxide reacts with O_2 forming SO_4^-.[7] The g values of the radical obtained in the present work ($g_z=2.030$, $g_y=2.006$, $g_x=2.001$) are similar to those for SO_4^-.[7,28-30] Since the SO_2^- signal intensity was restored by evacuation, the new radical formed on NaX by the reaction of SO_2^- with O_2 appears to be a complex which has an SO_4^--like structure, although SO_2^- combines rather weakly with O_2, thus

$$SO_2^- \underset{-O_2}{\overset{+O_2}{\rightleftarrows}} SO_4^- \ (SO_2^- \cdot O_2).$$

It is suggested that SO_2^- on decationated zeolites transfers electrons to O_2 to form O_2^-.[13] However, this formation of O_2^- appears to be difficult on NaX since no O_2^- is formed by only thermal treatment. Even with γ-irradiation, the O_2^- radicals obtained have different g tensors from this signal (Table 1). In addition, O_2 has a lower electron affinity compared with that of SO_2.[6,31,32] Thus, an electron transfer reaction, such as

$$O_2 + SO_2^- \longrightarrow O_2^- + SO_2,$$

is difficult to proceed, although the reverse reaction can easily occur.

On the other hand, when O_2 was introduced into this NaX sample, the decrease in the total SO_2^- spin reached about 65% and was accompanied by the appearance of an SO_4^--like signal. This means that the reaction of SO_2^- with O_2 also leads to the formation of diamagnetic compounds as in the case of the reaction of O_2^- with SO_2. However, when O_2 was introduced onto NaX which had been heated to 773 K in the presence of SO_2, the signals due to the existing SO_2^- and polysulfur radicals were scarcely affected. This result indicates that the state of SO_2^- is different from that of the radical formed on NaX heated below 573 K. SO_2^- may exist in the sodalite unit since the radical does not react with O_2, which is held in the supercage at room temperature,[15] while, below 573 K, SO_2^- is formed in the supercage. The SO_2 molecule must be able to penetrate into the sodalite unit at high temperature as well as does O_2.[15]

The presence of polysulfur radicals indicates that SO_2 on NaX decomposes above 673 K. As the intensity of the radical increases, the SO_2^- radicals decrease in number (Fig. 7) and exist only inside the sodalite unit.

The SO_2^- in the supercage may be converted to a polysulfur radical, while the SO_2^- in the sodalite unit may not change into this radical because the cavity is too small for polymeric formation.

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