We define ϕ as the phase of [Ce^{4+}] with zero at the maximum of the concentration (the minimum of the transmission) and principal values in the interval $-180° < \phi \leq 180°$. Figure 4a,b shows the result of adding the *same* (carefully chosen) amount of Br$^-$ to the system at two distinct phases differing by 180°, namely, at $-110°$ (a) and $+70°$ (b). In (a) the oscillation is temporarily quenched whereas in (b) there is a barely visible increase in amplitude lasting only about one period. (The accuracy of the angles is estimated to $\pm 15°$.)

Traces c and d show the quenching of oscillations by addition of Ce^{4+} (at $-140°$) and BrMa (at $-120°$). The amount of BrMa required was about 25 times that of Ce^{4+}; nevertheless, the response to the addition showed the same phase dependence as was found with the other additions. Trace e illustrates how sensitive the response can be to the phase of the addition. At the time marked by a triangle HOBr was added at $-90°$ whereas at the arrows the same amount was added at $-110°$. Trace f shows a quenching resulting from a dilution with the feed mixture. It makes no difference if the solvent was used instead. The result of an addition of Br$_2$ looks much the same as additions of Br$^-$ or HOBr, and it is not shown.

Discussion

The experimental results presented demonstrate that it is possible to quench harmonic chemical oscillations by addition of relevant chemical species or by dilution; compare ref 9. A crucial question in an analysis of the data is the choice of the smallest phase space that is sufficient to describe the dynamical system to the desired accuracy. From the data we have tentatively calculated amplitudes, phases, and transients for a three-dimensional model. The result indicates that the phases of the oscillations of the species tested (calculated from the vectors **u** and **v** in (2)) are not restricted to a narrow interval as suggested by the measured phases of the quenchings. However, the uncertainty of the measured phases does not permit a reliable deduction. We are preparing a study in which we can have simultaneous additions of several species with phases determined much more accurately through automated timing. We shall report a calculation of amplitudes, phases, and transients of the oscillating species from the more accurate data when it becomes available.

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Distribution of Hexamethylbenzene in a Zeolite Studied by Xenon-129 and Multiple-Quantum NMR[†]

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The distribution of hexamethylbenzene (HMB) molecules among the cavities of a Na-Y zeolite has been investigated by both xenon-129 and multiple-quantum NMR. For samples prepared at 523 K, xenon NMR shows that HMB molecules are dispersed nonuniformly, entering and remaining in the first available zeolite cavities. After further heat treatment at 573 K, the xenon spectrum collapses to one single line characteristic of a macroscopically uniform molecular distribution; multiple-quantum NMR "counting" indicates spin clusters of about 16 hydrogens, consistent with one HMB (18 hydrogens) per cavity.

Introduction

When molecules are chemisorbed in dehydrated zeolites, it is commonly assumed that a uniform dispersion is obtained among the cavities of the zeolite particles.[1,2] In this Letter, we demonstrate that by means of xenon-129 NMR, pioneered as a zeolite probe by Fraissard and co-workers,[3] together with "counting" by multiple-quantum NMR,[4] it is possible to determine a great deal about molecular dispersions within zeolite cavities and that care must be taken in assuming a specific type of distribution. In particular, careful heat treatment of the sample may be needed to ensure a homogeneous molecular distribution.

Experimental Section

Dehydrated Na-Y zeolite samples (ca. 0.4 g each) were prepared in NMR tubes by heating at 673 K under vacuum (ca. 10^{-6} Torr) overnight. In order to produce different loadings of the guest molecules, solid hexamethylbenzene (HMB) was introduced to the zeolites under an inert nitrogen environment at room temperature. After the addition of the adsorbent, samples were evacuated with the sample tube immersed in a liquid nitrogen bath. The samples were then heated to a specific temperature for a known period of time and cooled to room temperature over a period of several hours. For the xenon-129 experiments, xenon gas was introduced into the sample until it reach an equilibrium pressure of 300 Torr at room temperature. Xenon-129 NMR of adsorbed xenon was performed on a Nicolet spectrometer operating at a frequency of 49.8 MHz. Typically 2000-4000 FIDs were accumulated for each spectrum with an interval of 0.2 s between each 90° pulse. All of the chemical shift values reported were referenced to the xenon-129 signal of xenon gas extrapolated to zero pressure.[3] Proton multiple-quantum NMR data were obtained

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(2) For reviews of molecules adsorbed in zeolites, see: Resing, H. A. *Adv. Mol. Relax. Processes* **1972**, *3*, 199. Pfeifer, H. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: West Berlin, 1972; Vol. 7. Lechert, H. *Catal. Rev.—Sci. Eng.* **1976**, *14*, 1.

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(4) Pines, A. Lectures on Pulsed NMR in *Proceedings of the Fermi School on the Physics of NMR in Biology and Medicine*; Maraviglia, B., Ed., in press. LBL preprint No. 22316. Munowitz, M.; Pines, A. *Science* **1986**, *233*, 525.

