

Effects of Na^+ on Dynamics of *p*-Nitroaniline Molecules in Zeolite ZSM-5 Studied by Solid-State NMR

Yoshihiko Komori and Shigenobu Hayashi*

Institute for Materials & Chemical Process, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565

Received September 3, 2003; E-mail: hayashi.s@aist.go.jp

The dynamics of deuterated *p*-nitroaniline (*p*NA-*d*) molecules in zeolite ZSM-5 including Na^+ (NaZSM-5) were investigated by means of ^2H and ^{13}C solid-state NMR to clarify the effects of Na^+ and hydrated Na^+. The adsorbed amount of *p*NA-*d* was four molecules per unit cell of NaZSM-5. ^2H NMR spectra of a dehydrated sample indicated that the motion of *p*NA-*d* in the micropore is a 180° flip-flop around the C_2 axis of the molecule. Another species with a faster flip-flop motion was distinguishable and assigned to *p*NA-*d* on the outer surface. When the sample adsorbed water molecules, ^2H spectra showed that the flip-flop motion of *p*NA-*d* was largely suppressed in the micropore and that *p*NA-*d* on the outer surface underwent an isotropic motion. These results indicated that the dynamics of *p*NA-*d* in NaZSM-5 depended on the interactions with Na^+ and hydrated Na^+ as well as on the location.

Highly ordered porous materials incorporating guest molecules have potential uses as new and intelligent materials. Zeolites are extensively used as inorganic host materials since they have advantages of rigidity as well as thermal and chemical stabilities, and since a wide variety of pore structures, sizes, shapes, and framework charge densities are available.[1–3] Guest molecules constrained in micropores present novel features, and the functional property of the molecule is varied by unique interactions with zeolites. Therefore, characterization of organic molecules in zeolites is one of the most important subjects from the viewpoint of a better understanding of the nature of the composite materials and efficient designs of functional materials with advanced performances.

Solid-state ^2H and ^{13}C NMR spectroscopies are advantageous for investigating the dynamics and chemical environments of guest molecules. Especially, solid-state ^2H NMR techniques have been utilized widely because both modes and rates of molecular motions can be determined. As for molecular motions in zeolites, studies of small organic molecules such as benzene,[4–18] *p*-xylene,[4,7,8,13,14,16,19] cyclohexane,[9,18,20] alcohol,[4,21] acetonitrile,[22] and *p*-nitroaniline (*p*NA)[23] have been reported. These reports demonstrate that the dynamics of guest molecules in zeolites are often constrained to exhibit unique motional behavior.

ZSM-5, an MFI type of zeolite, has straight channels crossing with zigzag channels, which consist of 10-membered rings with diameters of about 0.54 nm.[24] The unit cell of ZSM-5, $Na_nAl_nSi_{96-n}O_{192}$, contains four channel intersections of straight and zigzag channels. On the other hand, *p*NA is well known as a potential nonlinear optical material and second harmonic generation has been observed for *p*NA in various inorganic host materials such as zeolites,[25–32] mesoporous silica,[33] and layered materials.[34–36] The ZSM-5/*p*NA system is a typical example of the zeolite/organic compounds, and the structure[37–40] as well as optical effects[27,28,32,41,42] have been investigated extensively. X-ray diffraction (XRD) studies have indicated that the *p*NA molecules are located at the channel intersections when the adsorbed amount of *p*NA is less than four molecules per unit cell of ZSM-5.[37–39] Recently, we have studied the dynamics of *p*NA in micropores of siliceous ZSM-5 by means of ^2H NMR; we clarified that *p*NA molecules in the intersections undergo 180° flip-flop motion with a rate of 50 kHz at room temperature.[23,43]

On the other hand, it is generally believed that properties of adsorbed molecules in zeolites are strongly affected by the nature of extraframework cations.[44] Molecular mobility in high silica zeolites tends to decrease with decreasing the Si:Al ratio, especially for nucleophilic adsorbates which become trapped with long residence times at cationic sites.[45] Moreover, it was reported that Na^+ in ZSM-5 played an important role in hindering complete freedom of translational diffusion of *p*-xylene molecules at least up to 170 °C.[7] Recently, we have reported that the absorption band of *N*,*N*-dimethyl-*p*-nitroaniline is shifted to a longer wavelength by an interaction with Na^+ in zeolite, and that such behavior is reversible by the treatments of hydration and dehydration of Na^+.[46] However, how the extraframework cations affect the dynamics of the adsorbed molecules is little known.

In the present study, we have investigated motional behavior of *p*NA molecules in ZSM-5 including Na^+ (NaZSM-5). We have measured ^2H NMR, ^{13}C NMR, and UV–vis spectra of deuterated *p*NA in hydrated and dehydrated NaZSM-5. Based on the molecular motions, we discuss the roles of pore structures, Na^+, and water molecules.

