July, 1979] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (7), 1923—1927 (1979) 1923

# ESR Study of Molecular Oxygen Anion Radicals Produced on Cation-exchanged X-Type Zeolites by $\gamma$-Irradiation

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(Received December 20, 1978)

Molecular Oxygen anion radicals ($O_2^-$) were produced on X-zeolites by $\gamma$-irradiation in the presence of $O_2$. Their properties were systematically investigated by means of ESR spectroscopy. Two kinds of $O_2^-$ species with different $g_z$ values were formed on monovalent cation-exchanged (LiX, KX, RbX, CsX) zeolites and MgX, while three and single $O_2^-$ species were observed on divalent cation-exchanged (CaX, SrX, BaX) and trivalent cation-exchanged (LaX) zeolites, respectively. These $O_2^-$ radicals showed different reactivities with $N_2O$ or 1-butene, and their $g_z$ values were classified into four groups. By considering the results from the $g_z$ values and the effect of introduced high pressure $O_2$ on the $O_2^-$ spectra, the adsorption sites for the radicals on zeolites were determined.

Many Studies have been done about $O_2^-$ radicals adsorbed on various kinds of oxides and zeolites by the use of electron spin resonance technique.[1-11] Based on these studies, the influence of the electric charge of surface cations on the $g$-factor anisotropy for the adsorbed $O_2^-$ radicals has been discussed.[1,2,5,7] Kasai found that $O_2^-$ was formed on Y-type zeolites by $\gamma$-irradiation and the deviation of the maximum principal $g$ value ($g_z$) for the adsorbed $O_2^-$ on a monovalent zeolite NaY from that of a free electron ($g_e$) was twice as large as the deviation for $O_2^-$ on a divalent zeolite BaY.[6]

Wang *et al.* have attempted to explain the change of $g$ values for $O_2^-$ formed on Y-type zeolites by $\gamma$-irradiation in terms of the crystal field induced by the cations.[7-8] In the case of alkaline earth cation exchanged Y-zeolites, the $O_2^-$ radicals were found to be adsorbed on more than three different sites.[7] However, they could not clarify the nature of the respective sites. Not only on the alkaline earth Y-zeolites but also on NaY they observed three kinds of $O_2^-$ species having different $g_z$ values.[7] Kasai, on the other hand, reported his finding of single $O_2^-$ species on NaY. The difference between these results has not yet been well explained. The formation of $O_2^-$ radicals on trivalent cation-exchanged Y-type zeolites was also reported,[8] but no correlation among the changes of $g$ values in NaY, alkaline earth Y-zeolites, and trivalent cation-exchanged Y-zeolites has yet been found.

More detailed investigations are necessary to find the correlation between the $g_z$ values and the nature of adsorption sites for $O_2^-$ on various kinds of cation-exchanged zeolites. Especially, studies about $O_2^-$ on other monovalent cation-exchanged zeolites besides sodium-form zeolites should be done. In addition, no work has been carried out to examine the properties of $O_2^-$ formed on X-type zeolites by $\gamma$-irradiation except that on NaX.[12] In this paper, $O_2^-$ species formed on monovalent, divalent, and trivalent cation-exchanged X-type zeolites by $\gamma$-irradiation are systematically examined, and the properties of adsorption sites for the $O_2^-$ are discussed.

## Experimental

The cation-exchanged X-zeolites were prepared by immersing Linde 13X zeolite several times into the aqueous solutions of cations in the form of chloride, nitrate, or acetate. The obtained exchanged-zeolites were thoroughly washed with deionized water and dried at room temperature. The degree of ion exchange was determined by estimating the amount of sodium ions dissolved into the solution by means of flame spectrometry. The samples used and their exchange percentages are shown in Table 1.

The zeolite samples, placed in ESR quartz tubes, were degassed at 550 °C, and were exposed to oxygen after cooling to room temperature. The experimental details were similar to those described in the previous paper.[12] $\gamma$-Irradiation of samples was performed at room temperature by using a $^{60}Co$ source; the dose was 12 Mrad. Other samples were also irradiated by $\gamma$-rays without exposing them to oxygen. No ESR spectrum except a negligibly weak singlet line at $g=2.002$ was observed before $\gamma$-irradiation. Gaseous materials of high purity were obtained from Takachiho Chemical Co. and were used without further purification. The pressures of gases were adjusted to be within the range of 10—30 Torr when the samples were exposed to them. All gases were introduced into samples at room temperature. The ESR spectra were recorded at −196 °C with a JEOL JES-3BS X band spectrometer.

