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Electron Spin Resonance Studies of the Carbon Dioxide Anion Radical Adsorbed on X-Type Zeolites

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The hindered motion and the structure of the CO_2^- radical adsorbed on various zeolites were investigated by means of ESR spectroscopy. The adsorbed CO_2^- radical was obtained by the γ-irradiation of zeolites with carbon dioxide labeled with ^{13}C. The results show that the interaction of the CO_2^- radical with the zeolite surface changes with the electrostatic field on the surface. The motion and the structure of the adsorbed CO_2^- radical are affected by the properties of the zeolite surfaces; the former is also influenced by the extent of exchange of the cation on zeolite, regardless of the time of irradiation, before or after the introduction of carbon dioxide. The formation of the CO_2^- radical on zeolites was interpreted on the basis of such a mechanism that electrons are initially trapped by the surface of zeolite upon the irradiation and then transferred to carbon dioxide molecules. The results also show that the process of the electron transfer depends on the kind of cation.

The application of ESR spectroscopy to adsorbed molecules has been of considerable interest, since it permits detailed studies of their adsorbed state. Several works have been reported on the formation of the CO_2^- radical on an insulator, such as SiO_2 or MgO.[1-4] However, very little information has been obtained on the interaction between the radical and the solid surface.

Sharp and Symons[5] have recently investigated the CO_2^- radicals formed in various formates and shown that the ESR parameters for the CO_2^- radical depend markedly upon the nature of the host lattice. According to their results, the crystal field, which increases as the cation's charge increases or its radius decreases, causes a profound perturbation in the CO_2^- radical. Kasai[6] has studied the crystal-field interaction between an adsorbed paramagnetic species, O_2^-, and Y-type zeolites, and shown that the splitting of energy levels of the O_2^- is exactly twice as large with BaY as with NaY.

In this work, we will attempt to represent the crystal-field interaction in terms of the hindered motion and the structural variation in the CO_2^- radical adsorbed on zeolites.

Experimental

The X-type zeolite was furnished in the sodium form (Linde Lot No. 1380019). Ion-exchanged zeolites were prepared by exchanging the sodium ions with other kinds of

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cations in their chloride solutions by the conventional method.[7] The exchange process was then repeated in order to achieve a high degree of replacement. The exchanged zeolites were washed with distilled water in order to remove the excess chloride ions. Thus, Li-, K-, Mg-, Ca-, and BaX were obtained. The degree of ion-exchange was determined by measuring the amount of the exchanged sodium ions by means of atomic-absorption spectroscopy.

After the exchanged zeolite had been evacuated for 5 hr in a vacuum of 10^{-5} Torr at 500°C, it was slowly cooled to room temperature and transferred into an ESR sample tube. Carbon dioxide containing 59.1 atom% ^{13}C, which had been obtained from Merck Sharp & Dohme of Canada, Ltd., was used in order to observe the ^{13}C hyperfine structure. The carbon dioxide was introduced into the sample tube through a breakable seal at room temperature. After the zeolite had been exposed to the carbon dioxide gas of 20 Torr for 30 min, the physically-adsorbed carbon dioxide was removed by means of a liquid nitrogen trap. The ESR sample tube was sealed off *in vacuo* and then irradiated with ^{60}Co γ-rays (6×10^5 R/hr) for 30 min at 77°K.

The ESR spectra were measured at various temperatures by a spectrometer described elsewhere.[8] In order to study the mechanism of the formation of the adsorbed CO_2^- radical, a pre-irradiation process was also adopted.