Experimental

Preparation of Materials. NaZSM-5 was a reference catalyst distributed by The Catalysis Society of Japan, coded JRC-Z5-70Na ($Na_2Al_2Si_{94}O_{192}$). NaZSM-5 was dehydrated by evacuation at 473 K for 3 h before use. Deuterated *p*NA (ring-d_4, *p*NA-*d*) was ob-

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tained from Cambridge Isotope Laboratories (Andover, USA).

A weighted amount of *p*NA-*d* was mixed with the dehydrated NaZSM-5 under a nitrogen atmosphere. A Pyrex glass tube containing the mixture of *p*NA-*d* and NaZSM-5 was sealed in vacuo and then heated at 423 K for 72 h, after which the temperature was decreased to room temperature for 24 h. The XRD analysis showed no peaks of crystalline *p*NA-*d* and confirmed adsorption of *p*NA-*d* into the micropores and/or on the external surface of NaZSM-5. For ^{2}H NMR measurements of the dehydrated sample, NaZSM-5/*p*NA-*d* was transferred to a Pyrex NMR tube with an outer diameter of 5 mm under a nitrogen atmosphere and sealed it in vacuo. On the other hand, the hydrated NaZSM-5/*p*NA-*d* was prepared by keeping it in an ambient atmosphere. After the compound had fully adsorbed water molecules, it was transferred to the NMR tube and the tube was sealed. As for ^{13}C NMR and UV-vis analyses, it was difficult to measure sealed samples due to instrumental limitations. Therefore, a heat treatment at 393 K was conducted just before the measurements in order to remove the adsorbed water.

The amounts of *p*NA-*d* and water in NaZSM-5/*p*NA-*d* were checked in the hydrated sample. Thermogravimetry (TG) curves exhibited a continuous mass loss from room temperature to 770 K due to desorption of water and *p*NA-*d* molecules, which amounted to 13.3 mass%. The CHN elemental analysis showed carbon and nitrogen contents of 4.4 and 1.6 mass%, respectively. Based on the results, the adsorbed amounts of *p*NA-*d* and water molecules were 4.0 and 17 molecules per unit cell, respectively. The TG curve suggests that the heat treatment of 393 K removed at least 60% of the adsorbed water molecules.

Analyses. ^{2}H NMR measurements were carried out by a Bruker MSL400 spectrometer with a static magnetic field strength of 9.4 T. ^{2}H spectra were recorded at 61.42 MHz for static samples using a Bruker broadband probehead. The quadrupole echo pulse sequence was used, where the latter half of the echo signal was acquired and Fourier-transformed. The 90° pulse width was 3.4–3.6 μs for D_2O and the time interval between the two 90° pulses was set at 15 μs. The recycle time was varied between 1 and 10 s. The set temperature was varied from 140 K to 400 K. The temperature of the sample was calibrated by using CD_3OD.[47] Inversion recovery experiments were carried out at room temperature using the inversion recovery pulse sequence combined with the quadrupole echo pulse sequence. Time intervals between the 180° and 90° pulses were varied from 1 ms to 2 s with a recycle time of 10 s. Spectra were presented with respect to the signal of D_2O. ^{2}H line-shape simulations in motional states were carried out with the MXET1 program (a descendant of the MXQET program[48]).

^{13}C magic-angle-spinning (MAS) NMR measurements with the cross polarization (CP) method were carried out by a Bruker ASX400 spectrometer with a static magnetic field strength of 9.4 T. The Larmor frequency was 100.61 MHz. The spinning rate of the sample was set at 5 kHz with a zirconia rotor of 7 mm in outer diameter. The recycle time and the contact time were 15 s and 3 ms, respectively. Chemical shifts were expressed with respect to neat tetramethylsilane.

UV-vis spectra were measured by a diffuse reflectance method with a Shimadzu UV-3100PC spectrometer equipped with an integrating sphere unit. Samples were diluted with MgO powder to concentrations of 10 mass%. The sample and MgO powder were mixed in a mortar and the mixture was put into a sample holder with a sample thickness of 0.5 mm. MgO powder was used as a reference. Powder XRD patterns were measured by a Rigaku Miniflex diffractometer with Cu Kα radiation at room temperature.