## Results

*Monovalent Cation-exchanged Zeolites.* LiX $\gamma$-irradiated in the presence of $O_2$ gave a typical $O_2^-$ ESR spectrum, as shown in Fig. 1(a).[1-12] All the spectra obtained from $\gamma$-irradiated KX, RbX, and CsX in the presence of $O_2$ have similar lines. Figure 1(a) also shows the low-field lines of their spectra; the estimated values of $g_y$ and $g_z$ are 2.009—2.007 and 2.003—2.001, respectively. The low-field lines (B and D) indicate the presence of two kinds of $O_2^-$ species with different $g_z$ values.[7] The spectra shapes were not changed by evacuation at room temperature.

When these alkali-cation exchanged samples were exposed to 1-butene, the $O_2^-$(B) spectra of the samples disappeared, whereas the other ones, $O_2^-$(D), were kept unchanged (Fig. 1(b)). The contact with $N_2O$ only decreased the intensities of the $O_2^-$(B) spectra for RbX and CsX. All the $O_2^-$(B) spectra were broadened by exposing the zeolites to $O_2$ of 150 Torr. The $\gamma$-irradiation of LiX, KX, RbX, and CsX under vacuum gave ESR spectra almost similar to that for NaX,[12] though the relative intensity of each signal due to a V or F center was somewhat different in the respective samples.

*Divalent Cation-exchanged Zeolites.* Figure 2(a)

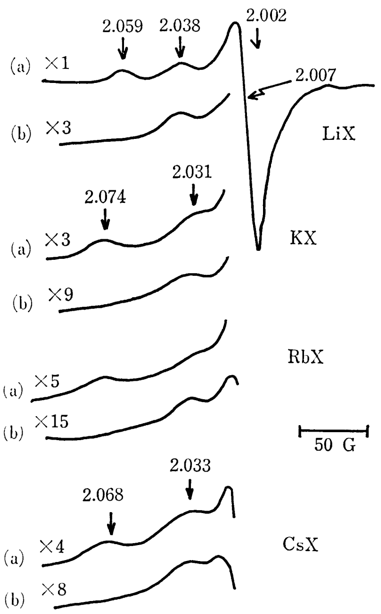

Fig. 1. ESR spectra of alkali cation-exchanged X-zeolites; (a) $\gamma$-irradiation in the presence of $O_2$, and (b) addition of 1-butene after (a) and evacuation.

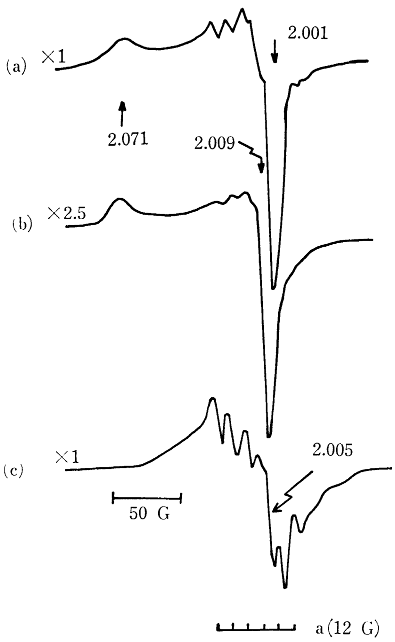

Fig. 2. ESR spectra of MgX; (a) $\gamma$-irradiation in the presence of $O_2$, (b) contact with $N_2O$ after (a) and evacuation, and (c) $\gamma$-irradiation under vacuum.

shows the ESR spectrum of MgX $\gamma$-irradiated in the presence of $O_2$. When $N_2O$ was added, the complicated lines in the central part ($g \approx 2.010$) of the spectrum disappeared and a typical $O_2^-$ spectrum was observed (Fig. 2(b)). In the case of MgX $\gamma$-irradiated under vacuum, several lines due to V and F centers were observed, as is shown in Fig. 2(c). The broad asymmetric signal with six hyperfine lines ($|a(\mathrm{Al})| = 12$ G) in the figure is the same as that observed by Sogabe *et al.*[13] and can be attributed to an electron hole trapped on an oxygen atom which is bound to an aluminum atom.[9,13–16] Accordingly, the ESR spectrum shown

