Dynamics of Water Molecules in Micropores of $AlPO_4$-5 and SAPO-5 Studied by ^{1}H NMR

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Dynamics of water molecules in one-dimensional micropores $AlPO_4$-5 and SAPO-5 frameworks was studied by measuring ^{1}H NMR spectra, second moment M_2 of line-width and spin-lattice relaxation time T_1. Although the presence of two kinds of water molecules free and bound on the capillary wall were reported in $AlPO_4$-5, our NMR T_1 results imply the absence of two kinds of H_2O motions, but the motional rate distributes from slow to fast jumps in both $AlPO_4$-5 and SAPO-5.

$AlPO_4$-5, one of typical aluminophosphate microporous crystals forms a one-dimensional homogeneous channel structure with a pore diameter of 0.73 nm. SAPO-5 has an analogous structure to that in $AlPO_4$-5, but a part of P (and Al) atoms in channel walls are replaced by Si, and hence, Brönsted acid sites are created on the pore surface. Molecules adsorbed in $AlPO_4$-5 and SAPO-5 can form one-dimensional molecular arrays which are expected to exhibit new structural and dynamical properties different from two or three dimensionally aggregated molecular systems.

From the measurement of ^{2}H NMR spectra of ^2H_2O in $AlPO_4$-5,[1,2] Goldfarb et al. reported the presence of two kinds of water molecules in pores: one is free and the other is fixed on the wall. To study dynamics of H_2O motions affected by the wall structures in $AlPO_4$-5 and SAPO-5, we measured ^{1}H NMR spin-lattice relaxation times (T_1), second moments of resonance lines (M_2) and spectra of H_2O adsorbed in $AlPO_4$-5 and SAPO-5.

$AlPO_4$-5 and SAPO-5 were synthesized according to the reported method.[3] Obtained fine crystals of ca. 100 µm long were calcined at ca. 990 K for 48 h and kept in vacuo at 393 K for 2 days, then exposed to saturated H_2O vapor. These specimens abbreviated to $AlPO_4$-5(H_2O) and SAPO-5(H_2O) were used for measurements.

X-Ray powder diffraction on calcined crystals were conducted for identifying the obtained samples. The Si/P atomic ratio in SAPO-5 was determined by a JEOL JXA-8621 electron probe microanalyser(EPMA) to be 9 ± 1 / 91 ± 1. The water content in $AlPO_4$-5(H_2O) was obtained by thermo-gravimetry affording a weight loss of 22% at 360–370 K corresponding to the water desorption. Comparing this value with 21.96%[4] reported, micropores in $AlPO_4$-5 are presumed to be almost filled with water molecules.

As shown in Figure 1, ^{1}H NMR spectra in $AlPO_4$-5(H_2O) and SAPO-5(H_2O) observed by a Bruker MSL-300 spectrometer exhibited a single peak with a width of 2.0 ± 0.1 kHz above room temperature. This implies that water molecules in both systems perform mostly the isotropic rotation in this temperature range. This result seems to be inconsistent with the reported ^{2}H NMR spectra[2] showing a doublet structure even at 353 K. An almost temperature independent small splitting also observed in our ^{2}H NMR measurement is attributable to the electric field gradient formed by charges on the pore wall. Our rough calculation based on the point charge model supported this explanation. Upon cooling, a gradually growing broad component with a width of ca. 60 kHz appeared accompanied by a slowly broadening narrow peak suggesting two kinds of water molecules as reported.[1]

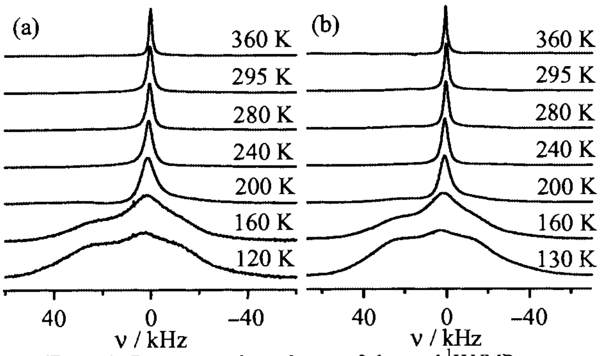

Figure 1. Temperature dependences of observed ^{1}H NMR spectra in H_2O adsorbed in (a) $AlPO_4$-5 and (b) SAPO-5.