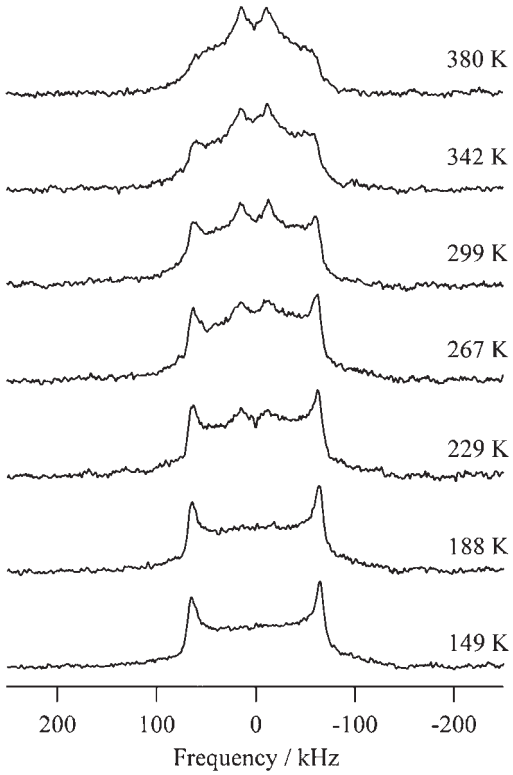


Fig. 1. Temperature dependence of ^{2}H NMR spectra of dehydrated NaZSM-5/*p*NA-*d*. Recycle times are 3 s at 149 and 188 K, and 1 s at the other temperatures.

Results and Discussion

^{2}H NMR of Dehydrated NaZSM-5/*p*NA-*d*. Figure 1 shows ^{2}H NMR spectra of dehydrated NaZSM-5/*p*NA-*d* at several temperatures. A Pake doublet pattern is observed at 149 K. The resolved doublet has a quadrupole coupling constant (QCC) of 180 kHz and an asymmetry factor (η_Q) of 0.02 ± 0.02, which is ascribed to *p*NA-*d* molecules in a rigid state. With increase in temperature, fine structures start to develop at the central region and the line shape stops changing above 380 K. It is supposed that the motion of *p*NA-*d* is much faster than 100 kHz above 380 K. On the basis of the profile change, the most plausible motion is a 180° flip-flop motion around the C_2 axis of the *p*NA-*d* molecule.[23]

Figure 2 shows spectra calculated assuming the 180° flip-flop motion with various rates. The flip-flop motion with the rate faster than 10 MHz gives a ^{2}H NMR pattern similar to that at 10 MHz. The experimental spectrum at 380 K (Fig. 1) agrees very well with the pattern calculated at 10 MHz with QCC of 170 kHz and η_Q of 0.04 (Fig. 2). The deviation in QCC from the experimental value of 180 kHz in the rigid state might be caused by contribution of wobbling motions.[23] The slight deviation of η_Q from 0 was also reported for crystalline *p*NA (*p*-nitroaniline-2,6-d_2) whose η_Q is 0.06 ± 0.02.[49] On the other hand, the spectra between 149 and 380 K cannot be simulated successfully by only adjusting the rate of the flip motion. It is reasonable to suppose that the spectra do not consist of a single component.

In order to demonstrate a presence of more than one component, we have utilized the inversion recovery measurement that

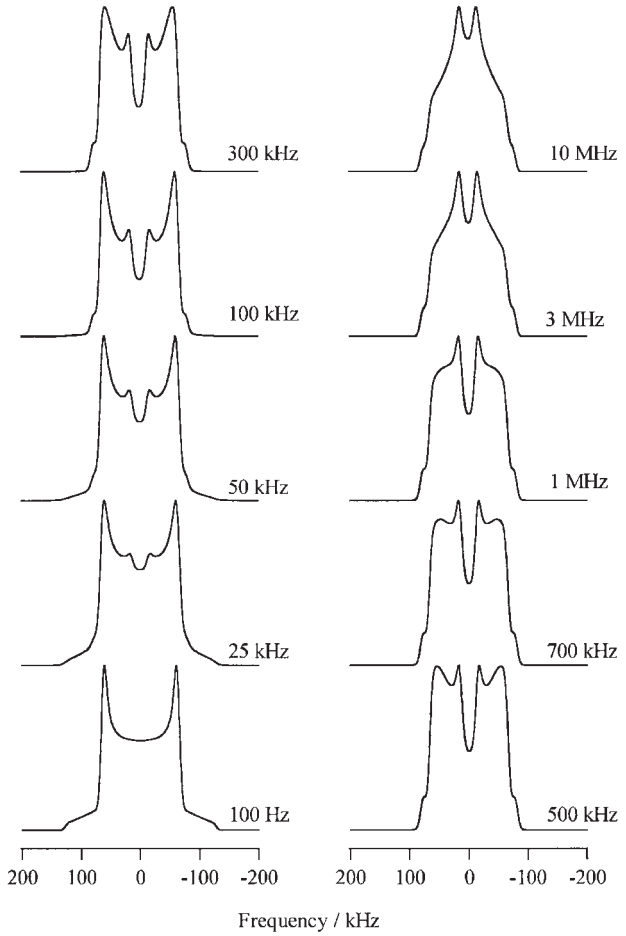


Fig. 2. Calculated spectra assuming the 180° flip-flop motion of *p*NA-*d* molecules around the C_2 axis. The values of QCC and η_Q are 170 kHz and 0.04, respectively. The motional rates are attached to the spectra.