Results and Discussion

The percentages of exchanged ions are shown in Table 1. In the case of MgX, only 59.6% of Na^+ was exchanged even when the exchange process was repeated; this seems to be due to the large hydration radius of Mg^{2+}.[9]

Formation and Identification of the CO_2^- Radical. The shapes of the hyperfine structures of ^{13}C in the spectra obtained for the zeolite exchanged by the Li^+ ion and the bivalent cation are very close to that of the $^{13}CO_2^-$ radical adsorbed on silica gel.[2] Each spectrum consists of a central line originating from the $^{12}CO_2^-$ radical and of two additional outer lines due to the $^{13}CO_2^-$ radical. However, no ESR spectrum of the CO_2^- radical adsorbed on NaX or KX was observed under the same experimental conditions as were used for the other zeolites. The CO_2^- radical on NaX or KX was obtained when these zeolites were irradiated for 16 hr at room temperature in the presence of carbon dioxide at 100 Torr. The formation of the radical on the NaX or KX may be interpreted as follows: the irradiation at room temperature enabled electrons to transfer from the surface to adsorbed carbon dioxide. The g-values evaluated from the hyperfine structure of ^{13}C are summarized in Table 1.

Structure of the CO_2^- Radical. Ovenall and Whiffen[10] have observed the ESR spectrum of the CO_2^- radical produced in γ-irradiated sodium formate and determined the structure of the radical by analyses of the g-values and the ^{13}C coupling constants. According to the molecular orbital theory, the unpaired 17th electron occupies the $4a_1$ molecular orbital:[10,11]

$$(4a_1) = c_1C(s) + c_2C(p) + c_3O(P_{z1}+P_{z2}) + c_4O(P_{y1}-P_{y2}) + c_5O(s_1+s_2) \qquad (1)$$

Actually, the ^{13}C coupling constants of the $^{13}CO_2^-$ radical are used for the estimation of the atomic orbital coefficient of Eq. (1).

$$A_{\mathrm{iso}} = C_1^2A_s, \quad A_{//} - A_{\mathrm{iso}} = C_2^2A_p \qquad (2)$$

where A_s and A_p are the coupling constants for the electrons in the pure carbon $2s$ and $2p$ orbitals, 1189 and 42.9 G[10,12] respectively, and where C_1^2 and C_2^2 are the spin densities in the carbon $2s$ and $2p$ orbitals respectively, which give information on the hybridization of the orbitals.

The OCO angle of the CO_2^- radical, θ, has been derived in terms of the hybridization:[13]

$$\cos\theta = -\frac{\lambda^2}{\lambda^2+2} \qquad (3)$$

where λ^2 is the ratio of hybridization, C_2^2/C_1^2. The anisotropic hyperfine structure of the $^{13}CO_2^-$ radical

Table 1. ESR parameters of CO_2^- radical adsorbed on the zeolites

CO_2^- radical on	g value			A value (gauss)			C_1^2	C_2^2	λ^2	Angle (θ)
	g_x	g_y	g_z	$A_\perp$	$A_{//}$	A_{iso}				
LiX (87.0%)	2.0036	1.9968	2.0036	118	160	132	0.111	0.653	5.88	138°
MgX (59.6% 42.8%)	2.0033	1.9989	2.0033	154	200	169	0.142	0.723	5.09	135°
CaX (96.4% 78.5%)	2.0026	1.9977	2.0026	151	199	167	0.140	0.746	5.33	136°
BaX (94.4% 70.9%)	2.0011	1.9948	2.0011	147	197	164	0.138	0.769	5.57	137°
NaX (—)[a]		$g_0=2.0011$			$A_0=133$					
KX (100%)		$g_0=2.0009$			$A_0=133$					
MgO[1]	2.0029	1.9974	2.0017	184	230	199	0.167	0.723	4.33	134°
SiO_2[a][2]	2.0024	1.9978	2.0024	190	215	204	0.172	0.256	1.49	116°

a) γ-Irradiation for 16 hr at room temperature in the presence of CO_2.

