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ESR Study on Molecular Motion of CO_2^- Radical Adsorbed on Zeolite

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Synopsis. Molecular motion of $^{13}CO_2^-$ radical adsorbed on zeolite was quantitatively analysed from the temperature variation of the separation of hyperfine structure of ESR spectra from $^{13}CO_2^-$ radicals.

CO_2 molecules enriched with ^{13}C were adsorbed on a Linde X-type zeolite, which had been heat-treated at 500 °C for 5 hr. Free radicals were produced from the adsorbed CO_2 by γ irradiation. ESR spectra of these systems were reported by one of the authors (K.S.) and his collaborators.[1] They found that the spectra change with temperature. In the ESR spectra consisting of three bands, the central part is the spectrum originated from the $^{12}CO_2^-$ radical and the wings are the doublet ascribed to the ^{13}C ($I=1/2$) coupling of $^{13}CO_2^-$ radical. The wings of the spectrum observed at 77 K show the so-called amorphous pattern,[2] the characteristic line-shape for an anisotropic hyperfine (hf) coupling of radicals trapped in an amorphous matrix. This pattern can be simulated by the program of Lefebvre and Maruani.[3] The principal value of the hf coupling tensor giving the best fit pattern to the observed one at 77 K were obtained as $A_x=150.0$ G, $A_y=156.0$ G, $A_z=197.5$ G. The principal values of the hf coupling tensors of the spectra observed at temperatures 180, 190, and 200 K were determined in a similar way and are listed with other ESR parameters in Table 1.

TABLE 1. THE PRINCIPAL VALUES OF THE g-TENSOR AND THE A-TENSOR, AND THE LINE WIDTH $\Delta H_{1/2}$, WHICH GIVE THE BEST FIT TO THE OBSERVED LINE-SHAPE, AND THE CORRELATION TIMES τ

Temp.	g-tensor		A-tensor (G)		ΔH (G)	$\tau\times 10^8$ (s)
77 K	g_x	1.9975	A_x	150.0	5.5	
	g_y	2.0032	A_y	156.0		
	g_z	2.0015	A_z	197.5		
180 K	g_x	1.99998	A_x	154.1	7.0	4.29
	g_y	2.00155	A_y	158.7		
	g_z	2.00073	A_z	190.7		
190 K	g_x	2.00073	A_x	157.5	7.0	2.09
	g_y	2.00073	A_y	161.0		
	g_z	2.00073	A_z	185.0		
200 K	g_x	2.00073	A_x	160.0	7.0	1.34
	g_y	2.00073	A_y	162.6		
	g_z	2.00073	A_z	180.9		

ESR spectra of free radicals produced from adsorbed CO_2 are shown in Fig. 1. The shapes of the wings of the spectra become more isotropic with increasing temperature. At 77 K the CO_2^- radicals are almost completely frozen, the anisotropy of the coupling tensor being clearly observed. At 200 K no shoulder appears in the wing peaks and the doublet appears nearly symmetrical. The symmetric pattern indicates that the anisotropy of the hf coupling tensor is almost averaged out by the random motion of the adsorbed radicals at such a high temperature. The results indicate that the radicals adsorbed on the zeolite become more mobile at higher temperatures. In the process from the frozen state to the mobile one, *i.e.* in the temperature range 77—200 K, the anisotropy of the coupling tensor is partially averaged due to the gradually activated molecular motion of the radical. We can obtain quantitative information on the molecular motion of the adsorbed radical from the observed partial averaging of the anisotropic hf coupling tensor, based on the theory developed by Moriuchi and Sohma.[4] According to their theory partial averaging of each principal value of the hf coupling tensor is given by

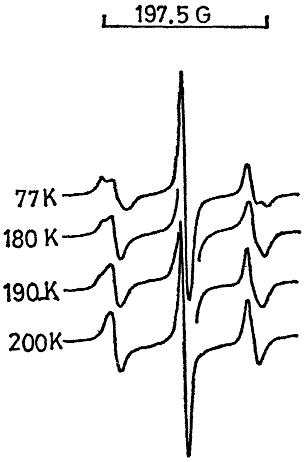

Fig. 1. Temperature variation of observed spectra of the CO_2^- radicals adsorbed on zeolite. The separation of the outermost peaks, 197.5 G, at 77 K, corresponds to the A_z principal values of the hyperfine coupling tensor.

$$\langle A_x\rangle_{Av} = a + A_{xo}\frac{2}{\pi}\tan^{-1}\frac{\tau}{T_2'}$$

$$\langle A_y\rangle_{Av} = a + A_{yo}\frac{2}{\pi}\tan^{-1}\frac{\tau}{T_2}$$

$$\langle A_z\rangle_{Av} = a + A_{zo}\frac{2}{\pi}\tan^{-1}\frac{\tau}{T_2'}$$

where a is the isotropic component of the coupling constant, A_x, A_y and A_z are the principal values of the

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hf coupling tensor, and A_{x0}, A_{y0} and A_{z0} the anisotropic components of each principal value in the completely frozen state; τ is the correlation time of the molecular motion and T_2' is related to the inverse of the experimentally determined line width, that is $T_2'=1/\pi\cdot\Delta H_{1/2}$ in Lorentzian line-shape, $T_2'=(\ln 2/\pi)^{1/2}\ 1/\Delta H_{1/2}$ in the Gaussain one. Experimentally determined principal values of the hf coupling tensor at each temperature result from partial averaging of the anisotropic hf coupling tensor due to the molecular motion of the responsible radical, $^{13}CO_2^-$ in this case, at this temperature. The isotropic coupling constant a was experimentally obtained by the equation $a=1/3(A_x+A_y+A_z)$ and the observed values of each component at 77 K, since one can assume that molecular motion at 77 K is completely frozen. T_2''s are determined from the line widths, experimentally determined by simulation with the observed spectrum at each temperature. The results are listed in Table 1. Since the peak corresponding to A_z appears most clearly in the doublet and changes distinctly with temperature, we used the observed value of the A_z-component at each temperature in order to estimate τ at this temperature. The correlation times are plotted against $1/T$ in Fig. 2. The activation energy for this molecular motion of the adsorbed CO_2^- radical on the zeolite was determined to be 4.1 kcal/mol.

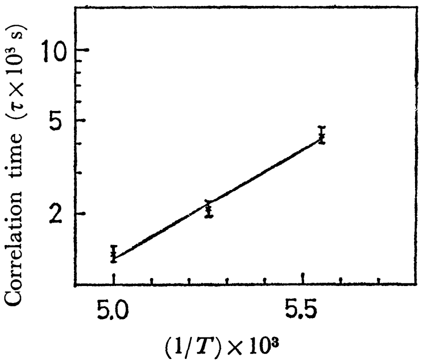

Fig. 2. The Arrhenius plot of the correlation times estimated from the partial averaging of the A_z component.

The observed ESR spectra and their analysis give us quantitative information on the molecular motion of the adsorbed CO_2^- radicals on the zeolite. The molecular motion of the adsorbed CO_2^- is completely hindered at 77 K but liberated gradually from 180 K until free random motion is attained at 200 K.

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