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Carbon-13 Nuclear Magnetic Relaxation Studies of Benzene Molecules Adsorbed on the Pillar Interlayered Montmorillonite

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Carbon-13 nuclear magnetic relaxation times of ^{13}C-enriched benzene have been determined in order to elucidate the adsorption properties of PILM (pillar interlayered montmorillonite) by varying temperatures and coverages. The activation energy of diffusion as small as 6.5 kJ mol^{-1} indicates that the majority of PILM adsorption sites exhibits a weak interaction with benzene. The pre-exponential factor of correlation time was exceptionally large, probably because the two-dimensional pore structure of PILM, in contrast to the three-dimentional zeolite or the open surfaces of graphitized carbon black and silica gel, restricts the chance for the adsorbate to diffuse. In the spin-lattice relaxation spectra at low temperatures, the internal and the external surfaces of PILM were discriminated, since the two adsorbed states on these surfaces give different T_1 and chemical shift values.

In recent years, there has been a growing interest in sheet silicates or aluminosilicates such as montmorillonite, vermiculite, kaolinite, and halloysite. The advantage of using montmorillonite is the easiness to accept an intercalating substance and to control the size of the generated interlayer (micropore) compared with the other clay minerals. Thus organic reactant molecules introduced into the interlayer space may undergo novel types of chemical reactions.[1)]

The basic layer structure of montmorillonite is threefold, consisting of a gibbsite Al_2O_3 layer (the octahedral layer) sandwiched by two $Si_2O_5^{2-}$ sheets (the tetrahedral layer). In the octahedral layer a part of the Al^{3+} ions are randomly substituted with Fe^{3+} or Mg^{2+} ions, the lack of the lattice charge being balanced with exchangeable cations (usually Na^+).

Thermal stability is endowed by substituting the exchangeable Na^+ with $[Al_{13}O_4(OH)_{24+x}(OH_2)_{12-x}]^{7-x}$ followed by a calcination treatment, since this polynuclear inorganic cation acts as a pillar substance and forms an interlayer network. Extensive investigations have been made on catalytic[2)] and adsorption[3)] properties of this new type of compound, *i.e.*, pillar interlayered montmorillonite (PILM).

As well established by the diffusion and shape-selective properties of zeolite,[4)] the mobility of molecules inside the pore is essentially important for catalysis and adsorption. Not only the mobility of molecules but also various interactions of the adsorbed molecules with the surfaces and other neighboring molecules are well elucidated by NMR relaxation measurements.[5—9)] In the present work ^{13}C nuclear magnetic relaxation study has been performed for the molecular dynamics of benzene adsorbed on PILM in order to gain a deeper insight into the characteristics of intercalation compounds.

Experimental

Montmorillonite. Otay montmorillonite, supplied from Ward's Natural Science Establishment, Inc., was used; the fraction less than 2 μm in diameter was separated by gravity sedimentation in water dispersion.

Intercalation. An aqueous solution of $AlCl_3$ (0.3 mol dm^{-3}) was vigorously stirred under reflux, followed by a slow dropwise addition of NaOH (1.0 mol dm^{-3}), until the OH/Al ratio of the solution became 2.37;[10—12)] by this procedure the polynuclear cation, $[Al_{13}O_4(OH)_{24}(OH_2)_{12}]^{7+}$,[13)] was formed. The resultant solution was added dropwise to the refluxing water suspension of montmorillonite (3%) upto about five times as much as the total cation exchange capacity (*ca.* 1 meq. g^{-1}) of montmorillonite. The boiling slurry was aged for 2 h, filtered, and washed with distilled water until Cl^- ions were undetected by the $AgNO_3$ test. The product was dried in an oven overnight at 393 K, calcined in air at 673 K for 2 h, and then kept in a desiccator containing the saturated aqueous solution of NH_4Cl. A schematic view of pillar interlayered montmorillonite (PILM) is shown in Fig. 1.

