Probing the Micropores in Linde-type A Zeolites by Helium-3 NMR

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NMR spectra of ^{3}He introduced in Linde-type A zeolites have been traced, which show that chemical shifts depend on the cations incorporated in the micropore. The chemical shift reflects the interaction with cations, the magnitude of which depends on the effective channel dimensions. ^{3}He NMR can probe the smaller pores with much shorter periods than the conventional ^{129}Xe NMR.

Microporous materials are widely used as catalysts, adsorbents, separation materials, and so on. The pore size is one of the key factors determining the function of these materials, because the sizes of the micropores are comparable to those of molecules. There are several methods to determine the pore size. Mercury porosimetry is used to determine the pore size with the diameter larger than several ten nm. The gas-absorption methods using nitrogen or krypton gas are widely used. The measurable pore size ranges from 2 to 50 nm. In the latter methods the total measurement time is of the order of ten hours because the time to reach equilibrium is necessary each time after the gas pressure is changed.

NMR can be used to explore the micropores by tracing the NMR spectra of substances confined in the micropores. Previously, we have reported that the ^{13}C chemical shift of tetramethylammonium ion confined in the pore is well correlated with the pore size.[1] ^{129}Xe NMR is also used to explore the pore using xenon as a probe. The ^{129}Xe chemical shift reflects the pore size.[2] The size of xenon is about 0.44 nm, and thus pores smaller than 0.44 nm are difficult to be characterized. For example, a long period of about 2 months and a high pressure are necessary to introduce xenon into NaA zeolite.[3] Furthermore, it took 3 to 30 h to trace one spectrum.[3]

^{3}He is NMR-visible and has a relatively high sensitivity. NMR of ^{3}He in porous glasses provides the pore shape but not the size.[4,5] NMR of ^{3}He dissolved in organic solids might yield valuable information on the intermolecular space, although the complicated spectra were not interpreted.[6] The diameter of He (about 0.28 nm)[7] is smaller than that of ^{129}Xe, and ^{3}He is much more NMR-sensitive than ^{129}Xe. Consequently, ^{3}He NMR is expected to be useful to characterize the smaller pores with the shorter time.

In the present work, the small micropores in Linde-type A zeolites have been explored by ^{3}He NMR. Linde-type A zeolites consist of two types of cages; sodalite cages (a diameter of 0.86 nm) and supercages (1.11 nm).[1,8] The channel combining the cages has a diameter of 0.41 nm.[8] We found that the peak position for the confined ^{3}He depends on the cation and consequently the effective channel dimension.

Three Linde-type A zeolites, KA (Molecular sieve 3A), NaA (Molecular sieve 4A), and CaA (Molecular sieve 5A) were obtained from Nishio Industries, Co., Ltd. (Osaka, Japan). Two other zeolites were also used; NaY and high-silica ZSM-5 supplied by The Catalysis Society of Japan, which were coded as JRC-Z-Y5.3 and JRC-Z-Z5-1000Na, respectively. ^{3}He gas was obtained from Isotec Inc. (Miamisburg, U.S.A.), whose purity was at least 99.95 atom %.

^{3}He NMR spectra were obtained with a Bruker ASX200 spectrometer (a static magnetic field of 4.7 T) at room temperature. The ^{3}He Larmor frequency was 152.45 MHz. A Bruker probehead for a liquid sample with a diameter of 10 mm was used without sample spinning. The $\pi/2$ pulse width was 27 μs. The ordinary single pulse sequence was used, in which the pulse width was set at 14 μs, the repetition time was 1 s and the typical number of accumulation was 32. The signal saturation was negligible under these conditions.

The sample tube was cylindrical with an outer diameter of 10 mm. The inner tube was coaxially inserted into the outer tube. The powder sample was packed into a space between the outer and the inner tubes. The inside of the inner tube was left empty. The sample tube was connected with a system of evacuation and gas supply through a 1/8-inch plastic tube. The gas pressure was controlled and monitored during the NMR measurements.

The samples was evacuated at 300 °C for a period longer than 1 h to remove water and air just before the NMR measurements. After cooling the sample to room temperature, ^{3}He gas was introduced at a required pressure. Usually, ^{3}He gas at a pressure of 100 to 120 kPa was first introduced, and then the pressure was gradually decreased.

Figure 1 shows ^{3}He NMR spectra at the gas pressure of 100 kPa. Each spectrum consists of two peaks. The peak marked by $*$ is ascribed to ^{3}He in the gas phase, because this peak is observed even when the sample tube was empty. The gas peak at 100 kPa is set at 0 ppm in this work. Another peak is ascribed to ^{3}He in the micropores, whose position depends on the sample. The peak shifts are 1.72, 0.28, and 0.03 ppm for KA, NaA, and CaA zeolites, respectively. It is well known that the effective channel dimensions increase in the order of KA (about 0.3 nm) $<$ NaA (0.4 nm) $<$ CaA (0.5 nm), although the framework structures are the same. With the decrease in the channel dimension, the peak shift increases.

