

^{129}Xe NMR Spectrum of Xenon in the α -Cage of Zeolite A during Hydration and Ion Exchange

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Xenon was forced into the α -cage of dehydrated NaA zeolite by heating to 523 K, with sufficiently high pressure of xenon (e.g., 14 atm) to increase the xenon concentration. After the sample was cooled to room temperature, the xenon was isolated as occluded in the zeolite cage. The ^{129}Xe NMR spectra for such occluded xenon showed remarkable changes in the line shape and the chemical shift during hydration and ion exchange of the zeolite, serving as an in-situ internal probe.

Introduction

Xenon adsorption on dehydrated zeolites and the detection with ^{129}Xe NMR were extensively used during the past 10 years to probe the physicochemical nature of zeolites,¹⁻⁵ metal clusters encaged in zeolite cages,⁶⁻¹⁵ organic molecules adsorbed on zeolites,⁶⁻¹⁹ etc. In a previous experiment by Samant et al.,²⁰ xenon was adsorbed within the α -cage of dehydrated NaA zeolite at high pressure and temperature, e.g., 40 atm and 573 K. When the sample was cooled to room temperature (RT), ^{129}Xe NMR spectrum of the encaged xenon showed five lines in the range 70–180 ppm, which were successively assigned to as many xenon atoms in the α -cage. Recently, the distribution in the number of occluded xenon atoms in dehydrated α -cage was investigated by using the NMR signal intensities as a function of the xenon occlusion pressure.²¹⁻²³

Samant et al. reported that the ^{129}Xe NMR lines were collapsed to a single peak at 187 ppm upon addition of water. The chemical shift of 187 ppm may be due to the formation of a xenon–water clathrate inside the α -cage as interpreted by Samant et al. It is also probable that the NMR peak is characteristic of xenon dissolved in water for which a value of 196 ppm was given earlier, as suggested by Ripmeester and Ratcliffe.²⁴ The difference between 187 and 196 ppm may come from the electric field in the zeolite. If the ^{129}Xe NMR line from the hydrated NaA zeolite is due to the xenon–water clathrate inside the α -cage,^{24,25} the chemical shift of hydrated xenon will depend significantly on the zeolite hydration and accordingly on the cation, which can be of great interest in clathrate chemistry. We thus attempt to investigate the dependence of chemical shift in ^{129}Xe NMR on the cation in hydrated zeolite A during the hydration and ion exchange.

Experimental Section

High-purity NaA zeolite was prepared according to a standard procedure in the literature.²⁶ After evacuation for 2 h at 673 K, the sample was equilibrated with xenon gas under 14 or 1 atm at 523 K. The adsorbed xenon gas was trapped in the α -cage by cooling to RT as described previously.²⁰ The sample is designated as Xe/NaA-*P* where *P* denotes the pressure in atm used for the xenon occlusion. The sample was transferred into a commercial 10-mm-o.d. NMR tube inside a glovebox to prevent from hydration with air moisture. Hydration of the Xe/NaA was performed at RT by exposing the sample to air that was saturated

with water vapor. Ion exchange of K^+ , Cs^+ , or NH_4^+ into the hydrated Xe/NaA was performed by stirring the sample for 1 h at RT in a 0.1 M aqueous solution of chloride that contained the amount of cations exceeding 10 times required for the maximum exchange. The zeolite sample was filtered and washed with doubly distilled water at RT. Such an ion-exchange procedure was repeated three times to increase the degree of ion exchange. KA and NH_4A samples were also obtained by the same ion exchange procedure with K^+ and NH_4^+ , respectively. The samples were evacuated overnight at RT and then put in contact with 1 atm of xenon at 350 K for 1 h. This gave partially dehydrated Xe/KA and Xe/ NH_4A samples. Water was added into the samples at RT for full hydration. A number of ^{129}Xe NMR spectra were obtained at various steps of the above xenon adsorption and zeolite hydration in order to follow the sample change.

All the ^{129}Xe NMR spectra were obtained at 296 K with a Bruker AM-300 FT-NMR spectrometer operating at 83.0 MHz for ^{129}Xe . Relaxation delay of 0.5 s was used for quick observation of NMR lines from samples in air. In vacuum (i.e., without paramagnetic O_2 , which speeded up the relaxation), much longer repetition times were required. For quantitative measurement of NMR line intensities, a sufficiently long repetition time of 10 s was used for samples even in air. Sample spinning and field locking were not used. All the chemical shift values are referenced to that of xenon gas extrapolated to zero pressure.