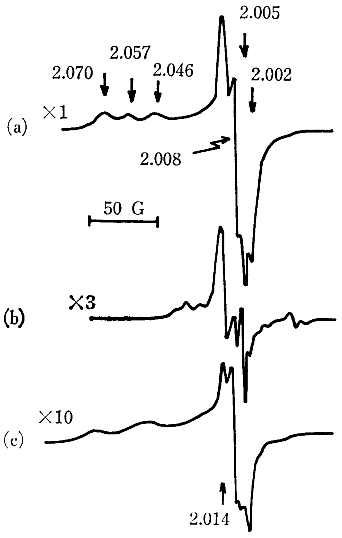

Fig. 3. ESR spectra of CaX; (a) $\gamma$-irradiation in the presence of $O_2$, (b) $\gamma$-irradiation under vacuum, and (c) addition of 1-butene after (a) and evacuation.

in Fig. 2(a) is recognized as this signal with hyperfine lines superposed on the signal due to $O_2^-$. The addition of $O_2$ (150 Torr) to the MgX $\gamma$-irradiated in the presence of $O_2$ confirmed this assignment, since the asymmetric signal with hyperfine lines became evident due to the broadening of the $O_2^-$ signal. It was observed that the introduced 1-butene destroyed all the signals except a singlet at $g=2.005$.

When CaX was $\gamma$-irradiated in the presence of $O_2$, the spectrum shown in Fig. 3(a) was obtained. From the low-field shoulders ($g_z=2.070$, 2.057, and 2.046), the presence of three $O_2^-$ species ($g_y \approx 2.008$ and $g_x \approx 2.002$) was confirmed.[1–12] Other signals ($g=2.014$, 2.005, 2.002 *etc.*) were ascribed to V and F centers,[7,9,12–16] since they were also obtained by $\gamma$-irradiation of CaX under vacuum (Fig. 3(b)). The complexity of the spectrum is due to the presence of the paramagnetic centers which interact with protons of the surface hydroxyl groups.[18,19] It was reported that the surface hydroxyl groups on alkaline earth zeolites remained even after evacuation at high temperature.[20–22]

Evacuation of the irradiated sample of CaX at room temperature decreased the intensity of the $O_2^-$ signal with $g_z=2.070$ by 50%, but did not affect those of the other signals. When the sample was exposed to 1-butene, the intensities of the signals due to $O_2^-$ with $g_z=2.070$ and 2.046 and the lines at $g=2.014$ and $g=2.005$ decreased, and, further, the $O_2^-$ signal with $g_z=2.057$ disappeared (Fig. 3(c)). Upon heating at 200 °C, only the signal with $g_z=2.046$ ($g_y=2.008$ and $g_x=2.001$) remained. All the $O_2^-$ signals were broadened by introducing $O_2$ of 150 Torr.

The spectrum obtained after the irradiation of SrX in the presence of $O_2$ was found to be composed of signals due to three $O_2^-$ species ($g_z=2.062$, 2.054, and 2.048) and V and F centers (Fig. 4(a)). The contact with gaseous $N_2O$ improved the resolution of the $O_2^-$ signals, though their intensities decreased (Fig. 4(b)). By the addition of 1-butene, the $O_2^-$ signals with $g_z=2.062$ and $g_z=2.048$ disappeared, while $O_2^-$

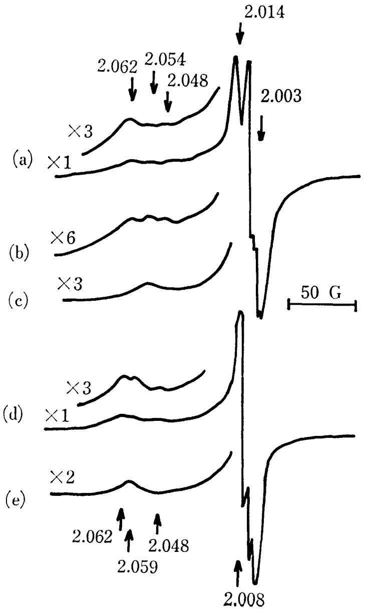

Fig. 4. ESR spectra of SrX; (a) $\gamma$-irradiation in the presence of $O_2$, (b) addition of $N_2O$ after (a) and evacuation, and (c) addition of 1-butene after (a) and evacuation. ESR spectra of BaX; (d) $\gamma$-irradiation in the presence of $O_2$, and (e) addition of 1-butene after (a) and evacuation.

with $g_z=2.054$ ($g_y=2.008$, $g_x=2.002$) remained (Fig. 4(c)). The spectrum recorded at −196 °C shows that the $O_2^-$ with $g_z=2.048$ was broadened by introducing $O_2$ (150 Torr). The broadening of other $O_2^-$ signals ($g_z=2.062$ and 2.054) was not remarkable at that temperature. However, the broadening of the latter was confirmed to occur by observing the change in ESR spectra recorded at room temperature before and after the addition of $O_2$ (150 Torr).

