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^{13}C and ^{1}H MAS NMR Study of Benzene and *p*-Xylene in Zeolites and a Mesoporous Material FSM-16

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^{13}C and ^{1}H MAS NMR spectra have been measured at room temperature for benzene and *p*-xylene adsorbed in H-ZSM-5, Na-, and H-type mordenites with different Si/Al_2 ratios, H-Y, Na-Y, Na-X, and FSM-16 to study the dynamics of the guest species in the host materials. The second moments M_2 evaluated from the SSB intensity in ^{13}C CP/MAS NMR spectra were used to predict the motion of the guest species. Benzene molecules rotate about the C_6 axis freely, and reorientation of the C_6 axis takes place in H-ZSM-5. The para axis of *p*-xylene molecule is fixed in H-ZSM-5. The reorientations of the guest species become isotropic in the faujasite-type zeolites, Na-Y, H-Y, and Na-X. In FSM-16, translation diffusion takes place in addition to the isotropic rotation like in the liquid state. The mobilities of benzene molecules are in the following order, mordenite < H-ZSM-5 < Na-Y < Na-X < H-Y < FSM-16, while those of *p*-xylene molecules are in the following order. H-ZSM-5 < mordenite < Na-Y < Na-X ≈ H-Y < FSM-16. There is a good correlation between the pore size and the mobility of the guest species, with the exception of the mordenite/benzene systems.

Zeolites have highly-ordered micropores, which are suitable for many applications such as molecular sieving, cation exchange, catalyst, and quantum confinement of guest compounds.[1] Recently, mesoporous materials such as FSM-16 and MCM have been synthesized,[2,3] which have pores with diameters of several nanometers.

Various kinds of organic molecules can enter into the pores of the above materials. NMR is a powerful method to study the dynamics of the guest species as well as the structure on an atomic scale. Benzene and *p*-xylene adsorbed in zeolites are systems extensively studied. Many works have used ^{2}H NMR to investigate the dynamics of the guest molecules,[4—14] while few reports using ^{13}C NMR have been published.[15—17] Some works have used ^{1}H NMR,[8,9,18] which gave supplementary information.

The present work uses ^{13}C magic-angle-spinning (MAS) NMR in addition to ^{1}H MAS NMR, and wants to discuss the dynamics of guest molecules. Those methods have been applied to benzene and *p*-xylene adsorbed in various zeolites and FSM-16. The guest compounds with natural abundance of ^{13}C have been used, demonstrating the sensitivity of ^{13}C NMR. Cross polarization (CP) from ^{1}H to ^{13}C is used to evaluate the residual dipole–dipole interaction between them, which is averaged partially by the motion of the guest species. Comparison of the signal intensities between the CP and single-pulse-excitation spectra enables us to discuss the dynamic behavior through the magnitude of the dipolar interaction. Spinning sidebands (SSB) caused by the ^{13}C chemical shift anisotropy are also useful to study the motion. The present work aims to survey ^{13}C NMR spectra for various zeolites and mesoporous materials. To our knowledge, no works have been published covering so many host materials using ^{13}C MAS NMR.

Experimental

Materials. Host materials were obtained from various sources. H-type ZSM-5 (coded H-ZSM-5) was a gift from Dr. K. Suzuki of this institute; its Si/Al_2 ratio was nominally 65. Six mordenites and two Y-type zeolites were Japan Reference Catalysts (JRC) supplied by Sansho-Shokubai-Iinkai, Catalysis Society of Japan. They were coded JRC-Z-HM10, HM15, HM20, M10, M15, M20, Y4.8, and HY4.8. The characters M and Y indicated mordenite and Y-type zeolite, respectively. H means that the cation is H^+, while no prefix means that the cation is Na^+. The numbers were Si/Al_2 ratios obtained by chemical analysis. FSM-16 was supplied by Toyota Central R&D Laboratories, Inc., whose pore diameter was 2.75 nm and whose surface area was 970 $m^2\,g^{-1}$. Na-X zeolite named 13X was purchased from Nishio Industries. Adsorbates, benzene and *p*-xylene, were obtained from Wako Pure Chemical Industries.

Adsorption procedures were as follows: The host materials were evacuated at 400 °C for 3 h. The guest compounds were subjected to three freeze-pump-thaw cycles to remove air. Vapor of the guest compounds was contacted with the host materials in a vacuum glass line overnight at room temperature. The amount of the adsorbate was controlled by after-heating only for the H-ZSM-5/*p*-xylene system.

Thermogravimetric and differential thermal analyses (TG/DTA) were carried out from room temperture up to 700 °C in air. Loading levels were estimated from the weight decrease from room temperture to 400 °C. They were expressed by the ratio of the above weight decrease to the weight of the dehydrated host, which were listed in Tables 1 and 2.

Table 1. Summary of Benzene-Adsorbed Samples

Host material	Loading level wt%	^{13}C			^{1}H	
		Shift (ppm)	FWHM (ppm)	M_2 (ppm^2)	Shift (ppm)	FWHM (ppm)
H-ZSM-5	10	129	2.0	300	7.5	0.3
M10	11	129	6	800	7.6	1.0
M15	15	129	5	500	7.4	0.9
M20	11	129	8	600	7.4	0.9
HM10	10	130	3	1400	7.3	[a]
HM15	11	130	4	1100	7.3	[a]
HM20	10	129	5	600	7.3	[a]
Y4.8	27	130	22	[b]	7.4	1.9
HY4.8	25	129.1	0.9	20	7.1	0.3
13X	15	129.5	2.1	60	7.4	0.9
FSM-16	72	128.6	0.2	0	6.9	0.1
No host[c]	—	128.475			6.771	

a) The signal was partially overlapped with the OH signal of the host. b) SSB's were masked by the broad isotropic peak. c) Neat liquid benzene.[23]

