Macroscopic or microscopic information of Y zeolite from ^{129}Xe n.m.r. line splitting

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The origin of ^{129}Xe n.m.r. line splitting observed in the study of Y zeolite has been investigated by comparing the n.m.r. spectra obtained before and after mixing various Y zeolites containing different cations or metal clusters at room temperature and also by low-temperature n.m.r. study of the zeolite mixtures. The results show that two ^{129}Xe n.m.r. lines separated by as much as 30 ppm apart can be completely coalesced at room temperature after mixing. The xenon exchange rate between ordinary Y zeolite crystallites of 1 μm size is usually so fast that the n.m.r. signal can only provide information averaged over many crystallites. Only at low temperatures, for very large chemical shift differences or for specially prepared Y zeolites with much larger crystal size, the xenon n.m.r. signal can be specific to the local environment inside the zeolite crystal.

INTRODUCTION

Xeon-129 is a nucleus suitable for n.m.r. study since it has a nuclear spin of 1/2, a relatively high natural abundance (26.44%), and a relatively high n.m.r. sensitivity (1.33 compared with ^{13}C). It is chemically inert in most cases. Its physical interaction with other species, through the collision or the van der Waals complex formation, brings about very large chemical shifts. Recently, its n.m.r. has attracted great attention in the study of zeolites. The ^{129}Xe n.m.r. chemical shift of xenon adsorbed on zeolites is very sensitive to the zeolite environment[1] and therefore serves as a useful probe for studying various problems with zeolites such as the exchange of cations,[2–5] clustering of transition metals,[6–10] the distribution of adsorbed species,[11–14] the zeolite crystallinity,[15,16] and the pore blocking.[17]

An important question raised in the study of zeolites by the ^{129}Xe n.m.r. method is whether the n.m.r. signal is always specific to a local environment inside the zeolite crystallite. Fraissard *et al.* noticed that the xenon atoms undergo fast exchange, on the n.m.r. time scale, over more than a few supercages of the Y zeolite. However, they assumed that motional average of the chemical shift occurred at room temperature over a region that was significantly

smaller than a Y zeolite crystallite[1,12,13] of normally 1 μm size. According to this assumption, two ^{129}Xe n.m.r. lines should be obtained from xenon adsorbed on the mixture of two different Y zeolites. Furthermore, if any physicochemical change occurs in a limited region as the chemisorption of hydrogen does within the outer rim of the Y zeolite crystallite containing platinum clusters (Pt/NaY),[13] the change in the local environment could easily be monitored by the appearance of the second n.m.r. line associated with the new environment for xenon.

In 1987, Schoemaker and Apple[8] reported partially coalesced ^{129}Xe n.m.r. lines on mixing of a NaY zeolite and a ruthenium-cluster containing Y zeolite (Ru/NaY). Their result indicates that Fraissard's assumption on the xenon exchange may not be applied at least to certain cases such as Ru/NaY. However, there is still uncertainty as to the origin of separate peaks in the ^{129}Xe n.m.r. of certain samples,[2] and therefore it will be of great interest in the zeolite field to clarify the general nature of the origin of the ^{129}Xe n.m.r. line broadening.

EXPERIMENTAL

The NaY zeolite samples used in this work and their crystal sizes are listed in *Table 1*. The CaY zeolite samples were prepared by exchanging Ca^{2+} into the NaY zeolite twice with an aqueous solution of $CaCl_2$ containing 2.5 times excess Ca^{2+}. The Pt/NaY sample (containing 2.0% Pt) was prepared via the ion-

Table 1 The chemical shift (ppm) of ^{129}Xe obtained at 296 K

Before mixing			After mixing	P_{Xe}/Torr	Crystal size /μm[a]
NaY[b]	83	CaY[c] 117	91	400	1.0
NaY[d]	82	CaY 117	90	400	0.8
NaY[e]	86	CaY 111	99	400	0.6
NaY[e]	86	Ru/NaY 129	97	400	0.6
NaY[d]	82	Pt/NaY 99	90	400	0.8
NaY[e]	79	HMB/NaY 111	99	300	0.6
NaY[f]	78	HMB/NaY 109	80,109	300	1.2

[a] Obtained by SEM
[b] Linde SK-40
[c] Samples in this column were prepared from the NaY zeolites listed in the first column, respectively
[d] Linde LZY-52
[e] Prepared by the procedure of Breck,[18] Si/Al = 2.4
[f] Used in the previous study of HMB/NaY[11,24]

exchange procedure reported by Gallezot *et al.*[19] The Ru/NaY sample (containing 2.4% Ru) was prepared according to the procedure reported previously.[20] The crystal size of these zeolite samples was determined by scanning electron microscopy (SEM).