The ESR spectrum of $\gamma$-irradiated BaX in the presence of $O_2$ indicated the formation of three $O_2^-$ species (Fig. 4(d), $g_z=2.062$, 2.059, and 2.048). The shape of the $O_2^-$ spectrum was more distinct in BaX as compared with other divalent zeolites, since the signals due to V and F centers were relatively weak. The intensity of the spectrum obtained in the $\gamma$-irradiated BaX under vacuum is about 15—20% of those obtained from the other divalent zeolites. The evacuation of $O_2$ attenuated the $O_2^-$ signal with $g_z=2.062$ to about 65%. The $O_2^-$ signals with $g_z=2.062$ and 2.048 disappeared after exposure of the zeolite to 1-butene (Fig. 4(e)). All the $O_2^-$ signals underwent the line-broadening in the presence of $O_2$ (150 Torr).

*Trivalent Cation-exchanged Zeolite (LaX).* When LaX was irradiated in the presence of $O_2$, the spectrum of $O_2^-$ with $g_z=2.034$, $g_y=2.007$, and $g_x=2.002$ was observed (Fig. 5(a)). Upon the addition of 1-butene, the $O_2^-$ signal disappeared, and an asymmetric signal with 6 hyperfine lines with weak intensity became visible (Fig. 5(b)). This shows that the spectrum in Fig. 5(a) is composed of this asymmetric signal and the overlapping one due to $O_2^-$. The asymmetric signal was also observed by $\gamma$-irradiating LaX under vacuum. It may be attributed to electron holes similar to those produced in MgX by $\gamma$-irradiation, though the resolution of the hyperfine lines was rather lower.[9,13–16] The addition of $O_2$ (150 Torr) broadened the $O_2^-$ signal.

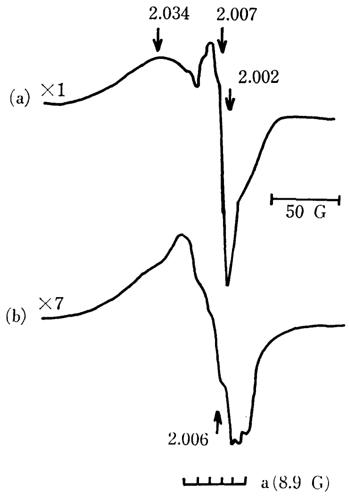

Fig. 5. ESR spectra of LaX; (a) $\gamma$-irradiation in the presence of $O_2$, and (b) addition of 1-butene after (a) and evacuation.

## Discussion

The ESR spectra observed on the cation-exchanged zeolites which were $\gamma$-irradiated in the presence of $O_2$ are sometimes complicated because of the overlapping of signals due to several $O_2^-$ radicals which are adsorbed on different sites. The formation of V and F centers makes the spectra more complicated. For example, the presence of some $O_2^-$, especially those with $g_z=2.035$—2.040 on NaY and alkaline earth zeolites was ambiguous, since it was suggested only from the shoulders in the complicated spectrum. These $O_2^-$ species and centers may show different stabilities on thermal treatments and reactivities with the introduced foreign gases.[12] By making use of these different reactivities and stabilities, we separated the spectrum for each individual $O_2^-$ from the other, and provided the convincing evidence for the presence of each $O_2^-$ species.

The $g_z$ values for $O_2^-$ obtained from $\gamma$-irradiated X-type zeolites in the presence of $O_2$ and those for NaX in our previous study[12] are classified into four groups, as is shown in Table 1. A theoretical analysis of the principal $g$ values for $O_2^-$ was carried out by Känzig and Cohen.[23] According to their result, the $g_z$ component which shows the largest deviation from $g_e$, that of a free electron, is expressed by

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

Where $\lambda$ is the spin-orbit coupling constant and is evaluated at 0.014 eV.[6] The z axis is chosen along the internuclear axis of $O_2^-$. The lowest electronic configuration of $O_2^-$ is $\sigma_g{}^2\pi_u{}^4\pi_g{}^{*3}$. The originally degenerated $\pi_u$ and $\pi_g{}^*$ levels are split respectively into $\pi_u(2p_x)$, $\pi_u(2p_y)$ and $\pi_g{}^*(2p_x)$, $\pi_g{}^*(2p_y)$ in the adsorbed state by the asymmetric crystal field.[1,5,6,24]