Nitrogen adsorption isotherm obeyed the Langmuir-type equation at 77 K for PILM, which was pretreated overnight under vacuum ($<10^{-1}$ pa) at 393 K. The surface area of 290 m^2 g^{-1} thus obtained was much larger than the external surface area of 40 m^2 g^{-1}, determined with the α_s-plot.[14)] The d-spacing (c_0) of PILM was 1.80 nm, whereas the interlayer spacing was 0.84 nm.[3)] This magnitude is acceptable because the pillar diameter is *ca.* 0.9 nm.[10)] These results support the view of PILM microporosity, with the structure shown in Fig. 1.

NMR Measurements. 0.4 g (dry basis) of PILM was placed in a Pyrex NMR sample tube (10 mm O. D.) and fixed with a Teflon plug. After the heat treatment at 393 K under vacuum ($<10^{-3}$ Pa) overnight, a given amount of gaseous dosage of ^{13}C-enriched (89%) benzene, supplied from Molécules Marquées France, was introduced to the sample at room temperature; the monolayer capacity of benzene on PILM (1.81 mmol g^{-1} at $\theta=1$) was determined from the adsorption isotherm at 298 K. In order to seal off the sample tube without losing any benzene molecule present in the vapor phase, the sample was frozen with liquid nitrogen.

^{13}C-NMR measurements were carried out at 15.04 MHz using a pulsed Fourier-transform spectrometer (Jeol JNX-FX60Q). The spectra of phisically adsorbed benzene were obtained as easily as liquid benzene with, however, about 100 times broader line width. Spin-lattice relaxation times T_1 were determined by the inversion recovery method following a π-t-$\pi/2$ pulse sequence.[15)] Spin-spin relaxation times T_2 were measured by means of the Carr-Purcell-Meiboom-Gill method under conditions of non-spinning and non-^{1}H-decoupling, which are required for this type of measurements.[16)] The absolute value spectra, $(u^2+v^2)^{1/2}$, instead of the conventional absorption ones, v,

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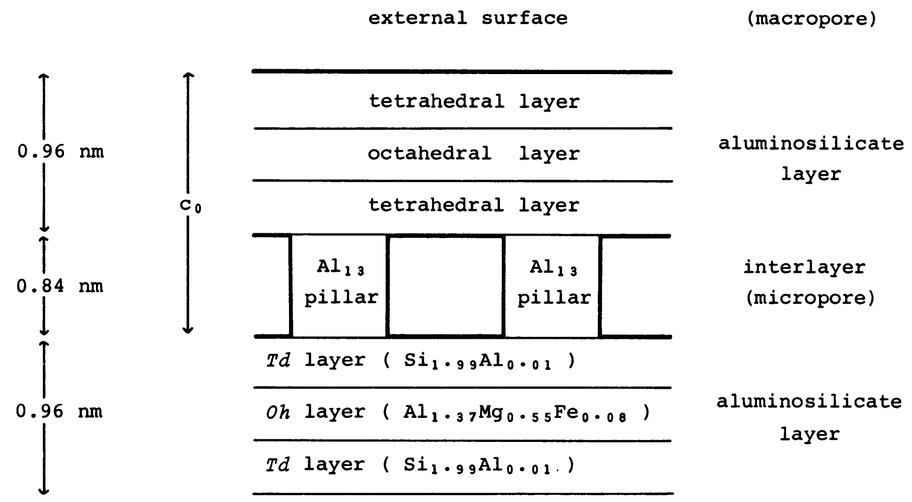

Fig. 1. Schematic view of pillar interlayered montmorillonite (PILM).

were adopted in determining T_2.[17] If not otherwise stated, the longitudinal and transversal relaxation were treated as purely exponential. The sample temperature was stabilized within the range of ±1 K (181—327 K).