The samples were pressed into a form of self-supporting pellets of 0.5–1.0 mm size and then placed in 8 mm o.d. Pyrex tubes that have specially designed ground-glass coaxial stopcocks. The Pt/NaY and Ru/NaY samples were re-reduced at 573 K by high-purity H_2 (99.99%) passed through a MnO/SiO_2 trap. All samples were separately dehydrated overnight at 1×10^{-5} Torr and 673 K. Sample mixing was then performed by grinding in a porcelain mortar inside a glove box. Natural xenon gas (Matheson 99.995%) was equilibrated with the sample for 30 min at 296 K. For low-temperature ^{129}Xe n.m.r. experiments, sample tubes containing the zeolite mixtures with xenon adsorbed at 400 Torr and 296 K was cooled by flowing cold N_2 into the n.m.r. probehead. The equilibrium pressure of xenon was not determined at other temperatures.

All the ^{129}Xe n.m.r. spectra were obtained with a Bruker AM-300 spectrometer operating at 83.0 MHz for ^{129}Xe. Deuterated water (or diethyl ether for the low-temperature n.m.r. experiment) was placed in the annular space between the 8 mm o.d. sample tube and a commercial 10 mm o.d. n.m.r. tube for field locking. Typically, a spectrum was acquired after accumulation of 500–2000 pulse transients with a repetition time of 0.5 s without sample spinning. The chemical shift was referenced with respect to the xenon gas extrapolated to zero pressure.

RESULTS AND DISCUSSION

Figure 1a is a ^{129}Xe n.m.r. spectrum obtained from xenon adsorbed at 296 K and 400 Torr on the macroscopic physical mixture of self-supporting granules of a NaY zeolite (Linde SK-40) and those of a CaY zeolite (prepared by calcium ion exchange into SK-40). The spectrum shows two well-separated lines; the resonance line appearing at 119 ppm in the

spectrum is the same as that obtained from the CaY zeolite under the same experimental condition, and the other line at 83 ppm is from the NaY zeolite. However, the two ^{129}Xe n.m.r. lines coalesced after the two kinds of zeolite pellets had been ground in a porcelain mortar under dry nitrogen atmosphere (*Figure 1b*). Such a coalescence of n.m.r. lines indicates that the xenon exchange rate between the adjacent CaY and NaY crystallites of approximately 1μm size should be much faster than $(119 - 83) \times 83.0$ Hz $\simeq 3000$ Hz under our experimental condition. Here it should be pointed out that the two zeolites had to be separately dehydrated before mixing to avoid ion exchange that otherwise took place during the high-temperature treatment and thus altered the chemical shift value.