Table 2. Summary of *p*-Xylene-Adsorbed Samples

Host material	Loading level wt%	^{13}C			^{1}H	
		Shift (ppm)	FWHM (ppm)	M_2 (ppm^2)	Shift (ppm)	FWHM (ppm)
H-ZSM-5	11	19.8	1		2.2	0.9
		129.2	2	1400	7.0	1.5
		134.7	2			
M10	8	20	2		2.6	2
		127[a]	10	900	7.8	1.5
M15	5	20	3		2.5	2
		129	8	800	7.4	2
		137	5			
M20	11	21	2		2.3	5
		130	5	500	7.3	4
		137	5			
HM10	10	20	1		2.3[b]	2
		132[a]	10	900		
HM15	11	21	2		2.4[b]	3
		129[a]	3	500		
HM20	11	21	1		2.3[b]	1
		130[a]	5	600		
Y4.8	30	21.3	2		2.4	1
		131[a]	7	0	7.0	3
HY4.8	32	21.1	1		2.4	1
		129.1	2	0	7.0	1
		135.1	2			
13X	15	20.7	0.5		2.5	1
		129.5	1	0	7.1	1
		136.7	1			
FSM-16	108	20.8	0.2		1.9	0.2
		129.2	0.2	0	6.7	0.1
		134.7	0.3			
No host[c]	—	20.78			1.84	
		129.09			6.59	
		134.46				

a) No clear signal of the aromatic carbon bonded with the methyl group was observed. b) The aromatic signal was overlapped with the OH signal of the host. c) Neat liquid *p*-xylene.

Adsorption in zeolites 3A, 4A, and 5A were tried, but no adsorption was observed for these three hosts.

NMR Measurements. NMR measurements were carried out by a Bruker MSL400 spectrometer with a static magnetic field strength of 9.4 T. Larmor frequencies were 100.61 and 400.14 MHz for ^{13}C and ^{1}H, respectively. The samples were spinning about an axis inclined at the magic angle (54.7°) to the static field. The sample temperature was ambient.

^{13}C spectra were measured using CP and the single pulse sequences without and with high power ^{1}H decoupling (named SP and HD, respectively) under MAS conditions at a spinning rate of 4.00 kHz. In the CP experiment, the flip angle of the first ^{1}H pulse was $\pi/2$, the contact time of CP was set at 1 ms, and the recycle time was 6 s. In the SP and HD experiments, the flip angle of the ^{13}C pulse was $\pi/4$, and the recycle time was 15 s. ^{1}H spectra were obtained using the single pulse sequence (named SP) under MAS conditions at a spinning rate of 8.00 kHz. The flip angle of the pulse was $\pi/4$. Rotors made of zirconia were used; their diameters were 7 and 4 mm for ^{13}C and ^{1}H, respectively. Spectra were presented with the signal of neat tetramethylsilane being 0 ppm. Higher frequency side of the spectra with respect to the standard signal was expressed as positive.

Results and Discussion

NMR Spectra of Benzene-Adsorbed Systems. Benzene molecule has a globular shape, and it rotates about the C_6 axis in the solid phase even at 200 K.[19] The principal values of the chemical shift tensor are 63, 63, and -117 ppm relative to liquid benzene.

Figure 1 shows ^{13}C MAS NMR spectra of H-ZSM-5/benzene. The isotropic peak is observed at 129 ppm with SSB's on both sides. The SSB's are originated from chemical shift anisotropy. The small sidebands suggest that the benzene molecules undergo some kind of motion in addition to the rotation about the C_6 axis. However, the motion is still anisotropic. If an isotropic motion is fast enough, no SSB is observed. The quality of the spectra is not sufficient to estimate chemical shift anisotropy from the SSB intensities.

Therefore, we use the second moment M_2 to evaluate the intensity of SSB or the magnitude of chemical shift anisotropy. The second moment is independent of the spinning rate in principle; it is expressed as[20]

$$M_2 = \frac{\delta_{\text{anis}}{}^2}{15}(3 + \eta_{\text{C}}{}^2), \tag{1}$$

where δ_{anis} and η_{C} are the magnitude of the chemical shift anisotropy and the asymmetric factor, respectively. The experimental value of the second moment M_2 is obtained from the CP/MAS NMR spectrum assuming that the line width of each SSB is zero, according to the following formula:

$$M_2 = \frac{\sum_n n^2 I_n}{\sum_n I_n} \left(\frac{\nu_{\text{r}}}{\nu_{\text{L}}}\right)^2, \tag{2}$$

where M_2 is in ppm unit, I_n is the intensity of the nth sideband, ν_{r} is the spinning rate, and ν_{L} is Larmor frequency. The obtained value is 300 ppm^2, which is listed in Table 1. The SSB intensities can be estimated theoretically from the chemical shift tensor.[21]. The second moment of solid benzene is estimated from the SSB intensities calculated using the above principal values of the shift tensor, which is 2900 ppm^2. The decrease in the second moment observed in H-ZSM-5/benzene is considered to be caused by reorientation of the C_6 axis. The intensity of the CP spectrum (Fig. 1A) is somewhat larger than that of the HD spectrum (Fig. 1B), indicating that the ^{13}C–^{1}H dipole–dipole interaction is present effectively.