Results and Discussion

NOE and Relaxation Mechanism. It was confirmed that the NOE (nuclear Overhauser enhancement) was unity (no enhancement of signal intensity under conditions of ^{1}H decoupling) for all the studied samples of benzene adsorbed on PILM. This fact clearly indicates that the ^{1}H–^{13}C dipolar interaction is completely ineffective[18] for the ^{13}C relaxation of the adsorbed benzene. Although high ^{13}C-enrichment in benzene (89%) may bring about the ^{13}C–^{13}C dipolar interaction, this interaction is much weaker than the ^{1}H–^{13}C dipolar interaction owing to a lower gyromagnetic ratio and a longer internuclear distance. Thus, the dominant mechanism for the relaxation is ascribed to the dipolar interaction with paramagnetic species. This view is supported by the quite high level of Fe^{3+} impurities in the aluminosilicate layer of PILM (13,000 ppm); it was pointed out for propene adsorbed on cation-exchanged X and Y type zeolites that NOE fell down to unity, when the Fe^{3+} content became beyond 700 ppm.[19]

Chemical Shift and Line Width. Figure 2 shows typical temperature dependence of the spectra (θ=0.23) for benzene adsorbed on PILM. Small resonance shift for the adsorbed benzene (about 1 ppm to higher field referred to the liquid) was observed for the adsorption coverage of $0.016 \leqq \theta \leqq 1.0$ within the limits of experimental error (±0.5 ppm). Since the order of magnitude of this shift is covered within the range of necessary corrections for medium effects, no further remarks will be given. It is apparent from Fig. 2 that the higher the temperature is, the narrower the width of the ^{13}C resonance is. This phenomenon is in accord with "motional narrowing",[18] and commonly observed for all other samples (θ=0.016, 1.0, and 1.9).

Figure 3 presents the effect of adsorption coverage (θ) on the spectra at 302 K.

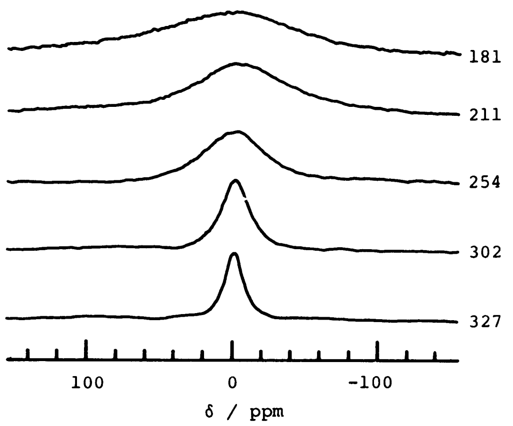

Fig. 2. ^{13}C-NMR spectra of benzene adsorbed on PILM (θ=0.23) as a function of temperature. Resonance frequency: 15.04 MHz. Standard for δ: liquid benzene.

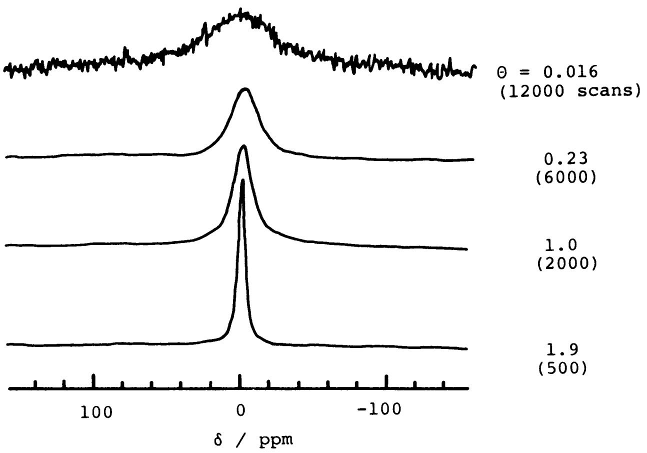

Fig. 3. ^{13}C-NMR spectra of benzene adsorbed on PILM as a function of coverage.
Temperature: 302 K. Resonance frequency: 15.04 MHz. Standard for δ: liquid benzene.