Results and Discussion

Hydration of Xe/NaA. Figure 1 shows changes in ^{129}Xe NMR spectra during hydration of Xe/NaA-14. Figure 1a was obtained before the hydration was started. The spectrum consists of five xenon NMR lines, which correspond to differences in the number of xenon atoms occluded within an α -cage, consistent with earlier results.²⁰⁻²² The NMR line at 80 ppm is assigned to a single xenon atom in the α -cage, and the other lines are shifted to low field because of increasing xenon–xenon interaction as the number of such xenon atoms increases within the α -cage. A narrow peak at 0.5 ppm is due to the small amount of xenon, which was slowly released from the sample into the gas phase over 1 year during the sample storage within sealed Pyrex tubing. The distribution in the number of occluded xenon atoms in α -cages can be determined from the relative signal intensities, as was recently done for the xenon occlusion as a function of pressure.²¹⁻²³ The present NMR data indicate that the most probable number of the occluded xenon atoms per α -cage was two under the experimental condition used to prepare the Xe/NaA-14 (i.e., 14 atm at 523 K), consistent with earlier results.²¹ We have also

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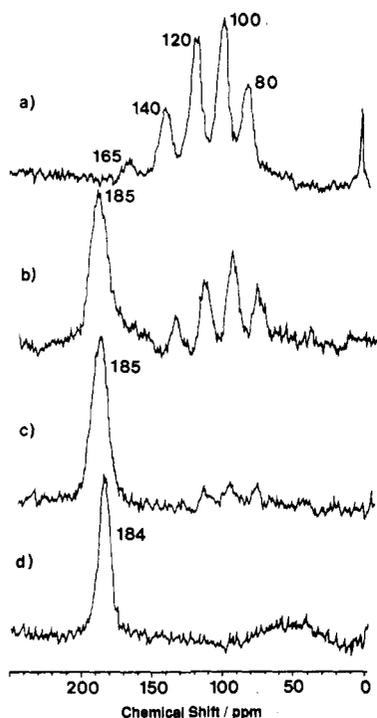


Figure 1. ^{129}Xe NMR spectra of Xe/NaA-14: (a) dehydrated; (b) hydrated for 12 h; (c) hydrated for 24 h; (d) in water.

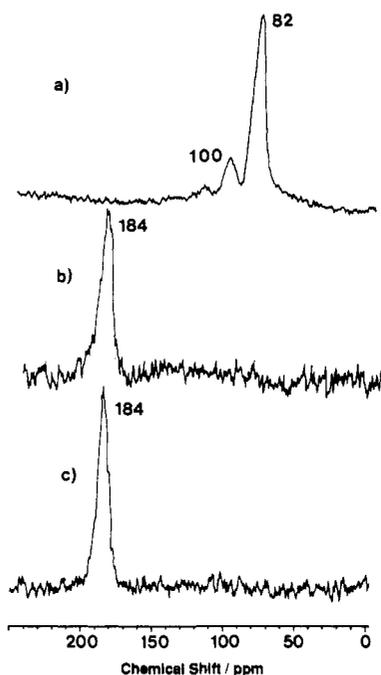


Figure 2. ^{129}Xe NMR spectra of Xe/NaA-1: (a) dehydrated; (b) hydrated for 24 h; (c) in water.

determined the average number of xenon atoms per α -cage by volumetric measurement of the xenon gas that was desorbed from the sample upon heating to 573 K and subsequently collected in a liquid N_2 trap. The result was 2.0 Xe/cage, in good agreement with the NMR line intensities. On the other hand, Xe/NaA-1 gave a ^{129}Xe NMR spectrum (Figure 2a) which indicates that most α -cages contain only one xenon atom or are empty when the xenon gas was adsorbed at low pressure.

Figure 1b was obtained after the Xe/NaA-14 sample was hydrated over 12 h. In the spectrum, all the aforementioned five ^{129}Xe NMR lines decreased in intensity remarkably without changing the chemical shift values, and a new peak appeared at 185 ppm as a result of the hydration. All the ^{129}Xe NMR lines between 70 and 170 ppm disappeared after such dehydration

over 24 h (Figure 1c). The chemical shift due to the zeolite hydration (185 ppm) did not change during the treatment, even after addition of water (Figure 1d). The intensity changes, which occurred without chemical shift variation for any of the NMR peaks, indicate that there existed a sharp boundary between the hydrated and dehydrated zones during hydration of the zeolite. Furthermore, the highly symmetric nature of the hydrated xenon peaks indicates that the content of hydrated water was nearly uniform throughout the hydrated zone. Otherwise, nonuniform partial dehydration should have brought about substantially broad peaks distributed between 185 and 80 ppm during the hydration. We consider that the hydration boundary exists between two macroscopic regions within the sample rather than within the same zeolite crystal with 1 μm in size. Such a sharp hydration front is consistent with hydration of NaY zeolite¹⁴ and adsorption of hexamethylbenzene (HMB) on NaY.¹⁶⁻¹⁹ The HMB adsorption at 523 K, on a densely packed bed of NaY with a depth greater than 5 mm, showed a sharp boundary between the two HMB-saturated and empty regions. Loose packings of the zeolite in a shallow bed indicated a wide distribution of HMB concentration over the entire sample. Thus, the ^{129}Xe NMR spectrum can be useful for the study of the diffusion and the concentration profile of adsorbed species on the zeolite cages.