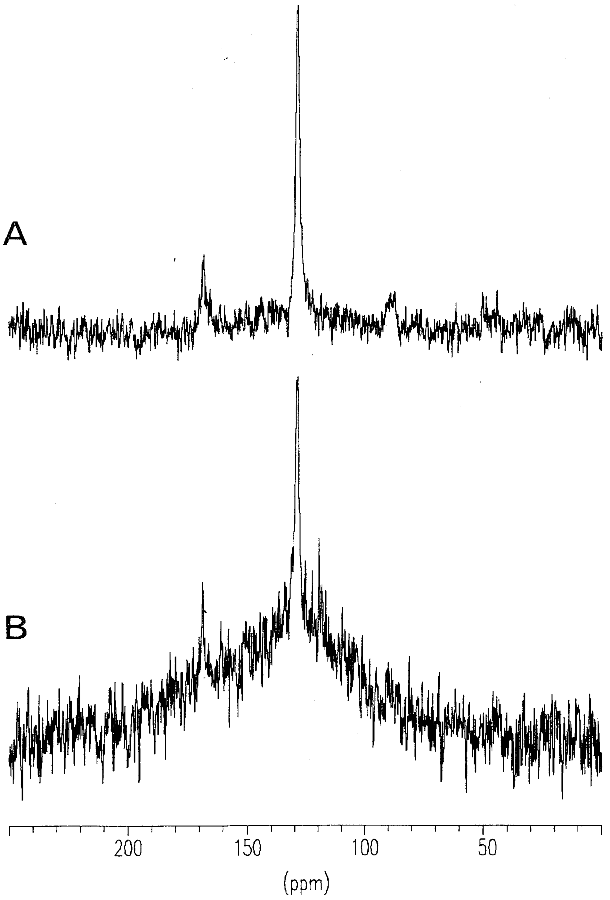

Fig. 1. ^{13}C MAS NMR spectra of H-ZSM-5/benzene. The pulse sequences were (A) CP and (B) HD. Spectral intensities are normalized. The broad signal underlying narrow peaks in B is a background signal of the probehead.

The six mordenite samples show a broad ^{13}C signal at about 130 ppm with line widths ranging between 3 and 8 ppm. The signal to noise ratios are bad, and no clear signal is observed in the HD/MAS spectra. These features might indicate an inhomogeneous nature of the adsorption sites in the mordenite channel. The intensity of SSB is larger than in the H-ZSM-5/benzene system. The second moments are 500 to 1400 ppm^2. These values demonstrate that the benzene molecules undergo a rotation about the C_6 axis as well as a reorientation of the C_6 axis. However, the motion of benzene molecules is much more restricted in mordenite than in H-ZSM-5. There are several trends in the M_2 value. The H-type mordenites have larger M_2 values than the corresponding Na-type ones when the Si/Al_2 ratio is low. The M_2 value decreases with increase in the Si/Al_2 ratio.

Figure 2 shows ^{13}C MAS NMR spectra of 13X/benzene. The intensities of SSB are negligibly small, indicating that the benzene molecule rotates almost isotropically. The signal intensity is much larger in HD than in CP. Although the ^{13}C–^{1}H dipole–dipole interaction is still present, its magnitude is small. The ^{13}C MAS NMR spectra of HY4.8/benzene are similar to those of 13X/benzene. Compared to the latter, the intensity of SSB is smaller, and the line width is narrower. The isotropic rotation is considered to be more free in HY4.8. The ^{13}C signal of Y4.8/benzene is very broad. The broad line width might suggest that the time scale of the motion is the same order of the ^{1}H decoupling field (about 50 kHz), which is supported by the ^{2}H NMR results.[6,10,13,14] ^{1}H decoupling is ineffective when the rate of the motion is of the order of the decoupling field.[22]

Figure 3 shows ^{13}C MAS NMR spectra of FSM-16/benzene. The SSB's are negligibly small. The line widths are extremely narrow like a spectrum of liquid. The SP spectrum shows a J-resolved pattern, which is the same as in liquid NMR. The intensity of the CP spectrum is 1/50 of that of the HD spectrum. Liquid does not give any signal in CP spectra. The small signal in the CP spectrum indicates that a small portion of the guest molecules are in a restricted motional state. These molecules might interact with the wall of the mesopores.

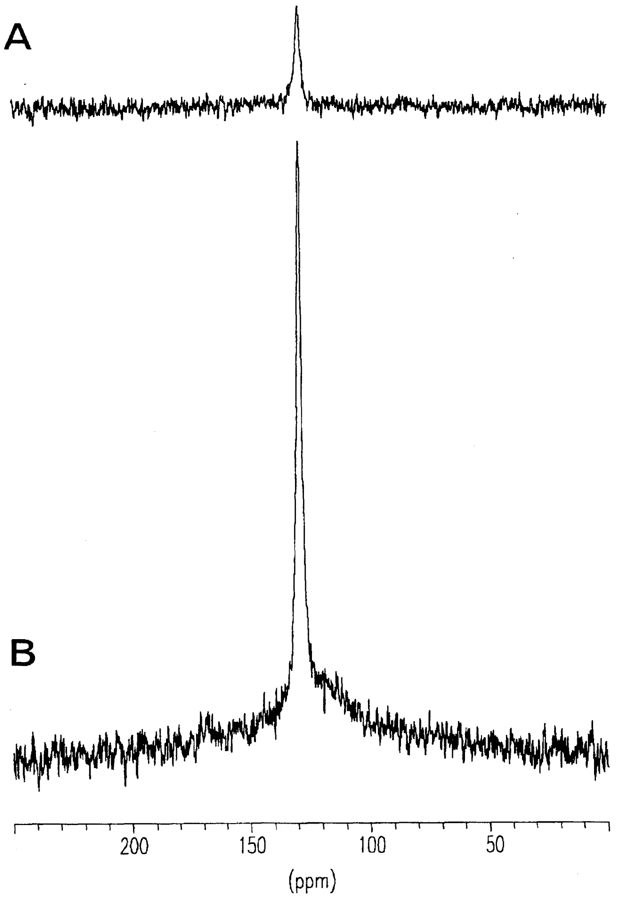

Fig. 2. ^{13}C MAS NMR spectra of 13X/benzene. The pulse sequences were (A) CP and (B) HD. Spectral intensities are normalized. A broad background signal underlies in B.

