

Undesorbed Dichloromethane in Zeolites Studied by Solid-State NMR

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We have studied the state of adsorbed dichloromethane molecules not removed by evacuation in several H-type zeolites, ZSM5, mordenite, β, and Y, by means of solid-state NMR. The amount of undesorbed dichloromethane was determined by quantitative analysis of ^{1}H MAS NMR spectra. The strength and the amount of Brønsted acid sites could not explain the amount of the undesorbed dichloromethane. The channel size is the most probable to determine the amount. The ^{1}H and ^{13}C MAS NMR spectra as well as the ^{2}H static NMR spectra demonstrated that undesorbed dichloromethane is rather mobile.

Evaluation of acid properties is important in order to develop new solid acid catalysts which can replace liquid acid catalysts such as sulfuric acid.[1,2] In the field of solid-state NMR, trimethylphosphine oxide (TMPO) has widely been used to probe surface acidity,[3–16] because ^{31}P has high sensitivity and the ^{31}P chemical shift of TMPO is sensitive to the acid strength. TMPO is a solid substance at room temperature, and anhydrous dichloromethane and tetrahydrofuran were used as a solvent when TMPO was adsorbed. Evacuation was carried out to remove the solvent after adsorption of TMPO.

Previously, we studied the surface acidity of several porous materials using TMPO as a probe molecule.[13,14,17] During the course of those studies, we found that some samples adsorbed the solvent molecules as strongly as TMPO. Consequently, the solvent molecules could not be removed without desorption of part of the adsorbed TMPO. Most of the previous work did not check whether the solvent molecules were removed completely or not.[3–12]

Dichloromethane is a good solvent, which can well dissolve organic substances. The solvent has been used when a solid substance was adsorbed on an adsorbent. It is generally believed that dichloromethane is easily removed by evacuation at room temperature.

In the present work, we have studied the state of adsorbed dichloromethane molecules not removed by evacuation in several types of zeolites by means of solid-state NMR. NMR is non-invasive and non-destructive. We observed ^{1}H and ^{13}C magic-angle-spinning (MAS) NMR spectra as well as ^{2}H NMR spectra. The amount of adsorbed dichloromethane was determined by quantitative analysis of the ^{1}H NMR spectra, because the NMR signal intensity is proportional to the atomic concentration. ^{1}H NMR is advantageous compared to macroscopic methods such as thermogravimetric analysis, because it can distinguish dichloromethane from other coadsorbed species such as water if present. We discuss the correlation between the amount of the undesorbed dichloromethane and the structural parameters such as the Si/Al ratio of the framework, the pore and channel size, and the acidity. We expect that the present results will show which substances we should be careful of, when a solid substance is adsorbed on an adsorbent using a solvent.

Experimental

Materials. Dichloromethane (CH_2Cl_2) and deuterated dichloromethane (CD_2Cl_2) were obtained from Kanto Chemical Co., Inc. and ISOTEC, Inc. respectively. Zeolite samples were reference catalysts supplied by The Catalysis Society of Japan, which had been characterized by a number of methods. They were coded as follows: H-type mordenite samples were JRC-Z-HM10, JRC-Z-HM15, JRC-Z-HM20; H-type ZSM-5 samples were JRC-Z5-25H, JRC-Z5-70H, JRC-Z5-1000H; H-type Y zeolite was JRC-Z-HY5.6; and H-type β zeolite was JRC-Z-HB25. JRC means Japan Reference Catalyst and Z is zeolite. H attached to the zeolite type means H^+ form. The number was a nominal SiO_2/Al_2O_3 molar ratio. The eight samples are named HM10, HM15, HM20, ZSM5-25H, ZSM5-70H, ZSM5-1000H, HY5.6, and HBEA25 in the present work. The as-supplied samples of HM10, HM15, HM20, ZSM5-25H, and ZSM5-1000H contained NH_4^+ ions and, therefore, those samples were calcined at 808 K under an air atmosphere to convert to H^+ form. The decomposition of NH_4^+ ions was confirmed by thermogravimetric analysis (TG).[17,18]

Dichloromethane was adsorbed, following the procedure of TMPO adsorption from a CH_2Cl_2 solution.[17] Neat dichloromethane was used instead of a CH_2Cl_2 solution of TMPO. The host samples were dried at 673 K for 3 h in an electric furnace under an air atmosphere. After cooling to 423 K, the dried sample was sealed in a vial with aluminum-faced silicone rubber septa while it was hot. After further cooling to room temperature liquid CH_2Cl_2 (or CD_2Cl_2) was injected into the sealed vial through an air-tight syringe, and then the samples were stirred for 4–5 h and kept static overnight. The sealed vial containing the sample was put in a vacuum desiccator, and the vial was opened by removing the septa under an N_2 atmosphere. The desiccator was closed and evacuated with an oil rotary vacuum pump (0.1 Pa). The sample was kept at room temperature under vacuum for 4 days with intermittent evacuation.