is useful to differentiate overlapped signals possessing different spin-lattice relaxation times. The inverted signal recovers, passing a null point, and finally reaches its equilibrium line shape. Figure 3 shows the spectra of the dehydrated sample at room temperature with various time intervals between the 180° and 90° pulses. The figure indicates a presence of two components possessing different relaxation times; an outer doublet with a split of 126 kHz (component I) and an inner doublet with a split of 26 kHz (component II). Component I passes the null point between 100–400 ms and its intensity recovers from 400 ms to 10 s, whereas component II passes the null point in the range of 20–40 ms. The relaxation times, T_1, are roughly estimated as 1.3 s and 40 ms for components I and II, respectively.

Component I corresponds to *p*NA-*d* with lower mobility. The outer doublets are observed clearly below 267 K, are gradually weakened above 267 K, and finally become obscure at 380 K (Fig. 1). The experimental spectrum at 380 K indicates that component I corresponds to the *p*NA-*d* molecules which undergo the 180° flip-flop motion. Comparison with the simulated results in Fig. 2 suggests that the rates of the motion are of the order of kHz at room temperature and MHz at 340–380 K. The estimated rate is comparable to that of *p*NA-*d* in the micropores of siliceous ZSM-5, which is 50 kHz at 297 K.[23] Consequently, component I can be ascribed to *p*NA-*d* in the micropores of NaZSM-5.

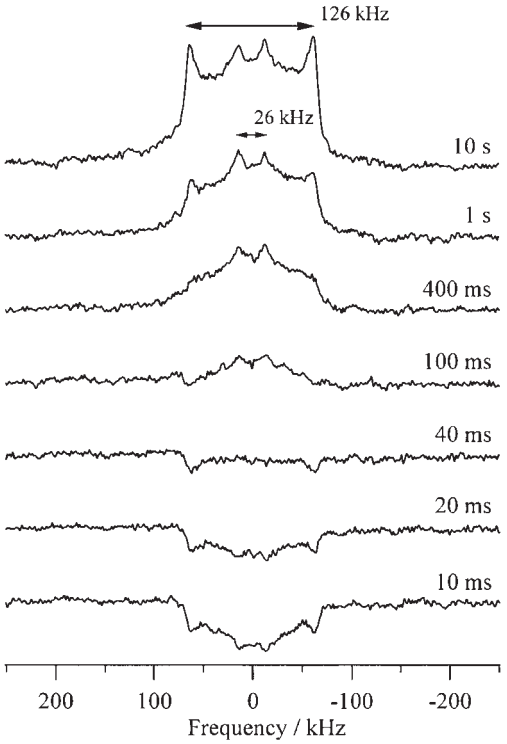


Fig. 3. Inversion recovery spectra of dehydrated NaZSM-5/*p*NA-*d* with various time intervals between 180° and 90° pulses. The time intervals are attached to the spectra.

Component II has higher mobility than component I. The experimental spectrum at 380 K indicates that component II also undergoes the 180° flip-flop motion. The intensity of the central region increases with increase in temperature above 188 K, as shown in Fig. 1. Results suggest that the rate is of the order of kHz in the temperature range of 188–229 K. This rate is much faster than that of component I. Because *p*NA molecules in the micropores of ZSM-5 cannot undergo such a fast motion,[23] the motion can be ascribed to *p*NA molecules on the outer surface. The C_2 axis of *p*NA-*d* must be fixed to undergo the 180° flip-flop motion. Consequently, *p*NA-*d* is considered to interact with specific adsorption sites such as Na^+ of the outer surface.

Figure 4 shows an example of deconvolution into components I and II. The observed spectrum at room temperature is fitted very well with a sum of two spectra calculated using the flip-flop motional rates of 50 kHz and 10 MHz. The intensity ratio of component I to component II is roughly estimated as 3:2. However, it is difficult to determine the accurate rates and intensity ratios of the components because of a large arbitrariness in the simulation.

