

LETTERS

A ^{129}Xe NMR Spectroscopic Technique To Probe Exclusively the Internal Surface of Zeolite Crystallites by Coating of the External Surface

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A NaY + CaY or NaY + Pt/NaY powder zeolite mixture was soaked with liquid octamethylcyclotetrasiloxane (OMTS) *in situ* under an atmosphere of xenon. The OMTS coating on the zeolite crystallites blocked the intercrystal diffusion of xenon very effectively at room temperature, while it did not affect the interior of the zeolite matrix. ^{129}Xe NMR spectra of the two mixtures complexed with OMTS showed two distinct signals corresponding to the different components in the respective mixtures. The application of the ^{129}Xe NMR spectroscopic technique using OMTS to Pt/NaY and Ni/NaY samples distinguished the chemical shifts due to the xenon interaction with the metal clusters located inside the zeolite matrix from those on the external surface.

Introduction

The ^{129}Xe NMR chemical shift and line width are very sensitive to the physicochemical environment of xenon.¹ The intrinsic characteristics of xenon led to the use of ^{129}Xe NMR spectroscopy as a probe in many investigations of microporous solid materials having high specific surface areas. It is also particularly suitable for many of the zeolites.^{1,2} However, one considerable concern is the observation that the intercrystalline diffusion of xenon occurs on a rapid time scale compared to the NMR time scale.³⁻⁵ As a result, the xenon chemical shift is averaged from crystal to crystal including the external surface and void space between the crystals under this condition, thus complicating the interpretation of the NMR spectrum.⁶ The diffusion of xenon may be slowed by cooling.⁴ However, the NMR lines broaden at low temperature. Furthermore, the xenon adsorption from dead space in the NMR tube changes the chemical shift during the cooling, still complicating the situation.

We undertook this work in order to develop an experimental technique for obtaining highly resolved ^{129}Xe NMR signals coming exclusively from individual zeolite crystal particles of the sample at room temperature. We present in this study effective blocking of the interparticle xenon diffusion by treating the external surface of the zeolite particles with liquid octamethylcyclotetrasiloxane (OMTS).

Experimental Section

The zeolite samples used in this work consisted of NaY, CaY, Pt₈/NaY, and Ni₈/NaY. The preparation and characterization of NaY, CaY, and Pt₈/NaY were made in the same ways as described earlier.⁷ The Pt₈/NaY sample contained Pt clusters of about 1 nm in size inside the supercages. The subscript number 8 represents the number of Pt atoms per unit cell estimated from the nominal loading. The Ni₈/NaY sample was prepared by ion exchanging Ni²⁺ into NaY in aqueous solution at room temperature. The Ni₈/NaY sample was then calcined at 673 K and reduced at 723 K. All these treatments except for the temperatures were conducted in the same way used for the preparation of the Pt₈/NaY. The samples were exposed to air after preparation.

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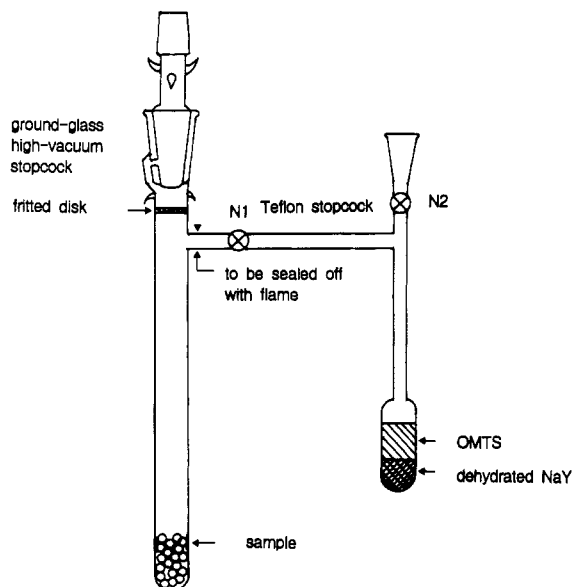


Figure 1. Schematic diagram of NMR cell used in this experiment.

The NaY and Pt₈/NaY samples were well mixed in 2:1 weight ratio in an agate mortar.⁵ This zeolite mixture was placed in a Pyrex NMR tube equipped with vacuum stopcocks and heated to 573 K over 2 h with repeated introduction of 1 atm of H₂ under static conditions followed by evacuation. The sample was cooled to 296 K after further evacuation at 673 K for 2 h. The sample was then equilibrated with 53.3 kPa of xenon gas (Matheson, 99.995%) at 296 K. The ¹²⁹Xe NMR spectrum was taken at 296 K with a Bruker AM-300 FT-NMR spectrometer operating at 83.0 MHz for ¹²⁹Xe.^{1,4,5}

The NMR tube containing the NaY–Pt₈/NaY mixture was open to air and joined to a second tube containing liquid octamethylcyclotetrasiloxane (Fluka, >99%), as shown in Figure 1. Afterward, the Teflon stopcock N1 in Figure 1 was closed. The OMTS was shaken with fully dehydrated NaY zeolite pellets and degassed by evacuation using stopcock N2 in an ultrasonic wave cleaner. The NaY–Pt₈/NaY mixture was reduced again by heating in H₂ and evacuating as described above. The zeolite sample was then equilibrated with 400 Torr of xenon gas at 296 K. After the Teflon stopcock N1 was opened again, the sample tube filled with xenon was tilted so that the liquid OMTS could be transferred onto the sample through the Teflon stopcock N1. Subsequently, the Teflon stopcock N1 was closed again. The NMR tube was flame-sealed after the sample with OMTS was frozen in a liquid N₂ Dewar. A ¹²⁹Xe NMR spectrum was taken again after the sample had thawed to 296 K. The NMR relaxation delay was taken as 0.5 s. The chemical shift was referenced to xenon gas extrapolated to zero pressure.