The trend of marked broadening of the resonance peak caused by the decrease of θ was noticed at all the

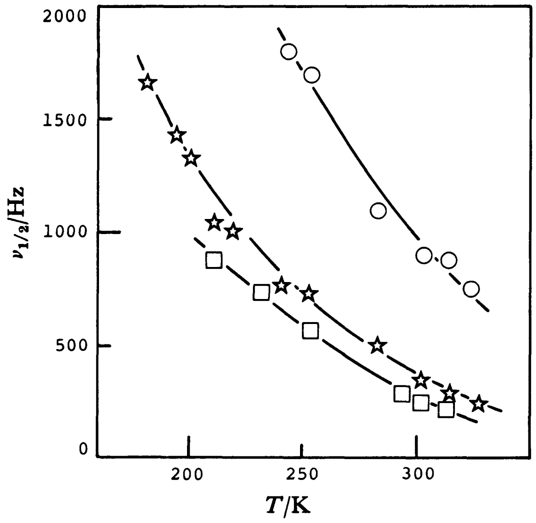

Fig. 4. Temperature dependence of ^{13}C-NMR half-height width ($\nu_{1/2}$) for benzene adsorbed on PILM. ○: θ=0.016, ☆: θ=0.23, □: θ=1.0.

temperature studied. Referred to the temperature dependence described above, the translational motion is considered to become more restricted as θ decreases (*vide infra*). The half-height width data are shown in Fig. 4.

Longitudinal and Transverse Relaxation Times. In order to consider the motional behavior of benzene adsorbed on PILM more precisely, we measured T_1 and T_2 varying both temperature and adsorption coverage θ. At higher coverage (θ=1.0, 1.9) T_1's were determined from the beginning of the decay ($0 \leqq t \leqq 2T_1$), since the relaxation functions were deviated from the exponential type at the later stage of the decay. The results of these measurements are summarized in Fig. 5.

Longitudinal and transverse relaxation times for the dipolar relaxations of ^{13}C near a paramagnetic center are given by[5,6,20,21]

$$\frac{1}{T_1} = \frac{\gamma_I^2\gamma_S^2\hbar^2 S(S+1)}{15 r_{IS}^6}\left(\frac{6\tau_c}{1+\omega_I^2\tau_c^2}\right) \qquad (1)$$

$$\frac{1}{T_2} = \frac{\gamma_I^2\gamma_S^2\hbar^2 S(S+1)}{15 r_{IS}^6}\left(4\tau_c+\frac{3\tau_c}{1+\omega_I^2\tau_c^2}\right) \qquad (2)$$

where γ is gyromagnetic ratio, $\omega_I = \gamma_I H_0$ resonance frequency of nuclear spin I, r_{IS} distance between the spins I and S, and τ_c correlation time for the diffusion of the adsorbate (the time between molecular jumps). Eqs. (1) and (2) imply $\omega_S \gg \omega_I$ and $\tau_{Si} (\simeq 10^{-6}\ \text{s}) \gg \tau_c$ (i=1,2), where $\omega_S = \gamma_S H_0$ is resonance frequency of electron spin S and τ_{Si} means the electron spin relaxation time.

Scalar interaction is prohibited, because Fe^{3+} ions are included only in the octahedral layer which is separated from the interlayer (micropore) by the tetrahedral layer.

As revealed in the systematic change of T_1 with adsorption coverage (Fig. 5), the mobility of benzene molecule is more restricted at a given temperature as the coverage is lowered, indicating the presence of strong adsorption sites on PILM. The amount of this site is certainly limited, since the change of T_1 is larger for θ=0.23→0.016 than for θ=1.0→0.23.