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observed at 77°K was analyzed in order to determine the OCO angle. The values of C_1^2, C_2^2, and λ^2 estimated from the spectra of the CO_2^- radicals adsorbed on the various zeolites are given in Table 1. The results on MgO[1] and SiO_2[2] are also listed in the table. The change in the value of θ, namely, the structural variation in the CO_2^- radical, has been ascribed to the difference in cation radius.[2] The charge of the cation as well as its radius, however, seems to affect the structure of the CO_2^- radical, as can be seen in Table 1.

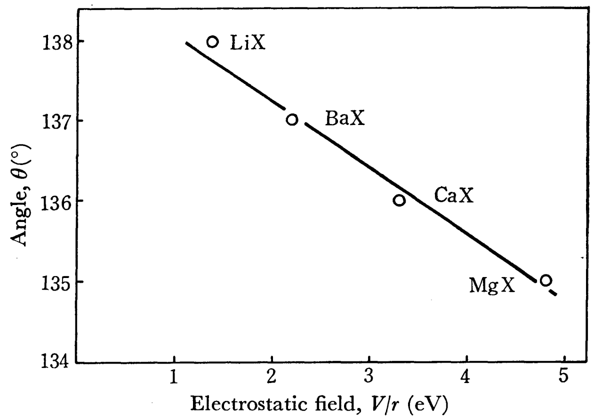

Fig. 1. Relationship between OCO angle of CO_2^- radical and electrostatic field on zeolites.

One aim of the present study is to investigate the interaction between the CO_2^- radical and the zeolite surface through the structural variation in the CO_2^- radical brought about by the change in the kind of cation on zeolite. Rabo *et al.*[14] have calculated the electrostatic fields characteristic of the cations on the zeolite surfaces. In Fig. 1, a good linear relationship can be seen between the electrostatic field on the zeolite surface and the OCO angle of the CO_2^- radical adsorbed on the zeolite. This means that the structure of the adsorbed CO_2^- radical is strongly affected by the electrostatic field; the OCO angle of the CO_2^- radical decreases as the charge of the cation increases or as its radius decreases. These results are consistent with those obtained by ESR studies of the CO_2^- radical trapped in formates.[5] However, the perturbation on the structure of the CO_2^- radical observed in this study is more remarkable than that in formates.

Motion of the CO_2^- Radical. In order to obtain some information on the interaction between the adsorbed CO_2^- radical and the zeolite surface, the motional behavior of the radical was investigated through the observation of the temperature variation in the spectrum of the $^{13}CO_2^-$ radical. It was found that the spectra of the radical on NaX and KX are isotropic even at 77°K, as can be seen in Figs. 2(a) and (b). There is little difference in these spectra, and their ^{13}C hyperfine coupling constants are both equal to 133G. Therefore, the CO_2^- radical on NaX and KX may be free from the cations on the zeolites and may still rotate or vibrate on the surfaces even at this temperature.[15] As may be seen in the figures, a signal having ΔH=10G and g=2.012 appeared. The same signal was observed when these zeolites were irradiated at 77°K in the absence of carbon dioxide. This may be ascribed to the hole generated by γ-irradiation, similarly to the cases of NaY reported by Stamires and Turkevich[16] and by Wang and Lunsford.[17] As regards LiX, the CO_2^- radical, as can be seen in Fig. 3, may weakly interact with the surface at 77°K.

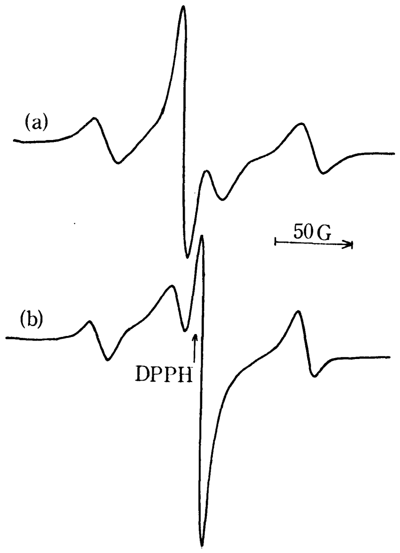

Fig. 2. ESR spectra of CO_2^- radical on (a) NaX and (b) KX at 77°K.