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The prepared samples were carefully handled without exposure to an air atmosphere because they easily adsorb moisture in air. For the measurements of MAS NMR spectra, all the samples were packed into a MAS rotor of a 4-mm diameter under an N_2 atmosphere. After packing into the rotor, the sealing of the 4-mm MAS rotor was rather good.[19] For the measurements of ^{2}H NMR spectra of static samples, the samples loaded with CD_2Cl_2 were transferred to a Pyrex tube with an outer diameter of 5 mm under an N_2 atmosphere, and then the tube was connected to a vacuum line, cooled in liquid nitrogen, and then evacuated to permit sealing with a torch.

NMR Measurements. ^{1}H and ^{13}C MAS NMR spectra were measured at room temperature with a Bruker MSL 400 spectrometer at Larmor frequency of 400.13 and 100.61 MHz, respectively. A Bruker MAS probehead was used with a zirconia rotor of 4.0-mm outer diameter. An ordinary single-pulse sequence was used for ^{1}H measurements. The parameters used were a ^{1}H $\pi/2$ pulse, a repetition time of 3 s, and the 16 accumulations. The pulse sequence for ^{13}C measurements was a single-pulse sequence with high-power ^{1}H decoupling during signal acquisition (HD). The parameters used were a ^{13}C $\pi/4$ pulse, a repetition time of 3 s, and 8000 to 76000 accumulations. The frequency scales of the ^{1}H and ^{13}C spectra were expressed with respect to neat tetramethylsilane (TMS) by adjusting the ^{1}H signal of adamantane spinning at 8.0 kHz to 1.87 ppm[20] and the lower-frequency signal of adamantane to 29.472 ppm.[21] The ^{1}H NMR spectra were analyzed quantitatively by using adamantane as an external reference.

^{2}H NMR spectra were measured for static samples with a Brucker MSL 400 spectrometer at Larmor frequency of 61.42 MHz, using a Bruker broadband probehead with a solenoid coil. The quadrupole echo pulse sequence was used, where the latter half of the echo signal was acquired and Fourier-transformed. The $\pi/2$ pulse width was 6 μs and the time interval between the two pulses was set at 15 μs. The recycle time was 1 s, and the number of accumulation was 19000 to 60000. The sample temperature was varied from 150 to 298 K. Spectra were presented with the signal of D_2O being 0 Hz.

Results and Discussion

^{1}H MAS NMR Spectra. Figure 1 shows ^{1}H MAS NMR spectra of H-type mordenites after CH_2Cl_2 adsorption followed by evacuation. The spectrum of HM20 consists of four components, which are centered at 9.0, 5.7, 5.3, and 1.8 ppm, as shown by chain lines in Figure 1C. The spectrum of HM15 is also composed of the four components, whereas the 1.8-ppm component is absent in HM10. According to previous work,[18] the 1.8-ppm component is ascribed to isolated Si–OH, and the 9.0-ppm component to hydrogen-bonded Si–OH. The broad 5.7-ppm component is dominant, being ascribed to Brønsted acid sites, Si–OH–Al. The sharp 5.3-ppm component was not observed in dehydrated samples,[18] where no CH_2Cl_2 was adsorbed. On the other hand, neat CH_2Cl_2 has a ^{1}H chemical shift of 5.443 ppm.[22] Consequently, the 5.3-ppm component is ascribed to adsorbed CH_2Cl_2 molecules which were not removed by evacuation. The amount of the residual CH_2Cl_2 molecules increases with decrease in the Si/Al ratio, that is, HM20 < HM15 < HM10.