The Ni₈/NaY sample was treated in the same way as shown in Figure 1 for the NaY+Pt₈/NaY mixture, except that the treatment with H₂ and under vacuum was performed at 723 K. The NaY and CaY zeolites were dehydrated separately and then mixed in 1:1 ratio using an agate mortar inside a glovebox. This mixture was evacuated in the NMR tube at room temperature. The ¹²⁹Xe NMR spectra of these samples were also taken under 400 Torr of xenon at 296 K. Then the same mixture was put in contact with OMTS as described before, and a new ¹²⁹Xe NMR spectrum was taken.

Results and Discussion

The ¹²⁹Xe NMR spectra for NaY, Pt₈/NaY, and their 2:1 mixture are shown in Figure 2. The NaY and Pt₈/NaY samples gave single NMR signals with the chemical shifts at 85 and 176 ppm in Figure 2, a and b, respectively. The observation of a single coalescent NMR peak from the NaY–Pt₈/NaY mixture

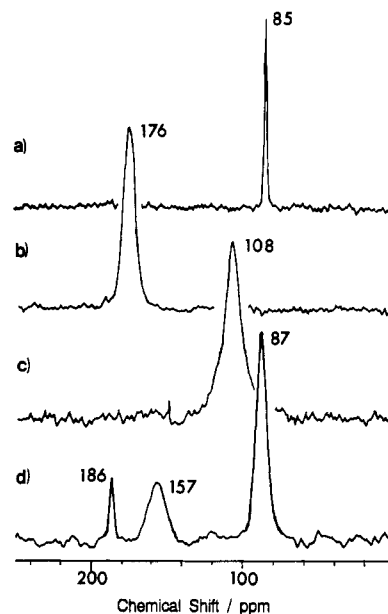


Figure 2. ¹²⁹Xe NMR spectra of adsorbed xenon at 53.3 kPa and 296 K: (a) NaY, (b) Pt₈/NaY, (c) NaY + Pt₈/NaY mixture, (d) NaY + Pt₈/NaY mixture after OMTS treatment.

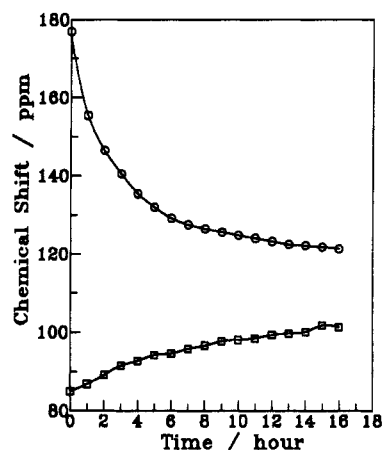


Figure 3. Variation of ¹²⁹Xe NMR chemical shift of NaY + Pt₈/NaY mixture with time after OMTS treatment.

in Figure 2c situated at 108 ppm is consistent with rapid intercrystalline xenon diffusion on the NMR time scale.^{3,4} Addition of OMTS into the NaY–Pt₈/NaY mixture resulted in the appearance of three NMR signals in Figure 2d. One narrow line at 186 ppm was due to the xenon gas dissolved in the OMTS phase. This dissolved xenon quantity was not large enough to affect the xenon pressure in the NMR tube. The other two NMR peaks came from adsorbed xenon in the NaY and the Pt₈/NaY crystals, respectively. Thus, the addition of OMTS *in situ* into the NaY–Pt₈/NaY mixture resolved the NMR signals by blocking the intercrystal xenon diffusion. A mixture of NaY and CaY showed similar ¹²⁹Xe NMR spectral resolution upon the addition of OMTS. The chemical shifts for NaY and CaY before mixing were 85 and 117 ppm, respectively. The 1:1 mixture showed a single ¹²⁹Xe NMR line at 93 ppm. When OMTS was added to the mixture, the NMR signal was completely resolved into two lines at 89 and 110 ppm.