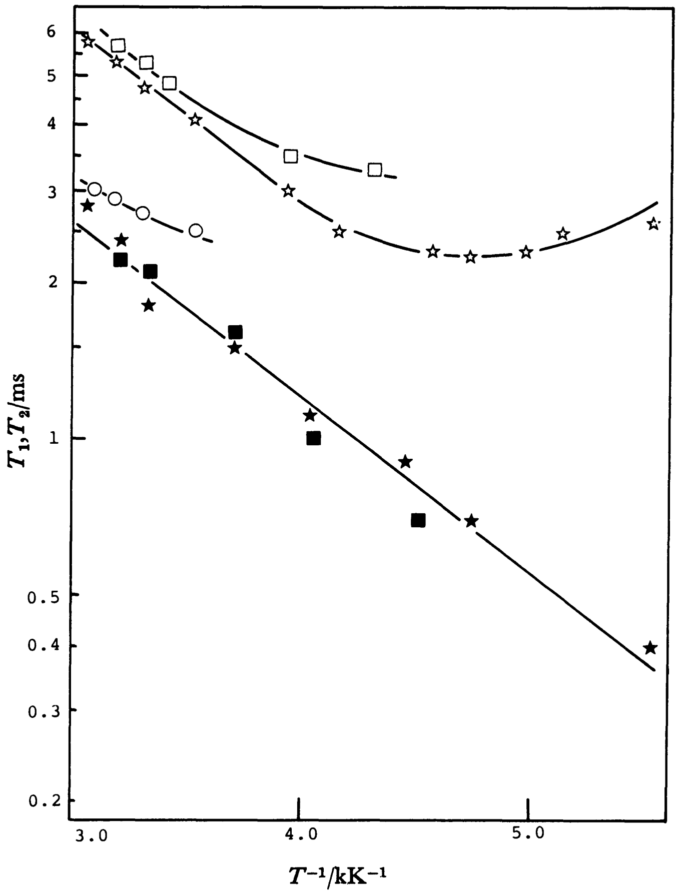

Fig. 5. Temperature dependence of ^{13}C relaxation times of benzene adsorbed on PILM; T_1 and T_2 indicated by open and solid symbols, respectively. ○: θ=0.016, ☆,★: θ=0.23, □,■: θ=1.0.

A similar behavior was reported for benzene adsorbed on silica gel.[22] However, an inverse trend was pointed out for cyclohexane adsorbed on NaY-zeolite, where intermolecular hindrance between cyclohexane molecules became dominant rather than particular interactions with adsorption sites, as the pore filling factor increased.[21]

Low-temperature T_1 measurements for θ=0.016 and θ=1.0 were encountered with experimental difficulties due to severe line broadening and peak separation (*vide infra*), respectively. However, a rather flat minimum of T_1 is clearly seen for θ=0.23 (Fig. 5), which suggest a distribution of correlation times.[6] Resing showed that many experimental data were put in order by the assumption of correlation times with a logarithmic Gaussian distribution:[5]

$$\tau_c' = \tau_c \exp\{(E' - \langle E\rangle)/RT\}$$

with

$$\tau_c = \tau_0 \exp(\langle E\rangle/RT)$$

and

$$\beta = [2\langle\{(E' - \langle E\rangle)/RT\}^2\rangle]^{1/2}$$

where E' is the activation energy of the motional pro-

TABLE 1. TRANSLATIONAL MOBILITIES OF BENZENE IN ADSORBED AND LIQUID STATES

System or adsorbent		$E^{a)}$/kJ mol^{-1}	$10^8\tau_c{}^{b)}$/s	$10^{12}\tau_0{}^{c)}$/s	Ref.
liquid	—	13	0.0015$^{d)}$	0.0089	26
graphitized carbon black	$\theta=1$	15	0.089	0.17	23
NaY-zeolite	$\theta=0.2$	16	40	42	25
	$\theta=0.83$	23	260	4.9	
silica gel	A site (4%)	13.4	3.0	14	27
	B site (15%)	7.7	0.16	19	
	C site (81%)	1.5	0.014	59	
PILM	$\theta=0.23$	6.5	1.1	270	this study

a) Activation energy for translational diffusion. b) Correlation time for translational diffusion at 210 K. c) Pre-exponential factor of τ_c. d) Extrapolated to 210 K in the equation for liquid benzene: $\tau_c=8.9\times10^{-15}\exp(1.3\times10^4/RT)$.

cess, $\langle E\rangle$ is the average value of E', R is the gas constant, and T is the absolute temperature. A theoretical curve was given for the relationship between β and the ratio T_1/T_2 at the minimum of T_1.[6] $T_1/T_2=1.83$ corresponds to $\beta=0$ with one correlation time. On the other hand, the value of 3.3 observed in this case leads to $\beta=1.3$, which supports the view that the correlation times are distributed within a certain range. On the basis of $\omega_I\tau_c=1$ at the minimum of T_1, τ_c was obtained as 1.1×10^{-8} s at 210 K.