TABLE 1. $g_z$ VALUES FOR $O_2^-$ ON CATION-EXCHANGED X ZEOLITES $\gamma$-IRRADIATED IN THE PRESENCE OF $O_2$ ($g_y=2.007$—$2.009$, $g_x=2.000$—$2.003$)

| Cation | Exchanged % | A | B | | C | D |
|---|---|---|---|---|---|---|
| Li | 72 | | | 2.059 | | 2.038 |
| Na[a] | 100 | 2.158 | | 2.059 | | 2.033 |
| K | 81 | | 2.074 | | | 2.031 |
| Rb | 67 | | 2.074 | | | 2.031 |
| Cs | 56 | | 2.068 | | | 2.033 |
| Mg | 67 | | 2.071 | | | |
| Ca | 80 | | 2.070 | 2.057 | 2.046 | |
| Sr | 81 | | 2.062 | 2.054 | 2.048 | |
| Ba | 85 | | 2.062 | 2.059 | 2.048 | |
| La | | | | | | 2.034 |

a) The values were obtained in our previous work[12] under the same experimental conditions as used for the others.

In the above equation, $\delta$ is the energy separation between the $\pi_g{}^*(2p_x)$ and $\pi_g{}^*(2p_y)$ orbitals. When $\delta \gg \lambda$, the energy separation $\delta$ is given by $\delta = 2\lambda/(g_z - g_e)$. Figure 6 shows the plot of $\delta$ values of the group B for alkali cation exchanged zeolites, the group C for alkaline earth zeolites and D for LaX against the charge of exchanged cation. The $\delta$ values summarized by Lunsford[5] are also shown in the figure as a measure of the distribution range for each value of cation charge. The $\delta$ values obtained in the present study fall almost in the ranges indicated by Lunsford. This result suggests that $O_2^-$(B) was adsorbed on the monovalent cation, $O_2^-$(C) on the divalent cation, and $O_2^-$(D) on the trivalent cation.

Table 1 also shows that $O_2^-$(D) was produced not only on LaX but also on alkali zeolites. $O_2^-$(D) of alkali zeolites, however, has a different character from those of the other $O_2^-$. In the atomosphere of $O_2$ (150 Torr), all the $O_2^-$ spectra except $O_2^-$(D) of alkali zeolites were broadened. This indicates that the $O_2^-$(A, B, C, and D of LaX) are located in the supercage, while $O_2^-$(D) of alkali zeolites may be adsorbed on sites different from the others, possibly on those in the sodalite unit.[7] The signal of $O_2^-$(D) on NaX has the six hyperfine lines due to an Al nucleus,[12] and the $g$ values for $O_2^-$(D) on alkali cation exchanged zeolites coincide well with those for $O_2^-$ adsorbed on the aluminum ion in zeolite structure[8,10] and $Al_2O_3$.[25,26] From these facts, it can be concluded that these $O_2^-$(D) of the alkali zeolites were adsorbed by the lattice aluminum. The $g_z$ value of $O_2^-$(D) for LaX is close to those for ScY and LaY[8] and, therefore, is characteristic of $O_2^-$ adsorbed on the exchanged trivalent cation. The ScY and LaY have only one kind of adsorbed $O_2^-$ species, and the observed superhyperfine structure indicates that the exchanged trivalent cations correspond to the adsorption sites.

The states of exchanged cations such as $M^{2+}$, $M(OH_2)_n{}^{2+}$, $M(OH)^+$, MO, and $M^+$–O–$M^+$ were suggested from the IR and X-ray studies of alkaline earth zeolites.[20,21,27,28] The $O_2^-$(B) species formed on alkaline earth zeolites have similar $g_z$ values to those on alkali zeolites. These $O_2^-$(B) species may therefore be trapped on monovalent-like sites such as $M(OH)^+$ or $M^+$–O–$M^+$. It was confirmed that the $M(OH)^+$ site exists in the alkaline earth zeolites even after evacuation at high temperature.[29] The $M^+$–O–$M^+$ complexes were suggested to be formed in the sodalite unit upon mild dehydration; the $M^{2+}$ ions located at site I′ and site II″ in the zeolite frame work are joined by an oxygen atom.[28] However, considering the movement of the cation due to dehydration at high temperature and $\gamma$-irradiation, it seems possible that the complexes with one of the $M^{2+}$ ions in a supercage are also formed.