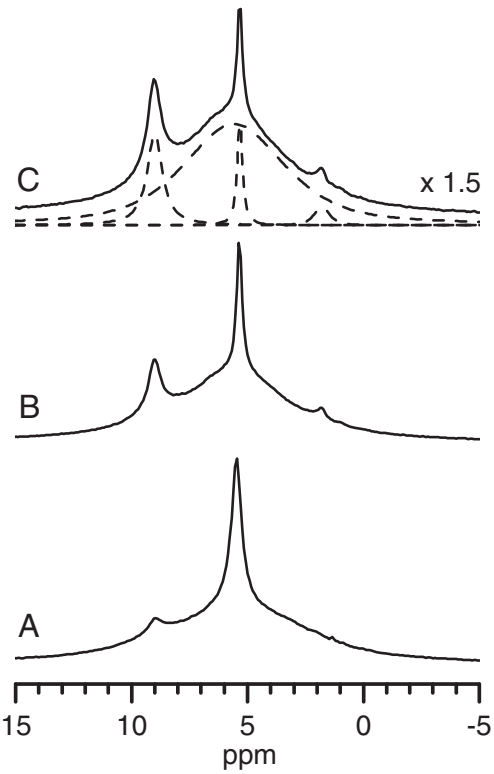

Figure 1. ^{1}H MAS NMR spectra of H-type mordenites after CH_2Cl_2 adsorption followed by evacuation; (A) HM10, (B) HM15, and (C) HM20. The spinning rates of the samples were (A) 10, (B) 8.7, and (C) 9.2 kHz. The signal intensities are normalized and the number in the figure is a multiplication factor. The spectrum of HM20 consists of four components shown by chain lines.

Figure 2 shows ^{1}H MAS NMR spectra of H-type ZSM-5 after CH_2Cl_2 adsorption followed by evacuation. The spectrum of ZSM5-25H consists of four components, as shown by chain lines in Figure 2A. The four components are the same as those in H-type mordenites. Among them, the 5.5-ppm component is ascribed to undesorbed CH_2Cl_2 molecules. A sharp peak at 5.3 ppm is dominant in the spectra of ZSM5-70H and ZSM5-1000H, which is also ascribed to undesorbed CH_2Cl_2 molecules. The amount of the undesorbed CH_2Cl_2 molecules increases with increase in the Si/Al ratio, that is, ZSM5-25H < ZSM5-70H < ZSM5-1000H. The dependence of the amount of the residual CH_2Cl_2 molecules on the Si/Al ratio is different between H-type moridenite and H-type ZSM-5.

Figure 3 shows ^{1}H MAS NMR spectra of H-type Y zeolite (HY5.6) and H-type β (HBEA25) after CH_2Cl_2 adsorption followed by evacuation. The spectrum of HY5.6 consists of two components at 4.8 and 8.6 ppm. The former is ascribed to Brønsted acid sites, Si–OH–Al and the latter is to hydrogen-bonded Si–OH. No signals due to undesorbed CH_2Cl_2 molecules are observed. The spectrum of HBEA25 consists of at least four components at 8.9, 5.3, 3.4, and 1.8 ppm. Among them, the small 5.3-ppm component is ascribed to undesorbed CH_2Cl_2 molecules. Its amount is only 0.45% of the total hydrogen content.

Table 1 summarizes the amounts of residual CH_2Cl_2 molecules not removed by evacuation in the order of the

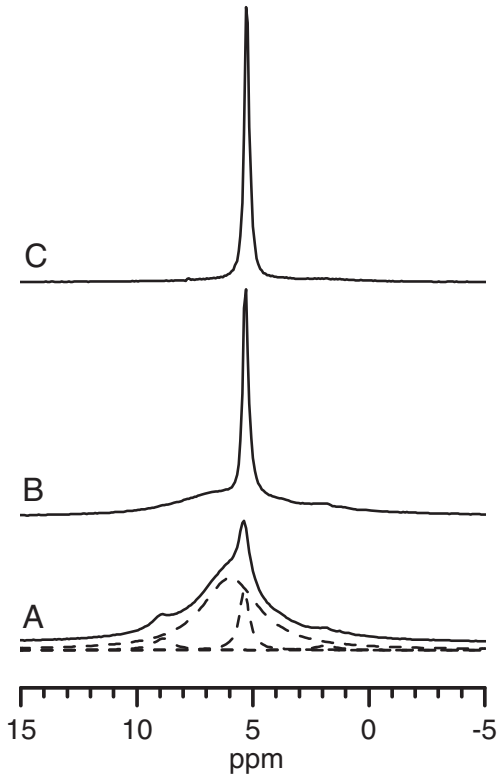

Figure 2. ^{1}H MAS NMR spectra of H-type ZSM-5 after CH_2Cl_2 adsorption followed by evacuation; (A) ZSM5-25H, (B) ZSM5-70H, and (C) ZSM5-1000H. The spinning rate was 8 kHz. The spectrum of ZSM5-25H consists of four components shown by chain lines. The signal intensities are normalized.