^{2}H NMR of Hydrated NaZSM-5/*p*NA-*d*. Figure 5 shows ^{2}H NMR spectra of hydrated NaZSM-5/*p*NA-*d* at several temperatures. The spectrum at 188 K shows a Pake doublet pattern with QCC of 180 kHz and η_Q of 0.02 ± 0.02; the doublets are observed in all temperatures. A signal with Lorentzian line shape appears in the central region; its height increases with increase in temperature. Figure 6 shows a deconvolution of the spectrum at 301 K. The spectrum consists of two components:

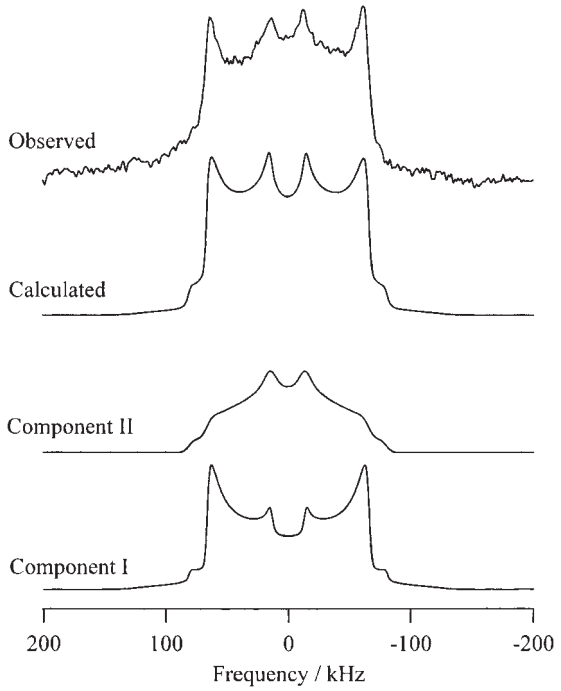


Fig. 4. Deconvolution of the ^{2}H NMR spectrum of dehydrated NaZSM-5/*p*NA-*d* measured at 299 K with a recycle time of 10 s. Components I and II are simulated by assuming the 180° flip-flop motion with rates of 50 kHz and 10 MHz, respectively. The values of QCC and η_Q are 170 kHz and 0.04, respectively, for both components.

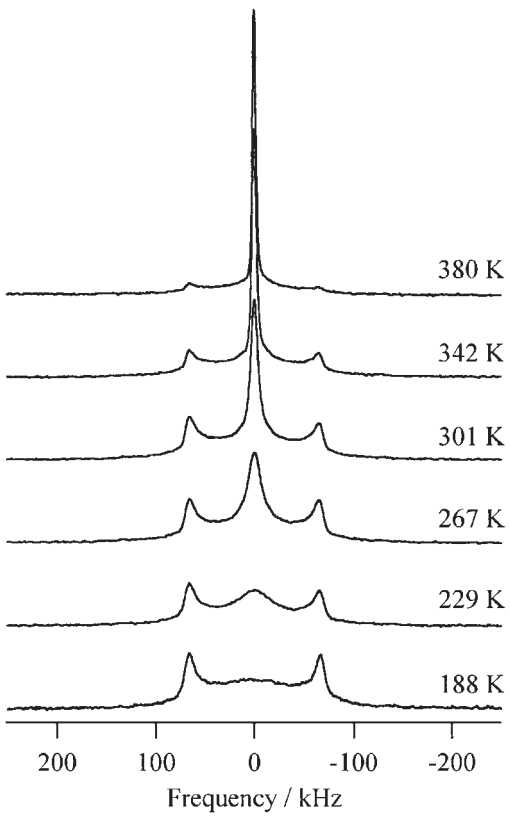


Fig. 5. Temperature dependence of ^{2}H NMR spectra of hydrated NaZSM-5/*p*NA-*d*. Recycle times are 5 s at 188 K, and 1 s at the others.