Figure 2 shows M_2 observed by the solid echo method with a Bruker SXP-100 spectrometer in $AlPO_4$-5(H_2O) and SAPO-5(H_2O). M_2 of ca. (30 ± 5) × 10^{-2} mT^2 observed at ca. 100 K agreed with 33.7 × 10^{-2} mT^2 calculated for the rigid water molecule. Above ca. 200 K, the echo signals in both systems showed barely separable two components in consistent with the foregoing ^{1}H spectra showing the superimposed broad and narrow signals. We could determine large M_2 components in both specimens and the small component of SAPO-5(H_2O). A small M_2 of (0.5 ± 0.1) × 10^{-2} mT^2 in SAPO-5 above 220 K implies the onset of the H_2O isotropic rotation, and the large component showing a width of ca. 2.5 × 10^{-2} mT^2 in both systems at room temperature is attributed to the restricted water. It is noted that the gradual M_2 change over 150 K observed in both systems is unexplainable by the usual thermal activation process of molecular motions.

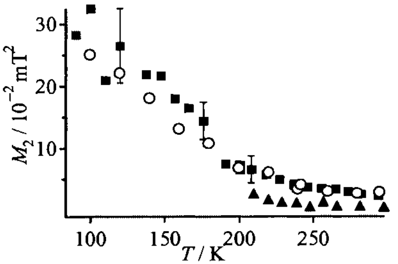

Figure 2. Temperature dependences of the second moment (M_2) of observed ^{1}H NMR absorptions in H_2O adsorbed in $AlPO_4$-5 (broad [○] component) and SAPO-5 (broad [■] and sharp [▲] components).

The small and the large M_2 observed below room temperature in both systems can correspond to the observed two ^{1}H spectrum components together with the reported narrow and broad ^{2}H spectra.[1] These results imply the presence of free and fixed two kinds of H_2O molecules in micropores in accordance with the result reported by Goldfarb et al.[1]

The recovery of ^{1}H magnetization in ^{1}H NMR T_1 measurement with a Bruker SXP-100 spectrometer showed nonexponential decay in the T_1 measurement. We divided this decay curve into two T_1 components, where the ratio of the short component vs the whole T_1 was ca. 1/10. Figure 3 shows the temperature and frequency dependences of only the long T_1. The long T_1 component was assigned to H_2O adsorbed in micropores, while the short is attributable to H_2O located near trace of amounts of paramagnetic impurities formed in the wall which was observed by ESR.

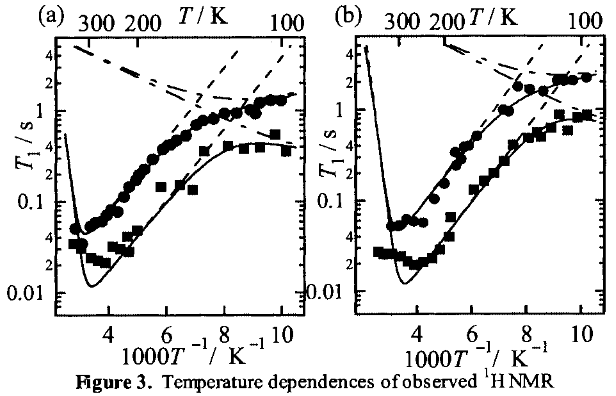

Figure 3. Temperature dependences of observed ^{1}H NMR spin-lattice relaxation times (T_1) of H_2O adsorbed in (a) $AlPO_4$-5 (b) SAPO-5, at 54.1 MHz [●] and at 14.1 MHz [■]. Solid lines are the best-fitted calculated values superposed by two T_1 components expressed as dotted and chain lines.