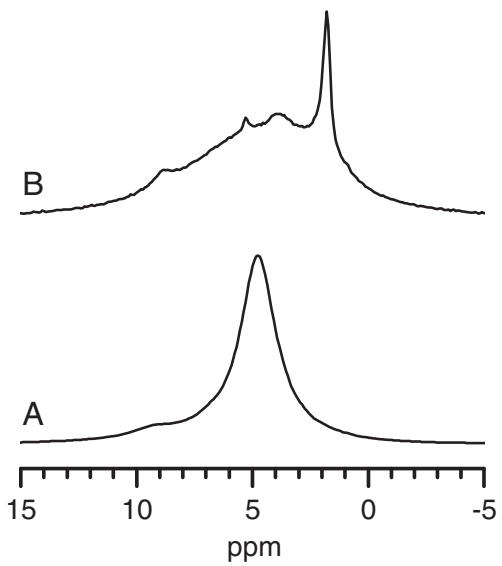

Figure 3. ^{1}H MAS NMR spectra of (A) HY5.6 and (B) HBEA25 after CH_2Cl_2 adsorption followed by evacuation. The spinning rates were (A) 8 and (B) 10 kHz.

amount. The sharp line shape of the residual CH_2Cl_2 molecules indicates that the molecules are rather mobile. If the molecules were in a rigid state, dipole–dipole interaction between ^{1}H spins would broaden the line width of ^{1}H static NMR spectra to several ten kilohertz. MAS of about 10 kHz can reduce the line width only partially. The observed sharp line width demonstrates that the molecules undergo a motion much faster than several ten kilohertz.

Table 1. Amounts of Undesorbed CH_2Cl_2

Samples	Amounts of CH_2Cl_2 /mmol g^{-1}	Nominal amounts of Brønsted acid sites /mmol g^{-1} a)
ZSM5-1000H	2.3	0.033
ZSM5-70H	0.85	0.47
HM10	0.70	2.8
ZSM5-25H	0.39	1.2
HM15	0.28	1.9
HM20	0.15	1.5
HBEA25	0.02	1.2
HY5.6	0.00	4.4

a) Calculated from the nominal SiO_2/Al_2O_3 molar ratio.

^{13}C MAS NMR Spectra. Carbon is contained only in the guest molecules and not in the host zeolites. Thus, the guest molecules can be observed selectively by ^{13}C NMR. Figure 4 shows ^{13}C MAS NMR spectra. HD pulse sequence was used instead of the cross polarization pulse sequence, because the sharp line shape of adsorbed CH_2Cl_2 in the ^{1}H MAS NMR spectra indicates that the guest molecules are relatively mobile. Cross polarization is ineffective in this case.[23] The ^{13}C signal intensity obtained by HD is proportional to the amount of the guest molecules in principle. As shown in the figure, the ^{13}C signal intensities agree fairly well with the ^{1}H signal intensities listed in Table 1.

The ^{13}C chemical shifts are 54.8, 53.6, and 53.7 ppm for HM10, HM15, and HM20, respectively. They are 54.1, 53.6, and 53.2 ppm for ZSM5-25H, -70H, and -1000H, respectively. The value decreases with increase in the Si/Al ratio. The interaction between CH_2Cl_2 and Brønsted acid proton might cause the high frequency shift. The ^{13}C chemical shift of neat CH_2Cl_2 is 54.548 ppm (The value reported previously (55.548 ppm)[22] was incorrect, and thus it is corrected here).

^{2}H Static NMR Spectra. The line shape of ^{2}H NMR spectra is sensitive to a motion with a rate of about 100 kHz. We have measured ^{2}H NMR spectra in order to ascertain the mobile state of the guest molecules. Figures 5A to 5C show ^{2}H NMR spectra of H-type mordenites after CD_2Cl_2 adsorption followed by evacuation. The signal intensity indicates that the amount of the adsorbed CD_2Cl_2 molecules is in the order of HM10 > HM15 > HM20. This order agrees with the results of ^{1}H and ^{13}C MAS NMR. The spectrum of HM10 consists of two components; a broad component and a narrow one. The line width reflects the mobile state of the guest molecules. The narrow component undergoes an isotropic rotation, whereas the broad one rotates anisotropically. Only the broad component is observed in HM15 and HM20. The full width at half maximum of the broad component is about 20 kHz, which is much smaller than the value in the rigid state. The ^{2}H quadrupole coupling constant is about 200 kHz for a C–D bond.[24,25] This means that even the broad component is rather mobile. Consequently, both the broad component and the narrow one undergo motions much faster than 200 kHz.