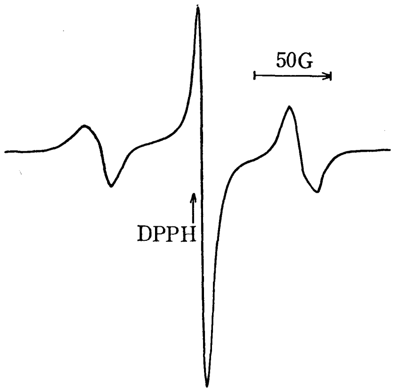

Fig. 3. ESR spectrum of CO_2^- radical on LiX at 77°K.

A distinct difference in the motion appeared on the zeolite exchanged with bivalent cations. The spectrum of the $^{13}CO_2^-$ radical on the MgX (59.6%) shown in Fig. 4 is anisotropic at 77°K. It was found, indeed, that the radical begins to rotate freely at about 200°K. When the sample was cooled down again from 298 to 77°K, the anisotropic spectrum was observed again; the spectral change is completely reversible with respect to the temperature variation. Also, the motion of the

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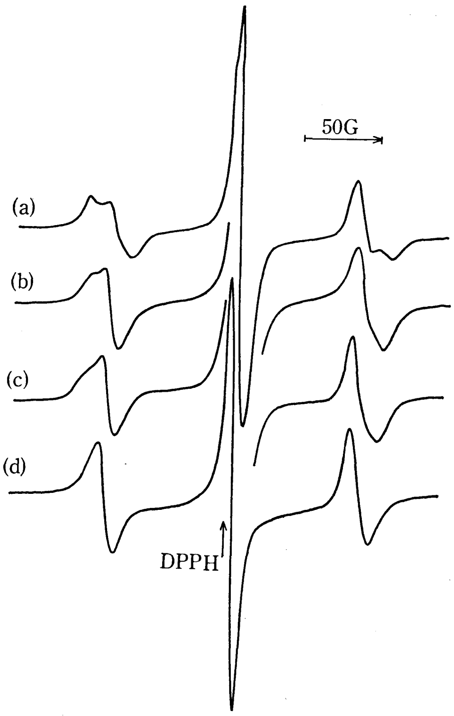

Fig. 4. ESR spectra of CO_2^- radical on MgX at (a) 77°K, (b) 180°K, (c) 190°K, and (d) 200°K.

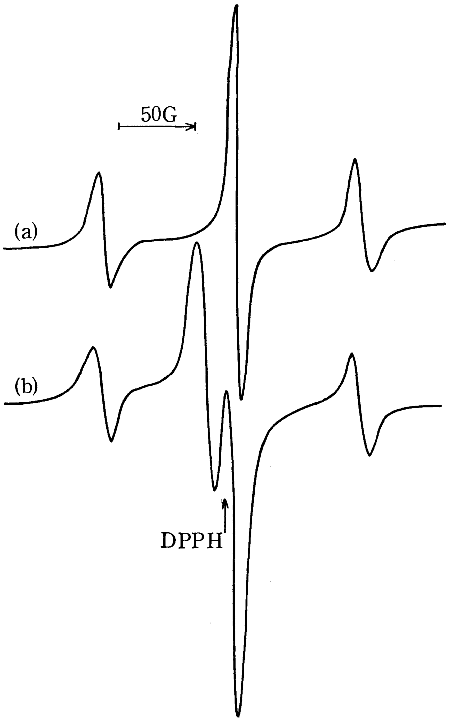

Fig. 6. ESR spectra of CO_2^- radical on MgX (a) at 298°K and (b) after standing for 48 hr at room temperature.