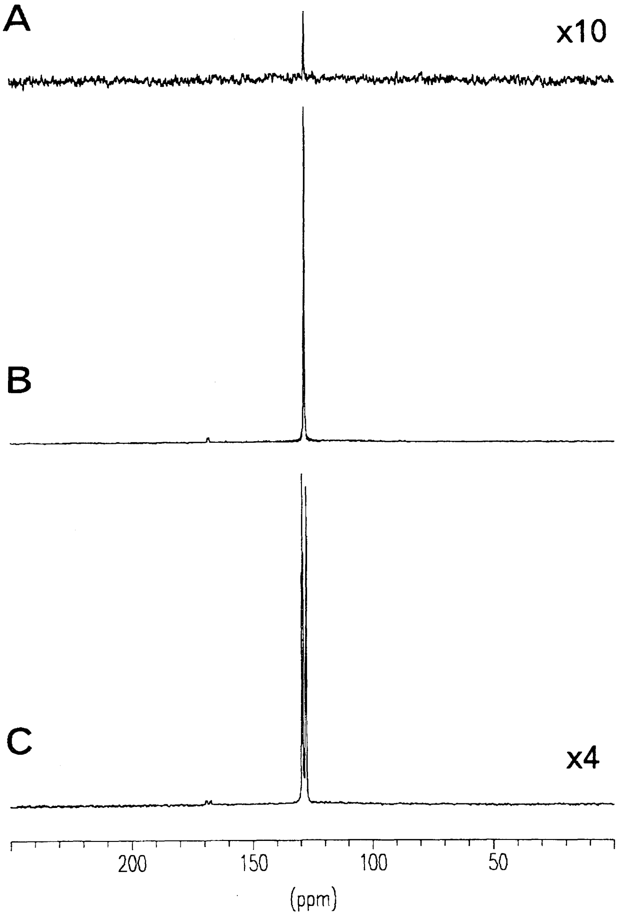

Fig. 3. ^{13}C MAS NMR spectra of FSM-16/benzene. The pulse sequences are (A) CP, (B) HD, and (C) SP. Spectral intensities are normalized.

The ^{13}C results are summarized in Table 1. The chemical shift does not depend on the host material very much. The line width and the SSB intensities change depending on the host, which reflect the dynamics of the guest species.

Figure 4 shows ^{1}H MAS NMR spectra of benzene adsorbed in H-ZSM-5, 13X, and FSM-16, and Table 1 summarizes ^{1}H results for various hosts. The signal at about 7 ppm is ascribed to benzene, and other signals come from the host materials. Only the signal of benzene is listed in Table 1. The SSB intensities are small, suggesting that ^{1}H–^{1}H dipole–dipole interaction is considerably averaged by the rotation of benzene molecules. The line width of the FSM-16 system is as small as for a liquid. ^{1}H chemical shift of neat benzene is 6.771 ppm.[23] The chemical shift for FSM-16 is 6.9 ppm, indicating the liquid-like property. Benzenes in the other host materials show small higher frequency shifts, reflecting the interaction with pore walls.

Motion of Benzene. Benzene molecules in H-ZSM-5 undergo reorientation of the C_6 axis in addition to rotation about the C_6 axis at room temperature, but not isotropic rotation. These results agree with those obtained by ^{2}H NMR.[5,6] Similar motions have been reported for Na-ZSM-5 and silicalite using ^{2}H and ^{13}C static NMR.[9,11,15] Some of the ^{2}H NMR

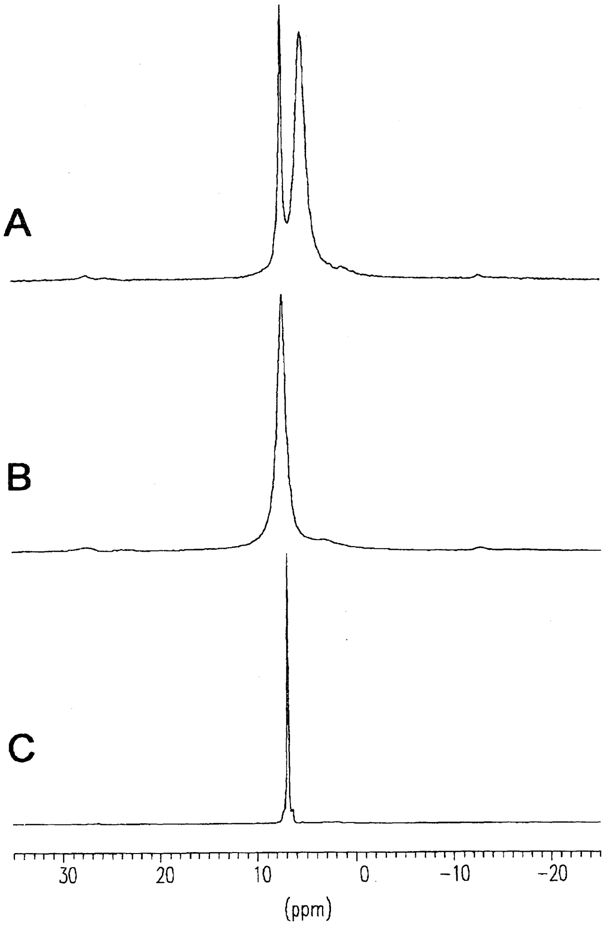

Fig. 4. ^{1}H SP/MAS NMR spectra of benzene in (A) H-ZSM-5, (B) 13X, and (C) FSM-16. Spectral intensities are arbitrary.

works suggest the presence of two or three components depending on the temperature and loading level.[6,9,11)]

Benzene molecules in mordenite undergo reorientation of the C_6 axis in addition to rotation about the C_6 axis at room temperture, similarly to the H-ZSM-5/benzene system. However, the reorientational motion is slower in mordenite than in H-ZSM-5. The Si/Al$_2$ ratio and the cation type affect the motion. The cation hinders the motion of benzene. As the number of the cation increases, the motion becomes slower. This hindrance effect is larger in H^+ than in Na^+. Eckman and Vega have reported from ^{2}H NMR study that the rate of the motion in mordenite is between those of H-ZSM-5 and HY.[5)] Their sample was H-type with a Si/Al$_2$ ratio of 18.1 and a loading level of 15 wt%. The high level loading might increase the fraction of benzene having the isotropic motion. The present results demonstrate that on the average the motion is slower in mordenite than in H-ZSM-5.

Benzene molecules in 13X and HY4.8 undergo almost isotropic rotation. The motion in Y4.8 is slower than in 13X and HY4.8. ^{2}H NMR studies have demonstrated hindrance of the motion by Na ion in NaY and enhancement of the motion by Na ion in NaX.[5—7,10,12—14)]

Benzene molecules in FSM-16 behave like liquid, and the motion is considered to be translational diffusion in addition to isotropic rotation. A small part of the guest molecules are slightly restricted in their motion due to the wall effect.