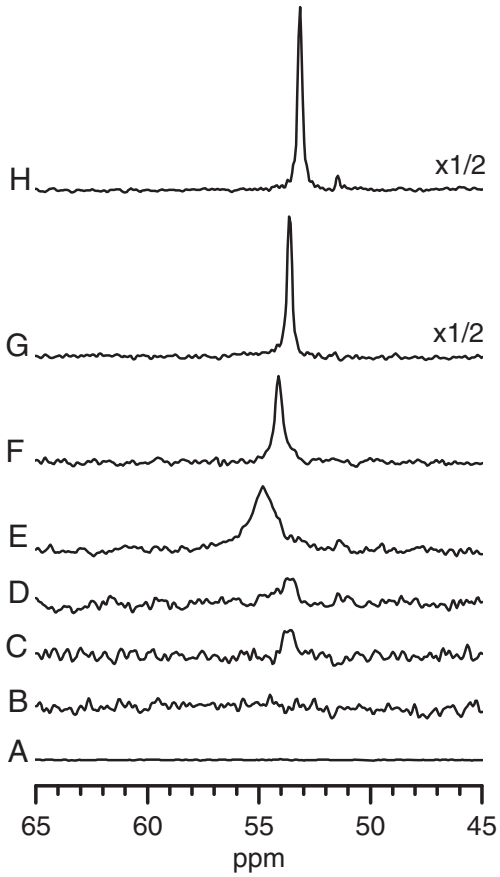

Figure 4. ^{13}C MAS NMR spectra of zeolite samples after CH_2Cl_2 adsorption followed by evacuation; (A) HY5.6, (B) HBEA25, (C) HM20, (D) HM15, (E) HM10, (F) ZSM5-25H, (G) ZSM5-70H, and (H) ZSM5-1000H. The spinning rates were (A, F, G, H) 10, (B, D) 8, and (C, E) 7 kHz. The signal intensities are normalized and the numbers in the figure are a multiplication factor.

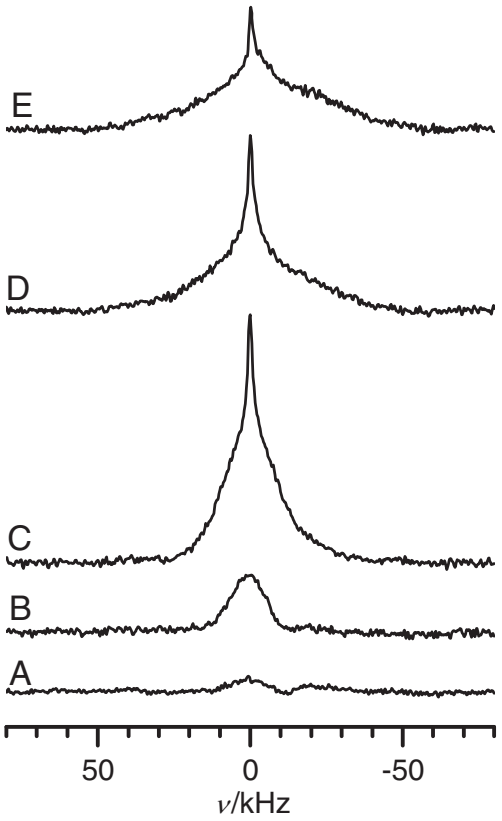

Figure 5. ^{2}H NMR spectra of H-type mordenites after CD_2Cl_2 adsorption followed by evacuation; (A) HM20 at 298 K, (B) HM15 at 298 K, (C) HM10 at 298 K, (D) HM10 at 200 K, and (E) HM10 at 150 K. The signal intensities are normalized for A–C.

Table 2. Channel Diameters and Acid Strengths in Zeolites

Samples	Framework type	Channel diameters/nm[2 a)]	Enthalpy change of ammonia adsorption/kJ mol^{-1} [b)]
ZSM-5	MFI	0.56 × 0.53, 0.55 × 0.51	134, 137
Mordenite	MOR	0.70 × 0.65, 0.57 × 0.26	142, 153
β	BEA	0.77 × 0.66, 0.56 × 0.56	128, 129
Y	FAU	0.74 × 0.74	119

a) Ref. 27. b) Ref. 26.