We tried to fit the observed long T_1 data by superposed two BPP-type minima originating from reported two kinds of H_2O molecules in pores, but could not obtain satisfactory fit. T_1 observed in both systems below room temperature could not be expressed by the ω^2 rule expected from the conventional BPP theory[5] in the range $\omega\tau_c >> 1$. Moreover, the T_1 minimum of 21 ms observed at 14 MHz was much longer than 3.9 ms calculated for the isotropic rotation model derived from the above M_2 analysis. These results together with the gradual M_2 decrease observed over 150 K as noted above, can be explained by assuming the Cole–Davidson type τ_c distribution[6] which can be expected from the presence of several kinds of water molecules with different environments in micropores. Conner has reported[7] a distributed τ_c given by

$$g(\tau) = \frac{\sin\beta\pi}{\pi}\left(\frac{\tau}{\tau_c - \tau}\right)^{\beta} \qquad \tau \le \tau_c \qquad (1)$$
$$= 0 \qquad \tau > \tau_c$$

where τ is the correlation time of the motion and β ($0 < \beta \le 1$) shows the distribution amplitude. Substituting eq 1 into the BPP equation, T_1 is given by

$$T_1^{-1} = \frac{2}{3}\gamma^2 \Delta M_2 \left\{ \frac{\tau_c \sin\left(\beta \tan^{-1}\omega\tau_c\right)}{\omega\tau_c\left(1+\omega^2\tau_c^2\right)^{\beta/2}} + \frac{2\tau_c \sin\left(\beta \tan^{-1} 2\omega\tau_c\right)}{\omega\tau_c\left(1+4\omega^2\tau_c^2\right)^{\beta/2}} \right\} \qquad (2)$$

where γ, ΔM_2 and ω are the protonic magnetogyric ratio, the M_2 reduction by the motion, and the Larmor frequency, respectively. The Arrhenius equation for the cut-off time τ_c is assumed by

$$\tau_c = \tau_0 \exp\frac{E_a}{RT} \qquad (3)$$

Here, E_a denotes the activation energy of the motion.

The observed values were fitted by superimposed two motional modes: the high-temperature mode **1** was assumed to have a τ_c distribution given by eq 1, while the low-temperature mode **2** is expressed by the BPP-type relaxation for simplicity. We assigned mode **1** to the H_2O isotropic rotation because M_2 less than 3×10^{-2} mT^2 above 250 K in $AlPO_4$-5(H_2O) was explained by this motion. Mode **2** was assigned to the 180°-flip because of the small ΔM_2 of 0.38×10^{-2} and 0.2×10^{-2} mT^2 observed in $AlPO_4$-5(H_2O) and SAPO-5(H_2O), respectively. This model is consistent with the reported ^{2}H spectrum at 148 K[1] with a narrow component explainable by this motion of a part of H_2O in pores. The best fitted T_1 and determined motional parameters are shown in Figure 3 and Table 1, respectively.

Table 1. Motional parameters of water molecules derived from T_1 data.

Sample	Mode	E_a / kJ mol^{-1}	ΔM_2 / 10^{-2} mT^2	τ_0 / s	β
$AlPO_4$-5 (H_2O)	**1**	50 ± 4	33.5 ± 2	4.0×10^{-17}	0.15 ± 0.03
	2	3.0 ± 0.5	0.38 ± 0.1	8.0×10^{-11}	1 (BPP)
SAPO-5 (H_2O)	**1**	40 ± 3	29.3 ± 2	4.0×10^{-16}	0.17 ± 0.03
	2	3.0 ± 0.5	0.21 ± 0.1	6.5×10^{-11}	1 (BPP)

It is noted that we obtained small β values of 0.15 ± 0.03 and 0.17 ± 0.03 in $AlPO_4$-5(H_2O) and SAPO-5(H_2O), respectively, indicating the presence of quite a wide τ_c distribution of the isotropic reorientation. This implies that the barrier for water rotation, i.e., the rotational jump rate is widely spread in capillaries. This conclusion is consistent with temperature dependences of M_2 in the present study and also reported ^{2}H spectra[1] exhibiting a gradual change in a wide temperature range. We showed from the ^{1}H NMR spectra the presence of two kinds of water, free one in the central part in capillaries and the other fixed on the wall. Here, we have to say, however, that H_2O in micropores above ca. 200 K cannot be divided into the two groups, but they distribute between these two extreme states, namely, freely rotating and fixed in both molecular sieves.

Any detectable difference on H_2O dynamics in SAPO-5 from in $AlPO_4$-5 was not observed in all NMR measurements despite of the existence of acid sites on the surface of micropores. The number of water molecules much larger than the acid site seems to smear out the effect of the site.

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