The pore size of the host materials used is in the following increasing order; H-ZSM-5 < mordenite < faujasite (Y4.8, 13X, HY4.8) <FSM-16. On the other hand, the mobility of benzene is in the following order; mordenite < H-ZSM-5 < Y4.8 < 13X < HY4.8 < FSM-16. There is a good correlation between the two orders, with the exception of mordenite. The mordenite samples have higher concentrations of cations than the H-ZSM-5 sample. The hindrance effect of the cations might play a greater role than the pore size in these systems.

NMR Spectra of *p*-Xylene-Adsorbed Systems. *p*-Xylene does not have a globular shape like benzene, and the rotation about an axis perpendicular to the ring plane is difficult. Instead, it can rotate about the C_2 axis connecting the two methyl carbons (called para axis). The results of the *p*-xylene systems are almost parallel to those of the benzene systems, with several exceptions.

Figure 5 shows ^{13}C MAS NMR spectra of H-ZSM-5/*p*-xylene (19 wt%). The isotropic peaks are observed at 134.7, 129.2, and about 20 ppm, being ascribed to the aromatic car-

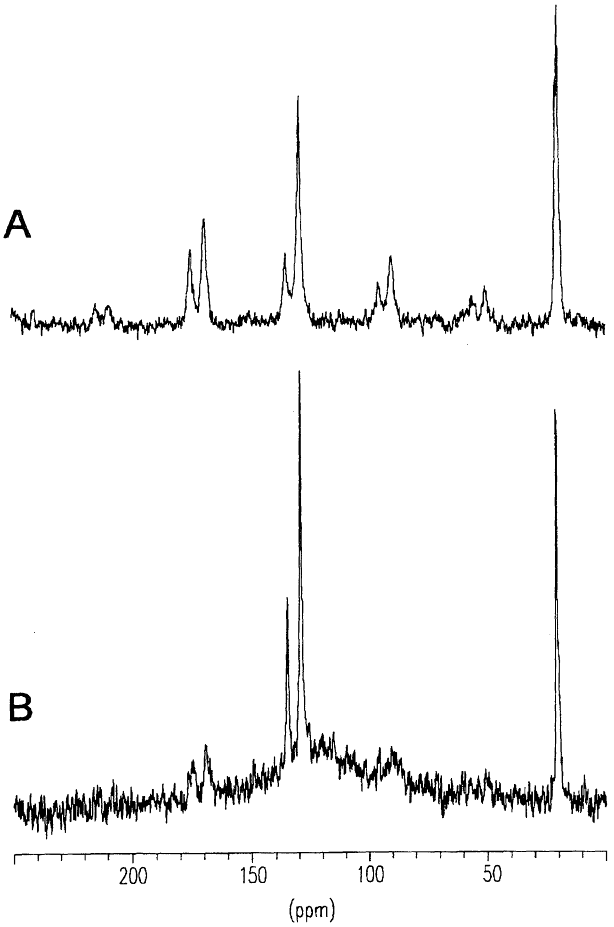

Fig. 5. ^{13}C MAS NMR spectra of H-ZSM-5/*p*-xylene with a loading level of 19 wt%. The pulse sequences are (A) CP and (B) HD. Spectral intensities are normalized. A broad background signal centered at 130 ppm underlies in B.

bon bonded with a methyl group, the aromatic carbon bonded with H, and the methyl carbon, respectively. Spinning sidebands up to the second order are clearly observed on both sides of the aromatic carbons. These sidebands suggest that the rotation of the *p*-xylene molecules is largely restricted. The HD spectrum has narrower isotropic peaks with higher intensities than the CP spectrum, and SSB's are weaker in HD than in CP. These facts demonstrate that two type of *p*-xylene molecules are present with different dynamic behavior. One is encapsulated in the zeolite channel, and the other is adsorbed on the outer surface. The outer-surface molecules undergo fast motion with isotropic character. The maximum loading level is 15 wt%, corresponding to eight molecules per unit cell or two molecules per intersection. The excess amount of *p*-xylene adsorbs on the outer surface. There are three methyl signals in the CP spectrum, which will be discussed later.

Loading levels were controlled by partial evolution at elevated temperatures. The following 5 samples were made additionally; loading levels of 15, 11, 10, 6, and 3 wt%. Figure 6 shows ^{13}C MAS NMR spectra of H-ZSM-5/*p*-xylene (11 wt%). The intensity of the CP spectrum is larger than that of the HD spectrum, indicating that the ^{13}C–^{1}H dipole–dipole interaction is effective. The 15 wt% sample shows spectra intermediate between Figs. 5 and 6, suggesting the presence of a small amount of the outer-surface molecules. The other three samples, 10, 6, and 3 wt%, have similar spectra to Fig. 6, with lower signal to noise ratios. Samples with loading levels of 11 wt% or less are considered to have no outer-surface molecules. The M_2 value of the 11 wt% sample is 1400 ppm^2. The M_2 value of the aromatic carbon for rigid *p*-xylene is estimated from the principal values of the chemical shift tensor at -170 °C,[24] which is 2800 ppm^2. Although the motion of *p*-xylene is restricted in the micropore, rotation about the para axis is considered to take place.