As shown in Fig. 5, a linear relationship was observed between T_1 or T_2 and the reciprocal absolute temperature in the high temperature range ($\omega_I^2\tau_c^2\ll1$). Since T_1 and T_2 are inversely proportional to τ_c in this region, the activation energy for diffusion $\langle E\rangle$ ($=E$) is therefore able to be determined from the temperature dependence of the relaxation times. From the T_1 measurements for $\theta=0.23$, the value of 6.5 kJ mol^{-1} was obtained. The validity of this value was confirmed, for the same value was obtained from the T_2 measurements in the whole temperature range studied.

Translational Mobilities of Benzene Molecules in the Adsorbed and the Liquid States. Table 1 summarizes translational mobilities of benzene molecules in the adsorbed and the liquid states. Benzene molecules adsorbed on the graphitized carbon black ($\theta=1$) are as mobile as liquid, probably due to the geometrical and electronic similarities between benzene and graphite.[23] Difference in the pre-exponential factor τ_0 may reflect the spatial limitation of motion in the adsorbed state.

Benzene molecules adsorbed in the supercage of NaY-zeolite are known to be extremely restricted in mobility. The adsorption center for benzene has been ascribed to the sodium ions at the S_{II}-sites (maximam number of 4 per supercage).[8,24] As a consequence of mutual hindrance between the adsorbed molecules, E increases with θ, exhibiting the largest E value of 23 kJ mol^{-1} at $\theta=0.83$.[25]

The activation energy of 6.5 kJ mol^{-1} for PILM at $\theta=0.23$ is small, probably because the interaction of benzene with the surface sites is weak comparable to those for B and C sites of silica gel.[27]

On the contrary, the observed pre-exponential factor τ_0 for benzene molecules absorbed on PILM was exceptionally larger than those on silica gel and NaY-zeolite. With regard to NaY-zeolite, a similar value was obtained for cyclohexane (1.5×10^{-12} s) as small as benzene (4.9×10^{-12} s), reflecting its geometrical structure.

The activation energy and the pre-exponential factor of diffusion for benzene adsorbed on NaX-zeolite were reported as 25 ± 7 kJ mol^{-1} and 8.2×10^{-4} cm^2 s^{-1}, respectively.[28]

The pre-exponential factor of the correlation time τ_0 is known to be related to that of diffusion D_0 by

$$\tau_0 = \langle l^2\rangle/6D_0$$

where $\langle l^2\rangle$ is the mean square jump length in diffusion. From the references of τ_0[25] and D_0[28], the value of $(\langle l^2\rangle)^{1/2}$ was deduced to be 1.5 nm, which is reasonable in magnitude from the geometrical viewpoint of NaX and NaY-zeolites. Provided that the magnitude of $\langle l^2\rangle$ of benzene on PILM is similar to that on NaY (NaX)-zeolite, the value of D_0 would become obviously smaller for PILM than for the zeolite. The two-dimensional lamellar structure of PILM seems to afford less chance for the adsorbed molecules to diffuse in contrast to the three-dimensional framework structure of NaY-zeolite.

Adsorption Sites on PILM. Besides the silanol and the abundant siloxane groups, possible candidates to be mentioned as the surface adsorption sites of PILM are as follows: (i) the exchangeable cations such as Na^+ and Ca^{2+} in the interlayer, (ii) the hydroxyl groups on the alumina pillar surface, (iii) the Al^{3+} ions as the substituting elements of the $Si_2O_5{}^{2-}$ network in the tetrahedral layer, and (iv) Lewis acid sites generated as the oxygen vacancies on the alumina pillar surface. The amounts of the exchangeable cations (i) and the hydroxyl groups on the pillar surface (ii) were estimated as 0.19 and 5 mmol g^{-1}, respectively, whereas the Al^{3+} ions in the tetrahedral layer (iii) amounted only to 0.049 mmol g^{-1}.[3] Since the amount of the strong adsorption sites is a little larger or smaller than $\theta=0.016$ (0.029 mmol g^{-1}) and at least far smaller than $\theta=0.23$ (0.42 mmol g^{-1}) (*vide ante*), the Al^{3+} ions in the tetrahedral layer as well as the oxygen vacancies on the alumina pillar surface introduced by the heat treatment could be the candidates of the strong adsorption sites. It is also highly probable that all these adsorption sites on PILM are related to the distribution pattern of the observed E and τ_c values.