As listed in *Table 1*, mixing of other Y zeolites similarly resulted in the coalescence of ^{129}Xe n.m.r. lines. The ^{129}Xe n.m.r. signal is thus confirmed to be averaged by rapid xenon exchange between more than two crystallites of the Y zeolites including the Pt/NaY and the Ru/NaY samples. This result agrees with a previous one reported by Shoemaker and Apple[8] from a mixture of NaY and Ru/NaY, for their two ^{129}Xe n.m.r. lines partially coalesced after only a gentle mixing with a glass rod. It seems that our mixing in a porcelain mortar was more uniform. Scanning electron microscopy showed that zeolite crystal damage did not occur under our experimental condition. However, excessive grinding in an agate mortar for longer than 10 min resulted in significant crystal damage. By applying the Einstein equation for diffusivity,[21] we also estimated that the xenon diffusivity should be at least on the order of $\sim 10^{-6}$ cm^2 s^{-1}. This value is comparable to $\sim 10^{-4}$ cm^2 s^{-1}
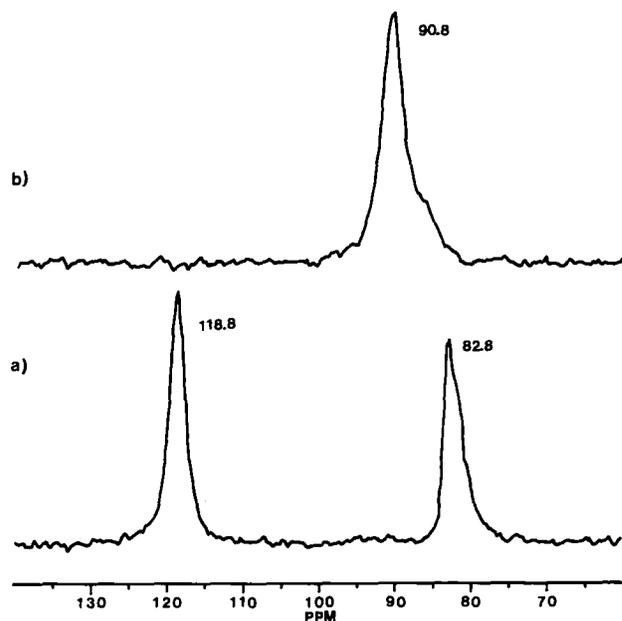
Figure 1 ^{129}Xe n.m.r. spectra obtained from xenon adsorbed at 296 K and 400 Torr on the mixture of NaY (SK-40, Linde) and CaY zeolite. (a) Mixture of two kinds of the zeolite pellets of 0.5–1.0 mm size; (b) zeolite well mixed in a porcelain mortar
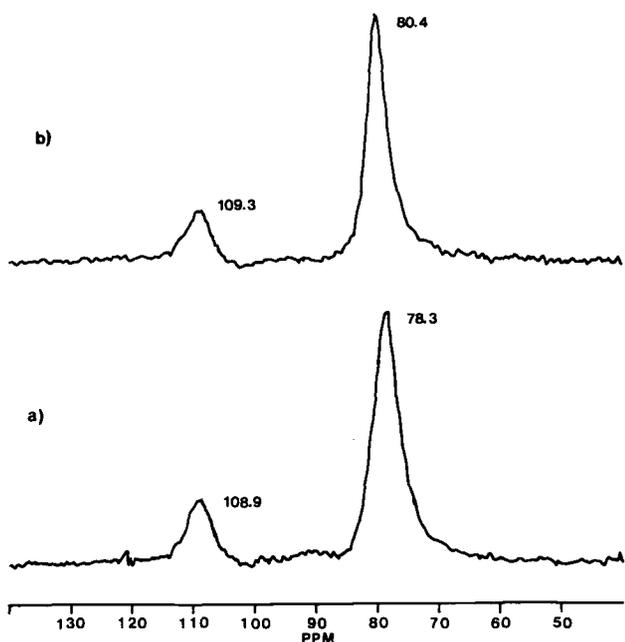
Figure 2 ^{129}Xe n.m.r. spectra obtained from xenon adsorbed at 296 K and 400 Torr on NaY and HMB/NaY zeolites. (a) Two samples vertically separated in the n.m.r. tube; (b) well mixed in a porcelain mortar

obtained by Caro *et al.*[22] for short-chain paraffins, which have weak interactions with the support and about same kinetic diameters as xenon, under similar adsorbate concentrations in a NaX zeolite.

Fraissard *et al.* reported the appearace of two ^{129}Xe n.m.r. lines at room temperature in the study of adsorption of H_2,[4] O_2,[13] CO,[13] and ethylene[12] on the Pt/NaY sample. They interpreted their results as evidence for two different regions in the zeolite crystallite as the chemisorption started to occur in the outer rim of the crystallite. However, rapid motional averaging of our ^{129}Xe n.m.r. signal, revealed in this work, suggests that their two lines could come from a rather macroscopic heterogeneity of the sample. A macroscopically heterogeneous adsorption of organic molecules was already noticed in a previous work where two of us (R.R. and B.F.C.) were involved. In their first report on the distribution of hexamethyl-benzene (HMB) adsorbed on NaY zeolite (HMB/NaY),[11] two ^{129}Xe n.m.r. lines were attributed to a heterogeneous distribution of HMB within the same zeolite crystal. But, further works have revealed the ^{129}Xe n.m.r. line came from the upper part of the sample tube where one HMB molecule was uniformly adsorbed per supercage.[23,24] The other ^{129}Xe n.m.r. line came from the lower part where no HMB was adsorbed. Similarly, a macroscopically heterogeneous adsorption of H_2O on NaY was observed by Gedeon *et al.*[25]

The same HMB/NaY sample used in the previous study was also tested in this work. The sample was an exceptional case that did not show the coalescence of the ^{129}Xe n.m.r. lines as shown in *Figure 2*. On the other hand, a similar HMB/NaY sample prepared from the NaY zeolite prepared here showed the

coalescence, independent of the mixing ratio (1:3–3:1) between the HMB/NaY and NaY samples. These different behaviors of the two HMB/NaY samples can be explained by the difference in their crystal sizes (1.2 and 0.6 μm, respectively). The separation of the two ^{129}Xe n.m.r. lines observed only from the mixture of HMB/NaY and NaY zeolites shows that xenon diffused more slowly in the HMB/NaY zeolite than in the NaY, CaY, Pt/NaY, or Ru/NaY sample studied in this work. It is likely that the adsorbed hexamethylbenzene molecules of 0.84 nm size hinder the diffusion of xenon along the zeolite channel.