Figure 7 shows expanded plots of the methyl region. There are three methyl signals in the 19 wt% sample; 20.6, 19.8, and 18.5 ppm. With the use of CP, the 19.8- and 18.5-ppm signal increases, whereas the 20.6-ppm signal decreases, as shown in Figs. 7A and 7B. This means that the 20.6-ppm signal is ascribed to molecules rotating freely and isotropically, i.e., to the surface-adsorbed molecules. When the loading level is lowered, only the 19.8-ppm signal remains undiminished, for which CP is effective. Both the 20.6- and 18.5-ppm signals disappeared. The 19.8-ppm signal is ascribed to molecules

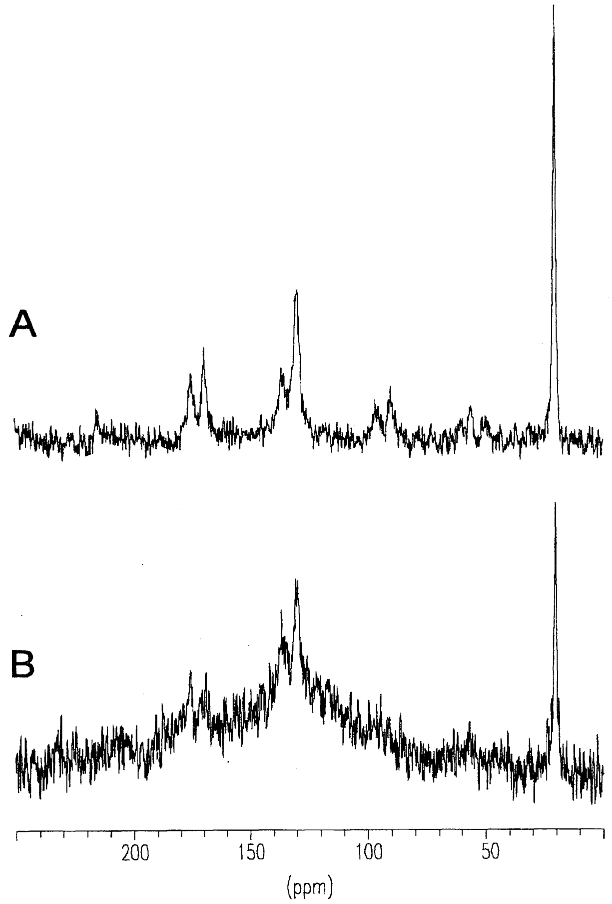

Fig. 6. ^{13}C MAS NMR spectra of H-ZSM-5/*p*-xylene with a loading level of 11 wt%. The pulse sequences are (A) CP and (B) HD. Spectral intensities are normalized. A broad background signal centered at 130 ppm underlies in B.

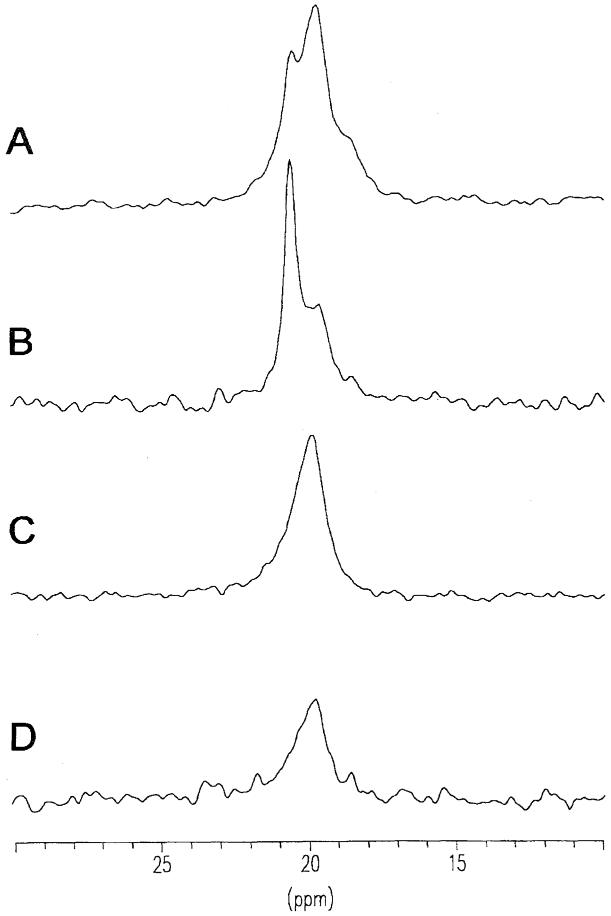

Fig. 7. Expanded plots of ^{13}C MAS NMR spectra of H-ZSM-5/*p*-xylene with loading levels of 19 (A,B) and 11 wt% (C,D). The pulse sequences are (A,C) CP and (B,D) HD. Spectral intensities are normalized for each pair, A-B and C-D.

in the channel. The assignment of the 18.5-ppm signal is not clear at the present stage. It might be ascribed to *p*-xylene on the second site in the channel or on a specific site of the outer surface.

The six mordenite samples show broad aromatic signals with line widths ranging between 3 and 10 ppm. The signal to noise ratios are bad, and no clear aromatic signal is observed in the HD/MAS spectra, which might suggest inhomogeneity of the adsorption sites again. The intensity of SSB is somewhat smaller than in the ZSM-5/*p*-xylene system. The second moments are 500 to 900 ppm^2. *p*-Xylene is considered to undergo the rotation about the para axis as well as the reorientation of the para axis, and the motion is a little more free in mordenite than in H-ZSM-5. The M_2 value decreases with increase in the Si/Al_2 ratio, and no significant difference is obtained between the H- and Na-type mordenites.

Figure 8 shows ^{13}C MAS NMR spectra of 13X/*p*-xylene. The intensities of SSB are negligibly small, indicating that the *p*-xylene molecule rotates isotropically. The signal intensity is much larger in HD than in CP. Although the $^{13}C-^{1}H$ dipole–dipole interaction is still present, its magnitude is small. The ^{13}C MAS NMR spectra of HY4.8/*p*-xylene are similar to those of 13X/*p*-xylene. The intensities of SSB are negligible, and the line width is a little broader. The isotropic rotation is as free in HY4.8 as in 13X. The aromatic signal of Y4.8/*p*-xylene is very broad. The broad line width might suggest that the time scale of the motion is the same order of the ^{1}H decoupling field, which is supported by the ^{2}H NMR results.[13)]

Figure 9 shows ^{13}C MAS NMR spectra of FSM-16/*p*-xylene. The SSB's are negligibly small, and the line widths are extremely narrow like the spectrum of a liquid. The SP spectrum shows a J-resolved pattern. The intensity of the CP spectrum is 1/42 of that of the HD spectrum. The small signal in the CP spectrum indicates that a small portion of the guest molecules are in a restricted motional state, interacting with the wall of the mesopores.