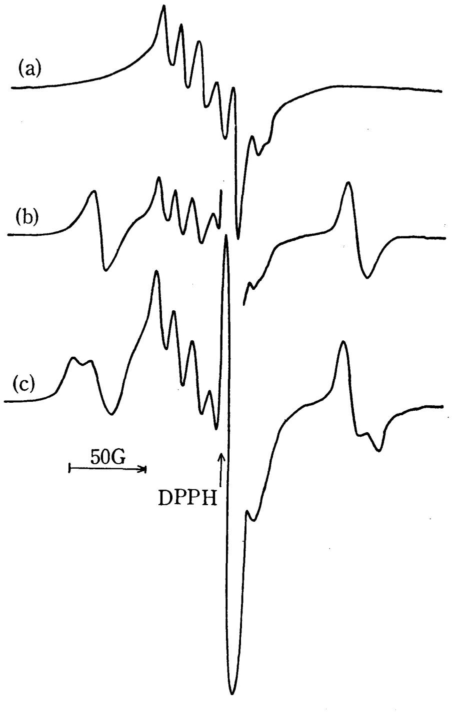

Fig. 5. (a) ESR spectrum of MgX irradiated for 2 hr at 77°K. (b) Spectrum of CO_2^- radical on pre-irradiated MgX at 298°K and (c) that at 77°K.

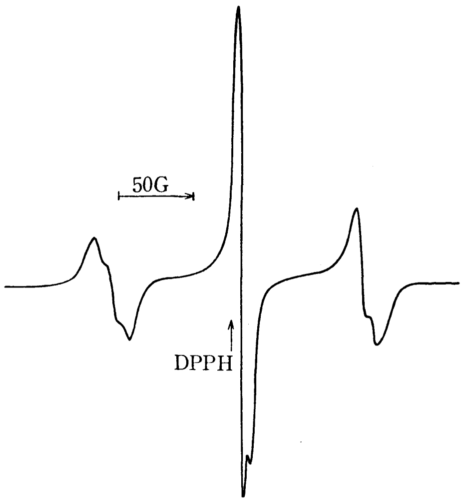

Fig. 7. ESR spectrum of CO_2^- radical on CaX (96.4%) at 77°K.

CO_2^- radical on pre-irradiated MgX was the same as that on post-irradiated MgX, as can be seen in Fig. 5. This indicates that the motional behavior of the CO_2^- radical on the zeolite is independent of the irradiation process.

The CO_2^- radical on the MgX was stable at room temperature for a few days, but bleached at about 420°K. However, an additional line (g=2.012) appeared after 48 hr at room temperature (Fig. 6(b)); the intensity of this line increased with a decrease in the intensity of the spectrum for the CO_2^- radical while it stood. This additional line may be due to the hole, as in the case of the zeolite irradiated in the absence of carbon dioxide, as has been described above. This increase in the amount of the hole may be accounted for by the electron capture of the CO_2^- radical in the process of the degradation of the radical. The anisotropic spectrum of the $^{13}CO_2^-$ radical on the CaX (96.4%) (Fig. 7) hardly changed between 77 and 420°K. This spectrum was still observed at 77°K even after the sample had been heated to 600°K in

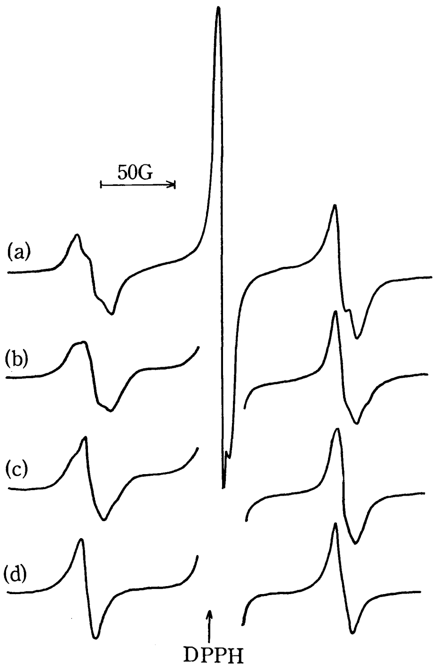

Fig. 8. ESR spectra of CO_2^- radical on CaX (78.5%) at (a) 77°K, (b) 127°K, (c) 150°K, and (d) 163°K.