Figure 2 shows ^{129}Xe NMR spectra obtained during hydration of Xe/NaA-1 in the same way as for the Xe/NaA-14. Since the ^{129}Xe NMR lines from more than one occluded xenon atom in the same α -cage (e.g., at 100 ppm, 120 ppm, etc.) are negligible, there must be very few cages containing more than one xenon atoms. This means that the NMR signals in parts b and c of Figure 2 came practically from single xenon atoms occluded in the α -cage of the hydrated NaA. The signals in Figure 2c and Figure 1d show that they have essentially the same chemical shift (i.e., 184 ppm) and line shape, which suggests that the additional xenon atoms might have escaped from the hydrated Xe/NaA-14 cages, leaving only one atom in the α -cage. In order to determine the number of the remaining xenon atoms per hydrated cage, the sample was evacuated at 573 K, while the desorbed xenon and water were collected in a liquid N_2 trap. Subsequently, the xenon gas was separated from water by repeated freeze-thaw cycles by using a dry ice trap. Volumetric measurement of the desorbed xenon gave 0.5 Xe/cage. Thus, the hydration of Xe/NaA-14 indeed decreased the xenon quantity from 2.0 to 0.5 Xe/cage, leaving possibly no more than one xenon atom per cage. The NMR signal intensity decreased continuously with time due to the loss of xenon after the hydration. Such xenon desorption by rehydration seems to indicate that the α -cage aperture is increased in size by hydration, probably due to the cationic positional change.

Ion Exchange in Xe/NaA. Figure 3 shows changes in the ^{129}Xe NMR spectra during ion exchange into the NaA in the presence of occluded xenon (i.e., during in-situ ion exchange). Figure 3a is the same as Figure 1d. It was obtained from fully hydrated Xe/NaA in water. When K^+ was exchanged into the Xe/NaA, the chemical shift was decreased to 150 ppm. When evacuated at 373 K, xenon was completely lost from the sample. The result suggests that xenon atoms can be adsorbed reversibly onto the hydrated KA zeolite under this condition. Fully hydrated KA with water did not adsorb xenon even after a prolonged exposure to xenon gas at 350 K and 1 atm, e.g., for 48 h. Such difficulty in the xenon adsorption was due to the presence of pore-filling water in the zeolite. After the pore-filling water was removed by evacuating for 12 h at RT, the sample began to adsorb xenon at 350 K. Figure 4a was obtained after such xenon adsorption at 350 K for 1 h. Addition of water into this sample gave the ^{129}Xe NMR spectrum in Figure 4b, which is essentially identical with Figure 3b. Thus, xenon can be put into the α -cage of the KA zeolite either before or after K^+ exchange. In-situ exchange of Cs^+ into the Xe/KA sample gave Xe/CsKA. Its ^{129}Xe NMR spectrum is shown in Figure 3c. Xenon was also

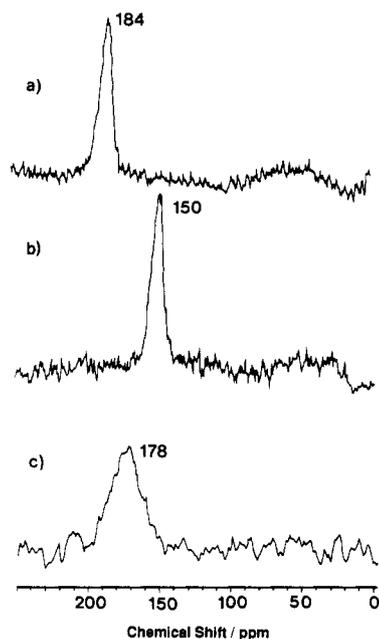


Figure 3. In-situ ^{129}Xe NMR of occluded xenon during ion exchange: (a) Xe/NaA; (b) Xe/KA; (c) Xe/CsKA.