The ^{13}C results are summarized in Table 2. The chemical shift does not depend on the host material very much. The interaction between the guest and host causes a slight lower frequency shift of the methyl carbon in the H-ZSM system. The line width and the SSB intensities depend on the host, as in the benzene systems.

Figure 10 shows ^{1}H MAS NMR spectra of *p*-xylene adsorbed in H-ZSM-5 (11 wt%), 13X, and FSM-16, and Table 2 summarizes ^{1}H results for various hosts. The signals

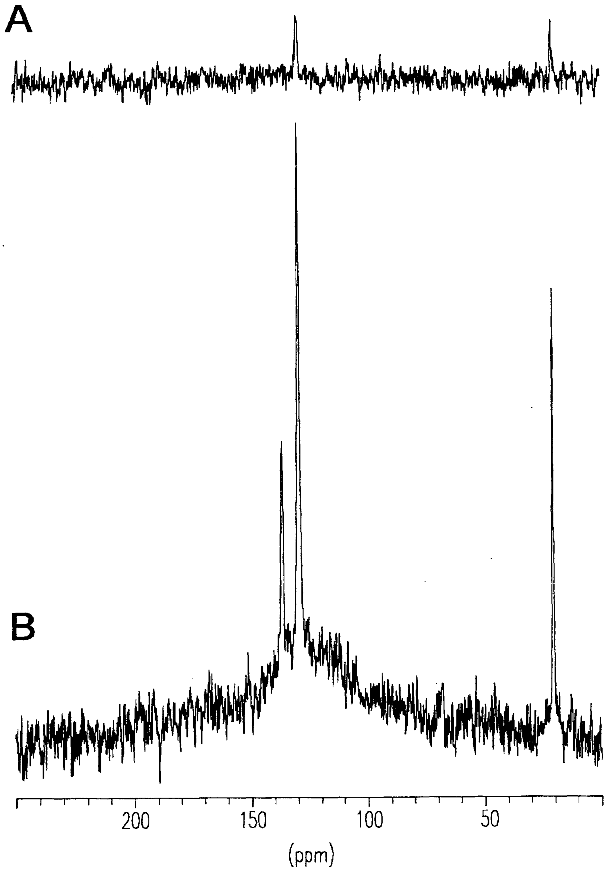

Fig. 8. ^{13}C MAS NMR spectra of 13X/*p*-xylene. The pulse sequences are (A) CP and (B) HD. Spectral intensities are normalized. A broad background signal centered at 130 ppm underlies in B.

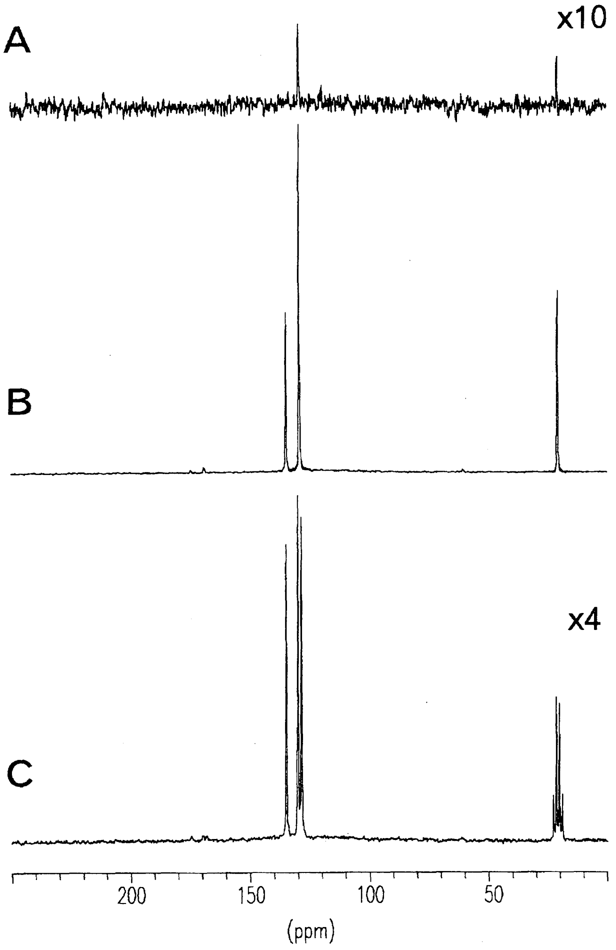

Fig. 9. ^{13}C MAS NMR spectra of FSM-16/*p*-xylene. The pulse sequences are (A) CP, (B) HD, and (C) SP. Spectral intensities are normalized.

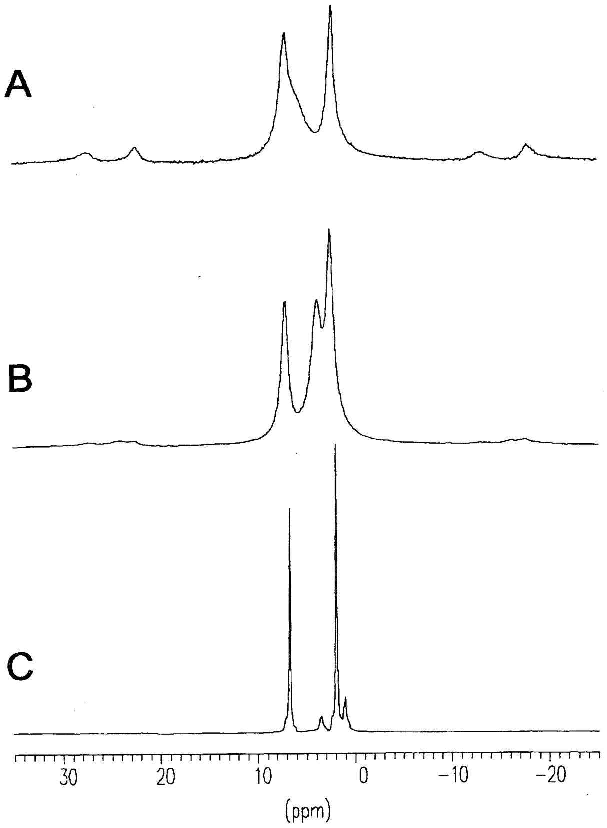

Fig. 10. ^{1}H SP/MAS NMR spectra of *p*-xylene in (A) ZSM-5 (a loading level of 11 wt%), (B) 13X, and (C) FSM-16. Spectral intensities are arbitrary.