The motion becomes slower at lower temperatures. Figures 5D and 5E show ^{2}H NMR spectra for HM10 measured at 200 and 150 K, respectively. The broad component becomes broader, while the narrow component is still narrow. The motion of the broad component becomes slower or more anisotropic. The line shape of the broad component has no fine structures, suggesting a distribution of the effective quadrupole interaction.

The Amount of Undesorbed Dichloromethane. Which factor determines the amount of dichlomethane not removed by evacuation? The acid strength, the acid amount, and the channel size are considered as candidates.

H-type zeolites have Brønsted acid sites. The acid strengths of H-type mordenite and ZSM-5 are stronger than those of H-type β and Y zeolite.[26] The enthalpy change of ammonia adsorption obtained by temperature-programmed desorption of ammonia is listed in Table 2. The above trend might suggest that the amount of dichloromethane depends on the acid strength. For the same type of zeolite framework the acid strength becomes stronger as the Si/Al ratio increases.[28] The amount of undesorbed dichloromethane increases with the acid strength for H-type ZSM-5. However, the inverse trend is observed in the case of H-type mordenite. Thus, the acid strength cannot explain the amount of undesorbed dichloromethane.

The amount of Brønsted acid sites depends on the Si/Al ratio. One Brønsted acid site is created by one fourfold-coordinated Al in the framework. The amounts of Brønsted acid sites are approximately estimated from the nominal SiO_2/Al_2O_3 molar ratios, as listed in Table 1. Among the samples studied, HY5.6 has the largest amount of the acid sites, while ZSM5-1000H has the smallest amount. In other words, HY5.6 is the most hydrophilic, and ZSM5-1000H is the most hydrophobic. CH_2Cl_2 is expected to prefer hydrophobic sites. The undesorbed dichloromethane increases with increase in the acid amount in the case of H-type mordenite, whereas it decreases for H-type ZSM-5. Thus, the acid amount cannot explain the amount of undesorbed dichloromethane.

Dichloromethane molecules are rather mobile, as demonstrated by the NMR results. This means that the interaction between dichloromethane and the host is weak. Thus, the channel size might be a dominant factor determining the undesorbed amount of dichloromethane, instead of the adsorption sites. Table 2 summarizes the channel sizes of the zeolite framework.[27] The van der Waals size of dichloromethane is $0.64 \times 0.45 \times 0.42\,nm^3$, being calculated from the molecular structure and van der Waals radii.[29] Dichloromethane can diffuse through the channels except for the smaller ones in mordenite. The cross sections of the larger channels in each zeolite are in the following increasing order, ZSM-5 < mordenite < β < Y. This order roughly explains the amount of undesorbed dichloromethane, which is roughly ZSM-5 > mordenite > β > Y. As the channel is smaller, the barrier of desorption becomes larger.

The amount of undesorbed dicholoromethane depends on the Si/Al ratio in mordenite and ZSM-5, although the framework structure is the same. In the case of mordenite the amount increases with decrease in the Si/Al ratio. The amount of Brønsted acid sites increases with decrease in the Si/Al ratio. The effective channel size becomes smaller due to Brønsted acid sites. The change of the effective channel size increases the undesorbed dichloromethane.

On the other hand, the amount of the undesorbed dichloromethane decreases with decrease in the Si/Al ratio. The channel size of the ZSM5 framework is very small. Brønsted acid sites reduce the effective channel size furthermore, inhibiting accommodation of dichloromethane molecules. Thus, the best channel size is present for keeping dichloromethane molecules in the channel. Fine tuning of the effective channel size is possible by controlling the amount of Brønsted acid sites.

We want to propose that the channel size is a dominant factor to determine the amount of undesorbed dicholomethane. As has been described in the Introduction, dichloromethane is often used when a solid substance is adsorbed on an adsorbent. Although it has been believed that dichloromethane is easily removed by evacuation at room temperature, it is not removed in some microporous materials with a channel size similar to ZSM-5.

Summary

We have studied the state of adsorbed dichloromethane molecules not removed by evacuation in several types of zeolites by means of solid-state NMR.

(1) The amount of adsorbed dichloromethane not removed by evacuation was determined by quantitative analysis of the ^{1}H MAS NMR spectra. We propose that the amount is determined dominantly by the channel size. The strength and the amount of Brønsted acid sites cannot explain the amount of the undesorbed dichloromethane.

(2) The ^{1}H and ^{13}C MAS NMR spectra as well as the ^{2}H static NMR spectra demonstrate that the adsorbed dichloromethane is rather mobile.

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