a furnace. The same result was obtained in the case of BaX. This suggests that the adsorbed CO_2^- radical strongly interacts with the zeolite surfaces and is stabilized on them. Such a stable anisotropic spectrum as obtained on the CaX or BaX could not be observed on the MgX, though the electrostatic field caused by the Mg^{2+} ion is generally expected to be stronger than that caused by the Ca^{2+} or Ba^{2+} ion.[14,18,19] This contradiction may be interpreted in terms of the very low degree of ion exchange on MgX, compared with that on CaX or BaX.

In this view, a series of zeolites differently exchanged by bivalent cations were investigated. For instance, the motional behavior of the radical adsorbed on CaX (78.5%) can be deduced from Figs. 8(a)—(d). The $^{13}CO_2^-$ radical on a zeolite with a lower degree of cation exchange shows almost the same spectrum as that on the zeolite with a higher exchange degree at 77°K, but the temperature at which the radical begins to move or bleach depends remarkably upon the exchange degree, as can be seen in Table 2. That is, an almost complete exchange with a cation such as Ca^{2+} or Ba^{2+} greatly restricts the motion of the radical. All the radicals adsorbed on zeolites of lower degrees of exchange bleach below room temperature. It can be deduced from these phenomena that the electrostatic field influences the motion of the CO_2^- radicals more effectively than the perturbation on the structure of the CO_2^- radicals.

TABLE 2. BEHAVIORS OF CO_2^- RADICAL ADSORBED ON THE ZEOLITES

CO_2^- radical on	Temperature at which the radical begins to		Decay time at R.T.
	rotate, °K	bleach, °K	
LiX (87.0%)	118	258	—
MgX (59.6%)	200	423	a few days
(42.8%)	116	252	—
(59.6%)[a]	202	—	a few days
CaX (96.4%)	420	420	a few months
(78.5%)	163	253	—
BaX (94.4%)	420	420	a few months
(70.9%)	179	271	—

a) Pre-irradiation for 2 hr at 77°K.

The Reaction of Carbon Dioxide with γ-Irradiated Zeolites. Wang and Willard[3] have reported that the addition of carbon dioxide to γ-irradiated silica gel results in the formation of the O_2^- radical, though the CO_2^- radical is formed on the post-irradiated gel, while Yamada *et al.*[2] have found that the latter radical is formed on the pre-irradiated gel. In the present study, the CO_2^- radical was generated on both post- and pre-irradiated zeolites. The results obtained in the case of MgX (59.6%) are shown in Figs. 4 and 5. On the other hand, a hyperfine structure attributed to the interaction of the trapped electron with the aluminum nucleus[16,17] was observed on irradiated MgX in the absence of carbon dioxide, as is shown in Fig. 5(a). However, when the MgX was irradiated in the presence of carbon dioxide, the hyperfine structure due to the ^{27}Al nucleus could not be observed. This can be interpreted as follows: the electrons formed during the irradiation are preferentially captured by the carbon dioxide molecule because this molecule traps electrons more deeply than aluminum does. Thus, the CO_2^- radical may be formed relatively easily on the surface of irradiated zeolite. In the cases of NaX and KX, no CO_2^- radical was observed when they were irradiated at 77°K, but it was generated by irradiation at room temperature. It may be deduced from these observations that the amount of trapped electrons formed during the irradiation is small, or that the ability to transfer the trapped electron to the carbon dioxide molecule is weak, at 77°K. Upon irradiation for 16 hr at room temperature, the amounts of sites sufficient to form the radicals may be obtained. Further work will be needed in order to discuss these sites.

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