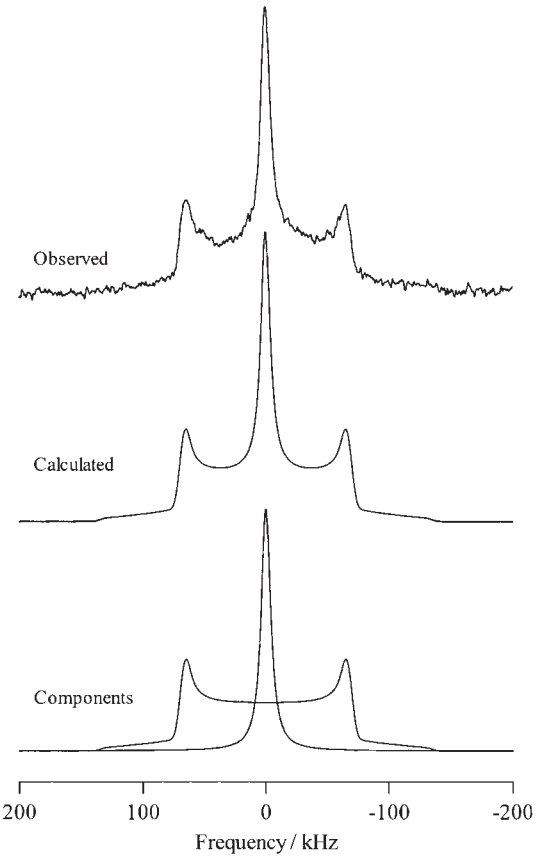


Fig. 6. Deconvolution of the ^{2}H NMR spectrum of hydrated NaZSM-5/*p*NA-*d* measured at 301 K with a recycle time of 10 s. The Pake doublet pattern is simulated assuming QCC of 180 kHz and η_Q of 0.04. The Lorentzian line shape is simulated assuming an fwhm of 9 kHz.

a Pake doublet pattern and a Lorentzian signal. Inversion recovery spectra at room temperature show that the two components possess different relaxation times, T_1: these are 650 and 10 ms for the Pake doublet and the Lorentzian components, respectively (spectra are not shown).

The Pake doublet does not disappear even at 380 K. The doublet pattern is assigned to *p*NA-*d* in the micropores of NaZSM-5. The presence of the patterns at high temperatures shows that the motion of *p*NA-*d* in the micropore is suppressed. It is reasonable to suppose that hydrated Na^+ coexisting with *p*NA-*d* in the micropore suppresses the motion of *p*NA-*d*.

The Lorentzian signal in the central region is assigned to *p*NA-*d* undergoing a fast isotropic motion on the outer surface of NaZSM-5. The full width at half maximum (fwhm) of the signal decreases with increase in temperature. The area intensity of the signal increases with increase in temperature, and becomes constant above 286 K. The *p*NA-*d* molecules on the outer surface are in a rigid state at low temperatures; a part of the molecules start to undergo some isotropic motion with increases in temperature. All *p*NA-*d* molecules on the outer surface undergo a fast isotropic motion above 286 K. The amount of *p*NA-*d* on the outer surface is estimated as 27% of the total molecules. It is suggested that *p*NA-*d* molecules on the outer surface are not transferred into the micropores during the hydration process because the adsorption of *p*NA is very slow

at room temperature.[38]

^{13}C CP/MAS NMR. Figure 7 shows ^{13}C CP/MAS NMR spectra measured at room temperature. The isotropic chemical shifts and their fwhm's are listed in Table 1 with the data for *p*NA in siliceous ZSM-5 (ZSM-5/*p*NA)[23] and crystalline *p*NA-*d*. There are four isotropic signals due to α (*C*-NH_2), β (*C*-D), γ (*C*-D), and δ (*C*-NO_2) carbons of *p*NA-*d*. The signals in the hydrated sample are broader than those in ZSM-5/*p*NA and crystalline *p*NA-*d*. This suggests that *p*NA molecules do not have an ordered arrangement but are adsorbed on various sites of the micropore and the outer surface.

The ^{13}C NMR spectrum is changed after heating at 393 K, as shown in Fig. 7b. The signals due to β and δ carbons appear to be split and the line widths of the other signals are broader than those in the hydrated sample, indicating a variety of adsorption sites. The chemical shifts of one of the split signals (116.1 and 140.4 ppm for β and δ carbons, respectively) are deviated significantly from others, which might suggest strong interaction between *p*NA-*d* molecules and Na^+.

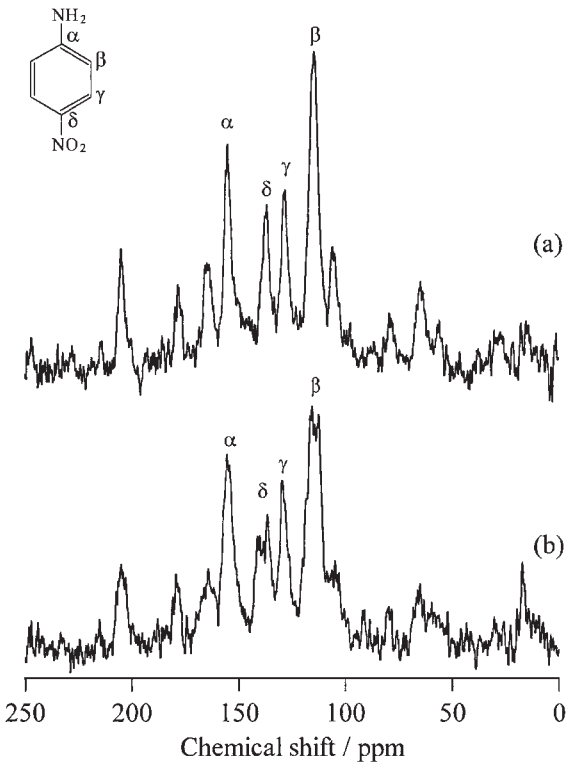


Fig. 7. ^{13}C CP/MAS NMR spectra of (a) hydrated NaZSM-5/*p*NA-*d*, and (b) after heating at 393 K for 3 h of (a). Spectra were measured at room temperature with spinning rates of 5 kHz.