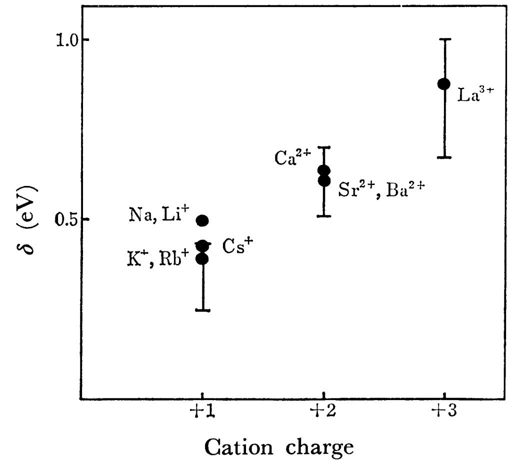

Fig. 6. Correlation between $\delta$ and the charge of metal ions. ●; cation exchanged X-zeolites: ├──┤ ; the range of $\delta$ values previously obtained.[5]

The $O_2^-$(C) species is characteristic of the divalent cation exchanged zeolites, and can be attributed to the $O_2^-$ adsorbed on the cations in the state of $M^{2+}$ (Fig. 6). The $O_2^-$(C) was not observed on MgX zeolite. It is known that the $Mg^{2+}$ ion has a large hydration radius, and can dissociate the bound water more strongly than other divalent cations in zeolites.[13,31] The monovalent-cation like sites are formed by dissociating the bound water of hydrated cations. Most $Mg^{2+}$ ions may take the monovalent-like form. The difference between MgX and other alkaline earth zeolites was also reported for the adsorbed states of $CO_2^-$ and $CO_2$.[13,31]

Table 1 shows that the $O_2^-$(A) species is only obtained on NaX. Such $O_2^-$ species with large $g_z$ values were observed on the pretreated NaY and KY with Na and K vapor respectively.[32] The exposure of NaY to Na vapor was found to form the paramagnetic center $Na_4{}^{3+}$, and the $O_2^-$ species is formed by taking an electron from the center. The paramagnetic center $Na_4{}^{3+}$ was also formed by $\gamma$-irradiation of NaY and the adsorbed $O_2^-$ has a large $g_z$ value of 2.113.[6] It was suggested by Bentarrit *et al.* that the induced migration of the cation by water leads to the generation of an $Na_4{}^{3+}$ center under $\gamma$-irradiation.[33] Stamires mentioned that $(Na_4)^{4+}$–$(H_2O)_x$ complex is formed in NaY zeolite after a proper degree of dehydration and is converted to $(Na_4)^{3+}$–$(H_2O)_x$ by trapping an electron.[17] As for NaX zeolite, $Na_6{}^{5+}$ was found to be produced by exposing NaX to Na vapor.[34] These findings predict that the $\gamma$-irradiation produces the

$(Na_n)^{(n-1)+}$ center which become non-paramagnetic by transferring an electron to $O_2$; the number of atoms $n$ depends on experimental conditions such as dehydration and $\gamma$-irradiation. The non-paramagnetic center may take the form of $(Na_n)^{n+}$ or a somewhat different configuration due to the movement of the cation after the adsorption of $O_2^-$, and induces a different crystal field from the usual monovalent $Na^+$ site. The $O_2^-$(A) seems to be that held at such a center. This assumption gives a reasonable explanation for the wide variety of $g_z$ values for $O_2^-$ on NaY. The pretreatments under different conditions may produce the sites of various configurations.[33] The $O_2^-$(A) species was not observed on the other alkali zeolites. The formation of $(M_n)^{n+}$ centers consisting of exchanged cations must be prevented by the remaining $Na^+$ cations.

By summarizing the consideration given above, the adsorption sites of $O_2^-$ on $\gamma$-irradiated zeolites in the presence of $O_2$ can be assigned to the exchanged $M^+$ ion and the lattice aluminum cation in monovalent cation-exchanged zeolites (LiX, NaX, KX, RbX, CsX), $M^{2+}$, $M(OH)^+$ and $M^+$–O–$M^+$ in divalent cation-exchanged zeolites (MgX, CaX, SrX, BaX), and $M^{3+}$ in trivalent cation-exchanged zeolites (LaX). The adsorption site $(M_n)^{n+}$ was also suggested for NaY zeolite. The lack of precise information on the electronic state and geometry of the zeolite surfaces makes the verification of these supposed adsorption sites difficult at present, but it is expected that their exact configuration and function will be revealed in the following studies using surface analytical techniques.

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