at about 7 and 2.5 ppm are ascribed to *p*-xylene, and other signals come from the host materials. Only the signals of *p*-xylene are listed in Table 2. The SSB intensities decrease in the following order of H-ZSM-5 > 13X > FSM-16. The SSB's of *p*-xylene in mordenites and Y-type zeolites are overlapped with the signals of the hosts, preventing any intensity evaluation. The H-ZSM-5 systems with larger loading levels (15 and 19 wt%) shows narrow lines ascribed to the outer-surface species in addition to the lines of the lower loading level samples. The line width for the FSM-16 system is so small that it is like a liquid. ^{1}H chemical shifts of neat *p*-xylene are 6.59 and 1.84 ppm. The chemical shifts for FSM-16, 6.7, and 1.9 ppm, agree with the liquid values, indicating the liquid-like property. The other host materials show small higher frequency shifts, indicating the interaction with pore walls.

Motion of *p*-Xylene. The motion of *p*-xylene molecules in H-ZSM-5 is largely restricted, but the rotation about the para axis is considered to take place. The 19 and 15 wt% samples have another component with nearly isotropic rotation, which is ascribed to the outer-surface species. Many works have been published on this system so far. Eckman and Vega have reported rigid nature of *p*-xylene in H-ZSM-5 using ^{2}H NMR.$^{5)}$ Portsmouth et al. have reported that the para axis is fixed in the silicalite/*p*-xylene system using ^{2}H NMR.$^{11)}$ On the other hand, Kustanovich et al. have reported that a part of *p*-xylene molecules undergo flip motion of the para axis in Na- and H-ZSM-5.$^{8,9)}$ Nagy et al. have suggested from the motionally narrowed ^{13}C static spectrum that rapid three-dimensional translational diffusion takes place in ZSM-5,$^{16)}$ but the S/N ratio of the ^{13}C spectrum was much worse.

Three methyl lines are observed at 20.6, 19.8, and 18.5 ppm in ^{13}C CP/MAS NMR spectra of H-ZSM-5/*p*-xylene with loading levels of 19 and 15 wt%. Reischman et al. have also reported three methyl lines for a 12 wt% sample at 22.0, 21.1, and 20.0 ppm.$^{17)}$ Single crystal X-ray diffraction study has demonstrated that there are two inequivalent *p*-xylene molecules in H-ZSM-5.$^{25)}$ Reischman et al. have ascribed the three signals to the two inequivalent guest molecules. The present work cannot support the assignment. At the high loading level samples, two types of *p*-xylene molecules with different dynamic behaviors are mixed. At least, the 20.6 ppm signal is ascribed to the outer-surface species.

p-Xylene molecules in mordenite undergo reorientation of the para axis as well as the rotation about the para axis, and the motion is a little more free in mordenite than in H-ZSM-5. The cations H^+ and Na^+ hinder the motion of *p*-xylene, and no significant difference is obtained between H^+ and Na^+.

p-Xylene molecules in 13X and HY4.8 undergo an isotropic rotation. The rotation is slower in Y4.8 than in 13X and HY4.8. Gonçalves et al. have concluded from ^{2}H NMR results that *p*-xylene motion is isotropic in H-Y, while it is a hindered isotropic motion in Na-Y.$^{13)}$ Kirschhock and Fuess have reported that the motion is continuous diffusion at room temperature in Na-Y from ^{1}H NMR line width.$^{18)}$

p-xylene molecules in FSM-16 behave like liquid, and the motion is translational diffusion in addition to isotropic rotation. A small part of the guest species are slightly restricted in their motion.

The *p*-xylene molecules are mobile in the following order; H-ZSM-5 < mordenite < Y4.8 < 13X ≈ HY4.8 < FSM-16. There is a good correlation between the pore size and the motion including mordenite.

Conclusions

^{13}C and ^{1}H MAS NMR spectra have been measured at room temperature for benzene and *p*-xylene adsorbed in H-ZSM-5, various mordenites, H-Y, Na-Y, Na-X, and FSM-16 to study the dynamics of the guest species in the host materials.

The second moments M_2 evaluated from the SSB intensity in ^{13}C CP/MAS NMR spectra were used in place of chemical shift anisotropy to predict the motion of the guest species. With the decrease in the M_2 value, the guest species are considered to be more mobile.

The pore size of the host materials used is in the following increasing order; H-ZSM-5 < mordenite < faujasite (Y4.8, 13X, HY4.8) < FSM-16. Benzene molecules rotate about the C_6 axis freely. Reorientation of the C_6 axis takes place in H-ZSM-5. With the increase in the pore size, the motion becomes isotropic in the faujasite-type zeolites. In the mesoporous material FSM-16, translational diffusion takes place in addition to the isotropic rotation like in the liquid state. The mobilities of benzene molecules are in the following order; mordenite < H-ZSM-5 < Y4.8 < 13X < HY4.8 < FSM-16.

The para axis of *p*-xylene molecules is fixed in H-ZSM-5. The reorientation of the para axis takes place with increase in the pore size, and the motion becomes almost isotropic in the faujasite-type zeolites. *p*-Xylene molecules behave like liquids in FSM-16. The mobilities of *p*-xylene molecules are in the following order; H-ZSM-5 < mordenite < Y4.8 < 13X $\approx$ HY4.8 < FSM-16.

There is a good correlation between the pore size and the mobility of the guest species with the exception of the mordenite/benzene systems.

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