As plotted in Figure 3, the chemical shift changed gradually with time after the OMTS addition for the two components of the NaY + Pt₈/NaY mixture. The chemical shift of xenon in the Pt₈/NaY matrix decreased with time, while an opposite trend was observed for xenon in NaY. The same changes were obtained when the unmixed samples were individually treated with OMTS. However, the absolute intensity of each NMR signal remained

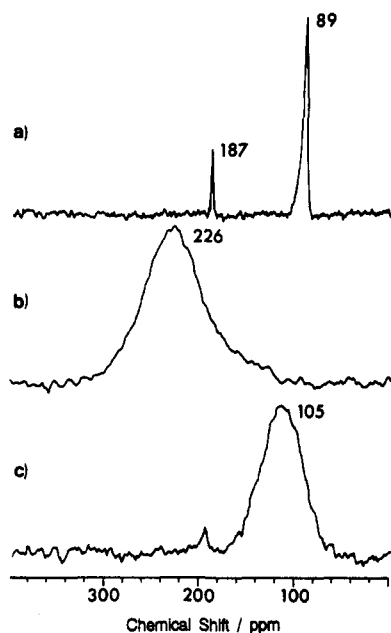


Figure 4. ^{129}Xe NMR spectra of adsorbed xenon at 53.3 kPa and 296 K: (a) NaY after OMTS treatment, (b) Ni_8/NaY , (c) Ni_8/NaY after OMTS treatment.

constant vs time. Moreover, the intensity ratio between the NaY and Pt_8/NaY lines remained as 2:1. These results lead us to speculate that the OMTS (estimated molecular size 0.8 nm) filled the zeolite pores from the outer rim of the individual zeolite crystallites toward the centers, compressing gradually with time the xenon in the zeolite matrix. It is thus supposed that the chemical shift⁸ changed according to the pressure increase. The values extrapolated to time zero in Figure 3 should be used in order to eliminate the time effect in the chemical shift measurement.

OMTS filled the void volume between zeolite particles and blocked the zeolite intercrystalline diffusion of xenon, thus resolving the ^{129}Xe NMR signals very effectively. The NMR spectral difference coming from the OMTS addition can be used to investigate the influence of the xenon exchange on the chemical shift. The ^{129}Xe NMR spectra shown in Figure 4 are given as examples of the spectral change.

The chemical shift of xenon increased from 85 to 226 ppm due to the nickel loading on NaY zeolite (Figures 2a and 4b). Transmission electron micrographs of the Ni_8/NaY sample showed many Ni particles of 5 nm in size located on the external surface of the zeolite crystal. It is very important for the characterization of the catalytic activity to determine whether the chemical shift difference between 226 and 85 ppm was due

to (1) the external Ni particles, (2) ionic nickel species, or (3) very small Ni clusters located in the zeolite matrix that could be difficult to see in the micrographs. This question can be answered by our OMTS addition experiment. In the ^{129}Xe NMR spectrum (Figure 4c) obtained after the OMTS addition on the Ni_8/NaY , the xenon chemical shift decreased to 105 ppm. Clearly, the chemical shift difference between Figures 2a and 4b was mostly due to the external Ni particles. The OMTS coating on the external surface inhibited the interaction of xenon with the external Ni particles. Moreover, it seemed that there was not enough Ni species in the zeolite supercages as to increase the chemical shift. The NMR line broadening in Figure 4b,c was clearly due to the external Ni particles. A quantitative explanation of the line width was beyond the purpose of the present work. The result with the Ni_8/NaY sample is in sharp contrast to that of the Pt_8/NaY . In the case of the Pt_8/NaY sample, the chemical shift was not considerably affected by the OMTS treatment. Thus, the Pt clusters located on the external surface was not significant.

We have also tested other liquid substances such as CCl_4 , tetraethyl orthosilicate, tetrabutyl orthosilicate, and diffusion pump oil (Corning 704) as blocking agents. However, these substances penetrated into Y zeolite crystals much faster than OMTS. In these cases, ^{129}Xe NMR signals from the zeolite phase disappeared before sufficient acquisition.

Conclusion

It is expected that the present technique using ^{129}Xe NMR together with OMTS coating will be very useful in solving problems such as the location of metal clusters, for example, in zeolites, and other microporous crystalline materials, molecular and ionic transport in zeolite powder particles, etc.

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References and Notes

- (1) Fraissard, J.; Ito, T. *Zeolites* **1988**, *8*, 350.
- (2) Dybowski, C.; Bansal, N.; Duncan, T. M. *Annu. Rev. Phys. Chem.* **1991**, *42*, 433.
- (3) Shoemaker, R.; Apple, T. *J. Phys. Chem.* **1987**, *91*, 4024.
- (4) Ryoo, R.; Pak, C.; Chmelka, B. F. *Zeolites* **1990**, *10*, 790.
- (5) Ryoo, R.; Pak, C.; Ahn, D. H.; de Menorval, L.-C.; Figueras, F. *Catal. Lett.* **1990**, *7*, 417.
- (6) Ripmeester, J. A.; Ratcliffe, C. I. In *Proceedings from the 9th International Zeolite Conference, Montreal*; von Ballmoos, R., Higgins, J. B., Treacy, M. M. J., Eds.; Butterworth: London, 1992; Vol. 1, p 571.
- (7) Ryoo, R.; Cho, S. J.; Pak, C.; Kim, J.-G.; Ihm, S.-K.; Lee, J. Y. *J. Am. Chem. Soc.* **1992**, *114*, 76.
- (8) de Menorval, L.-C.; Fraissard, J. P.; Ito, T. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 403.