The pressure of the gas phase was decreased gradually. The line shape is almost independent of the pressure. On the contrary, the signal intensity is proportional to the pressure, which is expected from the quantitative nature of NMR. This also suggests that absorption interaction between helium and the material is negligible. The signal positions of ^{3}He in the micropores were almost independent of the pressure down to about 10 kPa. Consequently, the interaction between ^{3}He spins does not affect the chemical shift.

When discussing the shift value, the effect of the volume magnetic susceptibility on the signal position should be taken into account because the shift range is very small. This effect

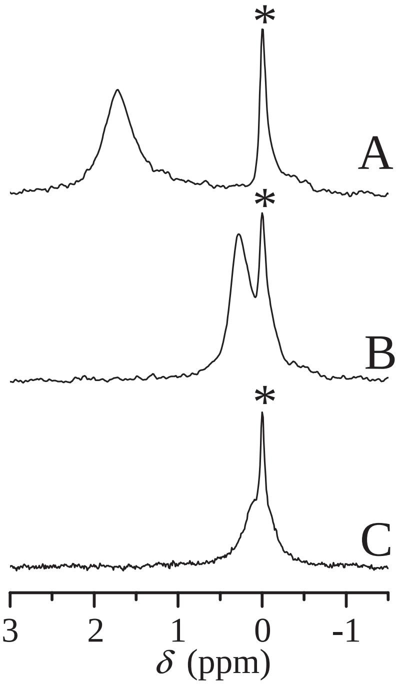

Figure 1. ^{3}He NMR spectra for (A) KA zeolite, (B) NaA zeolite, and (C) CaA zeolite. The pressure of the gas phase was 100 kPa. The $*$ marks indicate the signal of the gas phase.

is negligibly small for He gas because the density is very small. Thus, the 0-ppm position corresponds to a free ^{3}He atom. The sample tube made of Pyrex glass might affect the signal position slightly. However, this effect is the same for both the material and the gas. ^{3}He dissolved in porous glasses has a signal at about -3.4 ppm because of the diamagnetic susceptibility of the glasses.[4,5] The zeolites studied are diamagnetic, and thus a negative peak shift is expected if no other interactions are working.

The observed positive peak shift is considered to be caused by the interaction with cations. Generally, the chemical shift is a sum of a shielding term and a deshielding term. Because ^{3}He atoms have only 1 s electrons, the shielding term has a dominant effect on the ^{3}He chemical shift. Cations around the ^{3}He spin attract the electrons surrounding ^{3}He spins, leading to reduction of the shielding effect. The micropore enables close contact between a ^{3}He atom and cations. The smaller micropore makes the closer contact. Thus, the chemical shift increases with decrease in the effective channel dimensions.

The above consideration on the shift mechanism is validated by the following observations: NaY zeolite (the channel dimension of about 0.7 nm), which has larger micropores containing Na ions than A zeolites, shows a signal at -0.41 ppm (Figure 2a). High-silica ZSM-5, which contains negligible cations and has the channel dimension of about 0.54 nm, shows a signal at -0.58 ppm (Figure 2b). ^{3}He confined in fullerene dimer C120, which has many π electrons, gives signals around -10 ppm.[9]

In summary, NMR spectra of ^{3}He introduced in Linde-type A zeolites such as KA, NaA, and CaA have been traced in this work, whose peak shifts depend on the cation and consequently the effective channel dimension. Because He atom (0.28 nm) is smaller than Xe atom (0.44 nm), ^{3}He NMR can probe the smaller pores than ^{129}Xe NMR. The total experiment time becomes short, that is, several minutes, which consists of a waiting time to reach equilibrium after the gas introduction and the NMR measurement time. Thus, ^{3}He NMR is useful to probe the small pores, which is complimentary to ^{129}Xe NMR and the gas-absorption method. Application of ^{3}He NMR to other microporous and mesoporous materials is now in progress.

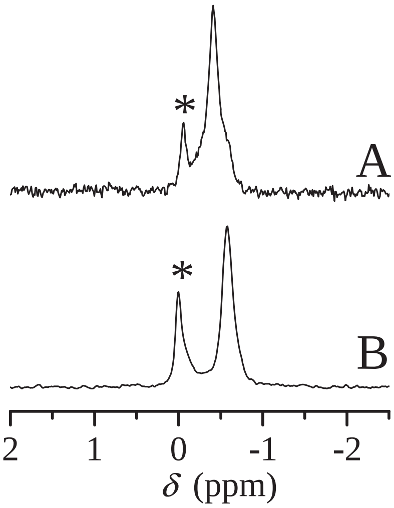

Figure 2. ^{3}He NMR spectra for (A) NaY zeolite and (B) high-silica ZSM-5. The pressure of the gas phase was 100 kPa. The $*$ marks indicate the signal of the gas phase.

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