UV–vis. Interaction of *p*NA-*d* with the host material is investigated by diffuse reflectance UV–vis measurements. Figure 8 shows UV–vis spectra of the hydrated and dehydrated NaZSM-5/*p*NA-*d* samples. The hydrated sample exhibits a band due to π–π^* transition at 400 nm, similarly to crystalline *p*NA-*d*. After a heat treatment of the hydrated sample at 393 K, the absorption intensity at 400 nm decreases and a new band clearly appears as a shoulder around 450 nm. Recently, we have demonstrated that UV–vis spectra of *N*,*N*-dimethyl-*p*-nitroaniline in zeolites show a large red shift of the absorption band by an interaction with cations.[46] In the same way, the red shift of *p*NA in the dehydrated sample is interpreted as a strong interaction between the *p*NA-*d* molecule and Na^+. However, the relatively large absorption intensity at 400 nm in the dehydrated sample indicates that all the *p*NA-*d* molecules do not interact with Na^+ effectively.

Structure and Dynamics. The *p*NA molecules are located in the micropores and on the outer surfaces. In the case of sili-

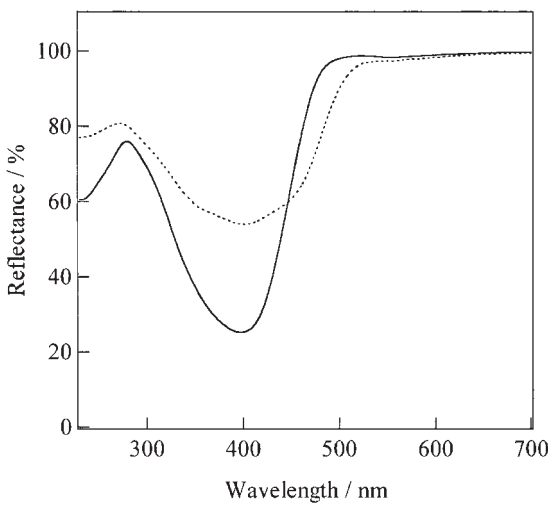
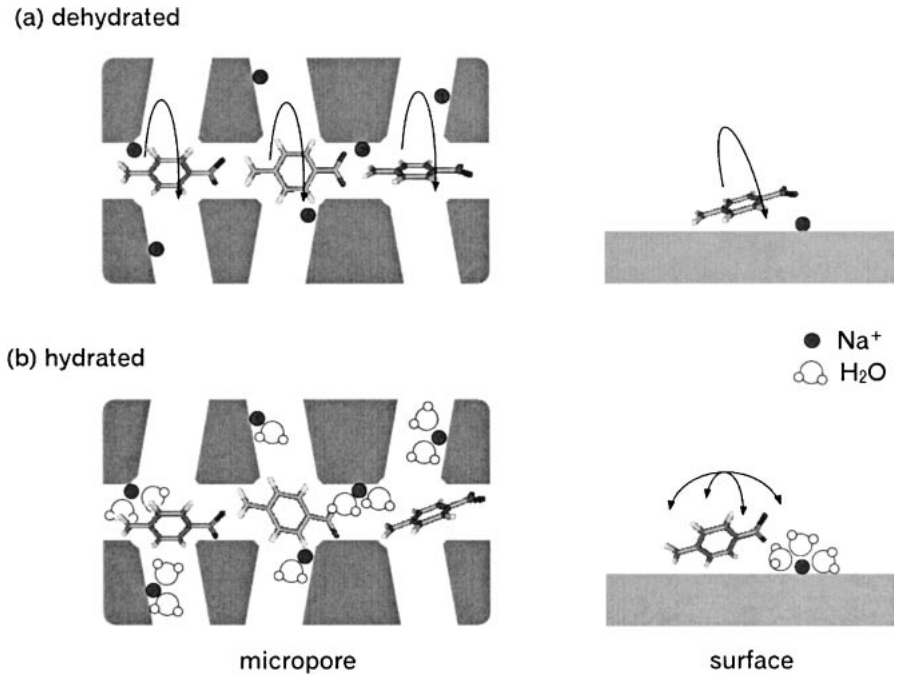


Fig. 8. UV–vis spectra of hydrated NaZSM-5/*p*NA-*d* (solid line) and the sample after heating at 393 K (dotted line).