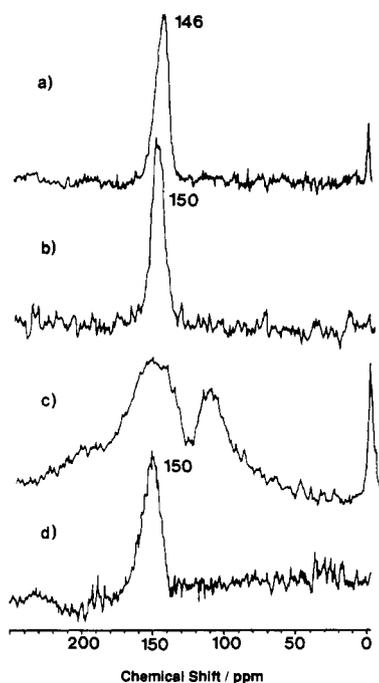


Figure 4. ^{129}Xe NMR of xenon adsorbed after ion exchange: (a) partially dehydrated Xe/KA; (b) Xe/KA in water; (c) partially dehydrated Xe/ NH_4A ; (d) Xe/ NH_4A in water.

introduced onto NH_4A after evacuation at 333 K for 5 h. The adsorption of xenon on this sample at 333 K for 5 h gave the spectrum in Figure 4c. The spectrum shows a very broad ^{129}Xe NMR peak, probably due to heterogeneous dehydration in the sample bed. Complete hydration by water indeed narrowed the linewidth as shown in Figure 4d.

Chemical shift for the hydrated xenon in the α -cage of A zeolite is listed in Table I. The data range between 150 and 184 ppm for the A zeolites that are exchanged with Na^+ , K^+ , Cs^+ , and NH_4^+ , respectively. The chemical shift of xenon may depend on the electric field effects due to cations in the zeolite cage, and the effect will be estimated by comparison of the chemical shift for xenon in dehydrated zeolite cages with different cations. However, no ^{129}Xe NMR data for dehydrated A zeolites with monovalent cations other than Na^+ are known to us. We assume to neglect

TABLE I: Free-Space Radius Available to Xenon Occluded in Clathrate Hydrate and Hydrated Zeolite Pore Structure

sample	chemical shift, δ , ppm	free-space radius R , nm	ref
hydrate, structure I, small	242	0.250	21
hydrate, structure I, large	152	0.293	21
hydrate, structure II, large	80	0.328	21
hydrated NaA	184	0.280 ^a	this work
hydrated KA	150	0.298 ^a	this work
hydrated CsKA	171	0.287 ^a	this work
hydrated NH_4A	150	0.298 ^a	this work

^a Obtained from ^{129}Xe NMR chemical shift by $R/\text{nm} = (0.375 - 0.515 \times 10^{-3})\delta/\text{ppm}$.²⁵ The total diameter of hydrated cage equals $2R$ plus the diameter of xenon atom (0.43 nm).

the electric field effect for the above A zeolites, since the effect is known to cause little difference for Y zeolites exchanged with monovalent cations.²⁷ We then attribute the chemical shift difference mostly to the difference in the free-space radius available for the xenon atoms trapped in the hydrated α -cage, as a correlation between the chemical shift and the free-space radius in the cages of clathrate hydrate was found by Ripmeester et al.^{24,25} from ^{129}Xe NMR. Table I summarizes the free-space radius obtained by using the correlation by Ripmeester et al.:^{24,25} $R = (0.375 \times 10^{-3})\delta$, where R is the radius in nm and δ is the chemical shift in ppm. The pore size variation in the hydrated A zeolite can come from the difference in the cation size, the cation position, and the number of hydrating water molecules in the α -cage, and therefore it seems to cause significant variation of the ^{129}Xe NMR chemical shift. Variable-temperature ^{129}Xe NMR for the occluded xenon may be useful to clarify if the zeolite hydration can result in the formation of a structurally well defined water cage within the α -cage like the clathrate hydrate cages. Further, previous results by Ripmeester and Davidson²⁸ indicate that the relaxation time for xenon dissolved in water is much longer than that for our hydrated xenon in A zeolite cages. The role of the zeolite framework and the cation on the relaxation will also be interesting.

Conclusion

The ^{129}Xe NMR spectra for the xenon atoms occluded in dehydrated and hydrated NaA zeolites have shown that the zeolite hydration can proceed with a sharp boundary between the hydrated and dehydrated regions when the dehydrated zeolite is exposed to humid air. The hydrated α -cage can contain only one xenon atom, even in the case where more xenon atoms were initially occluded before the hydration, which can probably be attributed to the pore volume decrease and the pore aperture expansion. The chemical shift of xenon in the hydrated α -cage showed a significant difference during the ion exchange with K^+ , Cs^+ , or NH_4^+ , probably due to a change in the hydrated pore volume. Such changes in the ^{129}Xe NMR spectrum during the hydration and the ion exchange of zeolite in the presence of the occluded xenon suggest the ^{129}Xe NMR as a probe for the study of the hydrated zeolite pore.

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