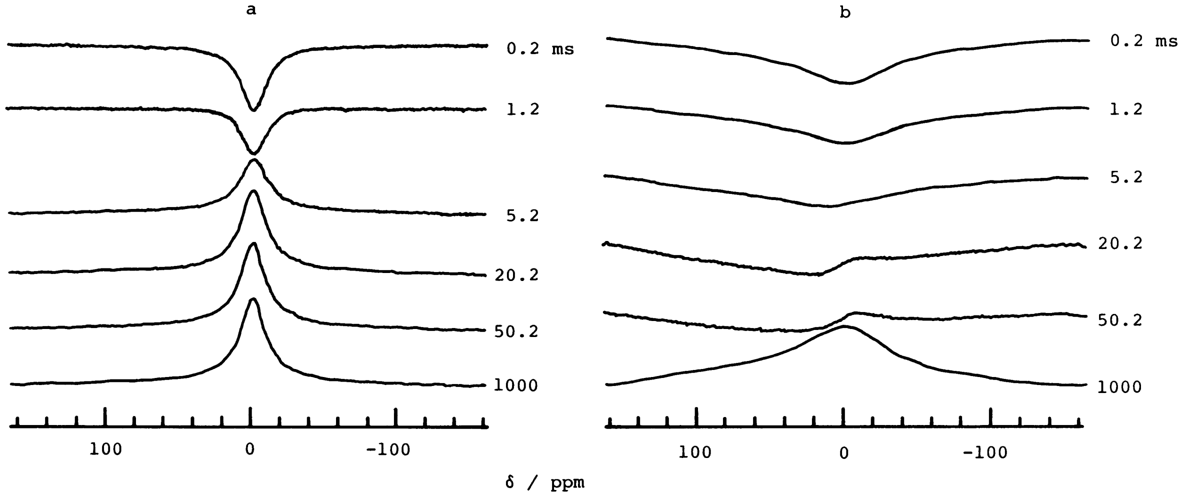

Fig. 6. ^{13}C spin-lattice relaxation spectra of benzene adsorbed on PILM (θ=1.9) at the temperatures of 282 K (a) and 220 K (b).
Resonance frequency: 15.04 MHz. Pulse sequenne: π-t-$\pi/2$. Standard for δ: liquid benzene.

Discrimination of Internal and External Surfaces. For lamellar adsorbents, discrimination of internal surface (micropore) and external surface (macropore) under dynamic conditions is important especially in relation to catalytic properties. Difference in T_1 between the adsorbed states enables peak discrimination in the spin-lattice relaxation spectra, which were observed for the samples with θ=1.0 under 203 K and θ=1.9 under 234 K. Illustrative spectra are presented in Fig. 6 (θ=1.9). It is apparent from Fig. 6 that there exist two peaks with different relaxation rates at 220 K, and that they are coalesced at 282 K into a single peak at the middle position. Accurate chemical shifts were determined from the absolute-value display of the spectra.

The high-field peak ($\delta \simeq -2$ ppm) exhibited shorter T_1 ($\simeq$7 ms) and narrower $\nu_{1/2}$ ($\simeq$1000 Hz) than the low-field peak ($\delta \simeq 8$ ppm, T_1>100 ms, $\nu_{1/2} \simeq 1700$ Hz). We assign the former to benzene molecules adsorbed in the micropore, and the latter to those adsorbed on the external surface on the basis of the following results. In the case of θ=1.0, the intensity of the low-field peak were very similar to those obtained for θ=0.23, whereas the pattern of exceedingly long T_1 and large $\nu_{1/2}$ exhibited in the low-field peak was quite exceptional.

Since long T_1 is indicative of high mobility, the low-field peak is naturally assigned to the external surface adsorption. At higher temperature than 254 K, discrimination of the two adsorbed states became difficult due to the onset of free exchange.

We consider that the NMR spin-lattice relaxation spectra of adsorbed molecules on intercalation compounds are useful to characterize the adsorbate mobility as well as the adsorption sites.

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