Table 1. Chemical Shifts and Fwhm's of ^{13}C CP/MAS NMR Signals for *p*NA[a)]

	$C_\alpha(NH_2)$		C_β(D)[b)]		C_γ(D)		$C_\delta(NO_2)$[b)]	
	shift	fwhm	shift	fwhm	shift	fwhm	shift	fwhm
NaZSM-5/*p*NA-*d*								
hydrated	155.1	3.8	114.5	5.9	128.4	3.7	137.2	4.4
heated at 393 K	155.2	6.0	112.3	3.1	129.2	4.1	136.6	2.7
			116.1	6.1			140.4	4.7
ZSM-5/*p*NA[c)]	154.9	2.2	112	6.5[d)]	127	6.5[d)]	138.2	1.2
*p*NA-*d*, crystalline	155.3	2.4	113.1	1.9	127.7	2.4	136.3	1.4

a) All values are expressed in ppm units. b) Values are obtained after a deconvolution assuming Lorentzian line shapes. c) The amount of *p*NA is four molecules per unit cell of ZSM-5. The ^{13}C NMR spectrum is shown in Ref. 23. d) The signal is broadened by interference between the flip-flop motion of *p*NA with a rate of 50 kHz and the ^{1}H decoupling field.[23]



Scheme 1. Models for dynamics of *p*NA molecules in the micropore and on the outer surface of (a) dehydrated and (b) hydrated NaZSM-5.

ceous ZSM-5, all *p*NA molecules are located in the micropores when the adsorbed amount is less than four molecules per unit cell of ZSM-5.[46] In the present study, a considerable amount of *p*NA locates on the outer surface, as clarified by ^{2}H NMR, although the total amount of loaded *p*NA corresponds to four molecules per unit cell. Consequently, the amount of *p*NA in the micropore is less than four molecules per unit cell. Na^+ reduces the *p*NA accommodated in the micropores.

The model of motion of *p*NA in NaZSM-5 is summarized in Scheme 1. ^{2}H NMR spectra in Figs. 1, 3, and 4 demonstrate that the motion of *p*NA-*d* in the micropore is the 180° flip-flop one for the dehydrated sample. A similar motion is also observed for *p*NA in the intersection of siliceous ZSM-5.[23] It is suggested that all *p*NA molecules locate at the intersections of NaZSM-5 and that Na^+ has little effects on the flip-flop motion of *p*NA. On the other hand, the flip-flop motion is suppressed in the hydrated sample, as indicated by ^{2}H NMR spectra in Figs. 5 and 6. Furthermore, the ^{13}C NMR results (Fig. 7 and Table 1) show broader signals than those of ZSM-5/*p*NA. It is reasonable to suppose that hydrated Na^+ affects the adsorbed sites of *p*NA-*d* and suppresses the motion because of the large volume of hydrated Na^+.

The motion of *p*NA molecules on the outer surface is also described in Scheme 1. The ^{2}H NMR spectra demonstrate the presence of a large amount of *p*NA-*d* molecules undergoing fast motion, which also demonstrates a number of adsorbed sites on the outer surface. The *p*NA-*d* molecules undergo the fast 180° flip-flop motion in the dehydrated sample, and Na^+ might work as a specific adsorbed site. On the other hand, the motion of *p*NA-*d* is an isotropic one in the hydrated sample (Figs. 5 and 6). Such results suggest that the specific adsorbed sites disappear due to hydration of Na^+. Weak interaction of *p*NA-*d* with hydrated Na^+ may cause the isotropic motion.

Conclusively, water molecules play an important role in the behavior of *p*NA in NaZSM-5. Hydration of Na^+ switches the motion of *p*NA from the flip-flop one to the rigid state in the micropore and to the isotropic motion on the outer surface. On the other hand, dehydration switches on the flip-flop motion in both locations. These behaviors show the possibility of a reversible control of dynamics of *p*NA. This mechanism may apply to other guest molecules when the desorption temperature of guest molecules is higher than that of water molecules.

Conclusions

The motion of *p*NA-*d* in ZSM-5 including Na^+ depends on both the location and the interactions with Na^+ and hydrated Na^+. The motion of *p*NA-*d* in the micropores is the 180° flip-flop one around the C_2 axis of the molecule in the dehydrated sample. On the other hand, such motion is suppressed when Na^+ is hydrated. The motion of *p*NA-*d* on the outer surface is different from that in the micropores. For the dehydrated sample, the 180° flip-flop motion takes place at a rate faster than in the micropores. Hydration switches the motion from the flip-flop one to the isotropic one. These results indicate that the effects of Na^+ and water molecules are important for the dynamics of *p*NA molecules in zeolites.

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