Figure 3 shows the low-temperature ^{129}Xe n.m.r. spectra of xenon adsorbed on the mixture of a NaY zeolite (SK-40) and a CaY zeolite (Ca^{2+}-exchanged into SK-40). The ^{129}Xe n.m.r. lines coming from the two kinds of zeolite crystallites were completely resolved at 173 K due to a decreasing exchange rate at low temperatures.[26] This result suggests that the xenon exchange rate at 173 K between two adjacent zeolite crystallites of 1 μm size was approximately
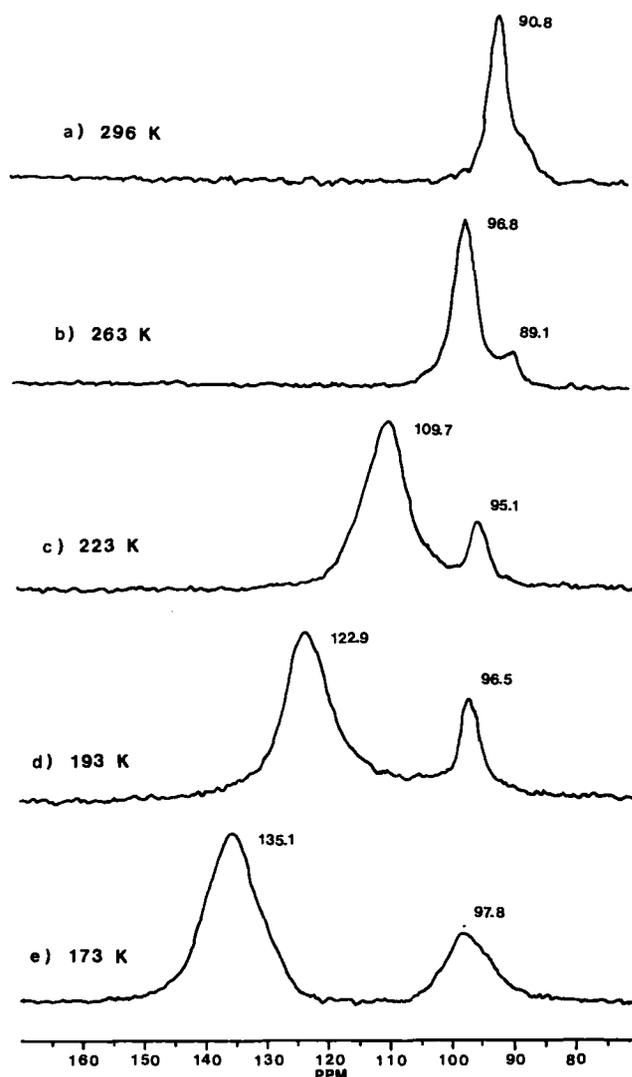
Figure 3 Low temperture ^{129}Xe n.m.r. spectra of well-mixed NaY (SK-40, Linde) and CaY zeolites

(135 − 98) × 83.0 Hz = 3000 Hz, from which the diffusivity in the NaY zeolite was calculated to be approximately 7×10^{-6} cm^2 s^{-1}. Since the diffusion constants in zeolite depend on the structure of zeolite, the type of exchanged cations, and the concentration of adsorbed molecules,[21] care should be taken to extrapolate our data to other cases.

CONCLUSION

The coalescence of the ^{129}Xe n.m.r. lines, observed by mixing our Y zeolites such as NaY, CaY, Ru/NaY, and Pt/NaY, indicates that the adsorbed xenon atoms exchange very fast between the zeolite crystallites under this circumstance. Therefore, the ^{129}Xe n.m.r. line can provide only macroscopic information averaged over many of the zeolite crystallites under this circumstance. Use of the ^{129}Xe n.m.r. method at temperatures lower than 173 K was found to be necessary to obtain the information specific to the local environment within the Y zeolite crystallite. However, the xenon n.m.r. signal can be specific to the local environment inside the zeolite crystal even at room temperature if the Y zeolite crystal size is much greater than 1 μm or if the chemical shift difference is much greater than those observed in this work. The microscopic information thus obtained will be very useful to study the zeolite intercrystal diffusion of exchanged cations, adsorbed molecules, or any other species.

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