Xe–HMB

χ = **Average number of HMB molecules per zeolite cavity**
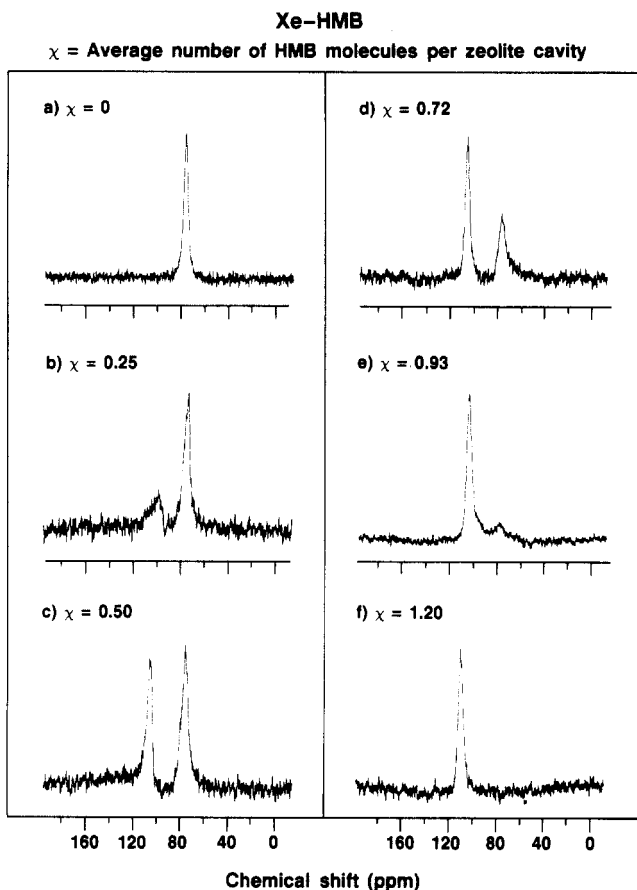

Chemical shift (ppm)

Figure 1. Xenon-129 NMR spectra of xenon (pressure 300 Torr) adsorbed in Na–Y zeolite with different loadings of hexamethylbenzene (HMB). Samples from (b) to (f) were prepared at 523 K for 2 h.

by using the phase cycling counting technique[5] on a home-built spectrometer operating at 180 MHz.

Results and Discussion

Figure 1 displays the room-temperature xenon-129 NMR spectra of xenon (pressure 300 Torr) adsorbed in a dehydrated Na–Y zeolite together with different loadings of HMB. The spectrum in Figure 1a, chemical shift value $\delta(Xe)$ 80, results from xenon adsorbed within zeolite supercages in the absence of HMB. The single line arises from the collisions of xenon atoms with the walls of the zeolite supercages and other xenon atoms as they move about the zeolite particles. This reminds us that while the xenon experiences numerous collisions at locally different sites, the xenon-129 resonance reflects only an average environment on the time scale of the NMR experiments, weighted by the collision probability at each site.[3] When HMB molecules are chemisorbed on the Na–Y zeolite (prepared at 523 K for 2 h), an additional line appears in the downfield direction, $\delta(Xe) \approx 107$, as shown in Figure 1b–f. Of the possible HMB distribution schemes shown in Figure 2, this behavior is clearly consistent with Figure 2A in which the xenon would experience two different average environments. The HMB molecules appear to adopt a nonuniform distribution within the zeolite crystallite, with each molecule entering and remaining in the first available empty supercage. Similar heterogeneous distributions of water molecules during the rehydration of zeolites has been observed by Fraissard and co-workers.[6]

After the samples were heated again at an elevated temperature of 573 K for 2 h, the xenon-129 NMR spectra all displayed one single line. An example is shown in Figure 3 in which a single

(5) Baum, J.; Pines, A. *J. Am. Chem. Soc.* **1986**, *108*, 7447. Munowitz, M.; Pines, A.; Mehring, M. *J. Chem. Phys.* **1987**, *86*, 3172. Shykind, D. N.; Liu, S.-B.; Pines, A.; Garroway, A. N. *J. Magn. Reson.*, in press.

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HMB (x) in NaY–Zeolite
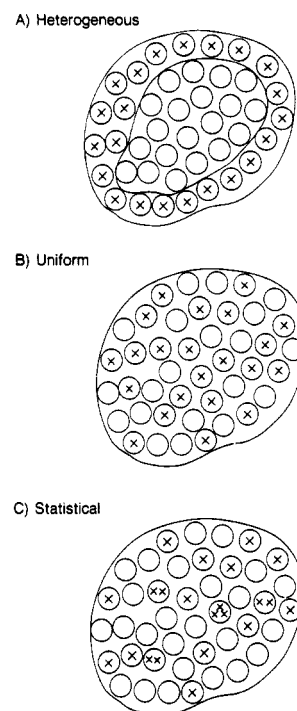
A) Heterogeneous

B) Uniform

C) Statistical

Figure 2. Possible dispersions of guest molecules among cavities of a zeolite particle when the average coverage is less than one molecule per cavity: (A) heterogeneous distribution in which the molecules remain in the first exposed empty cavities; (B) uniform distribution in the particle with at most one molecule per cavity; (C) uniform distribution in the particle but with statistical clustering among the cavities. The open circles represent empty zeolite cavities, and the guest molecules are indicated by the symbol X.
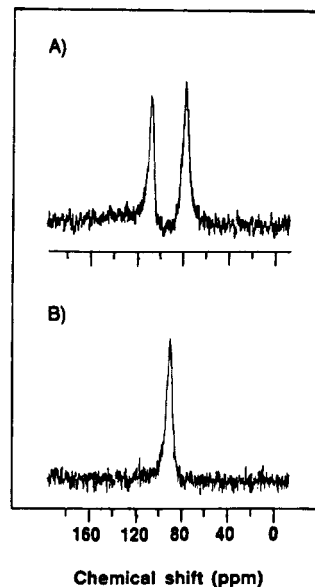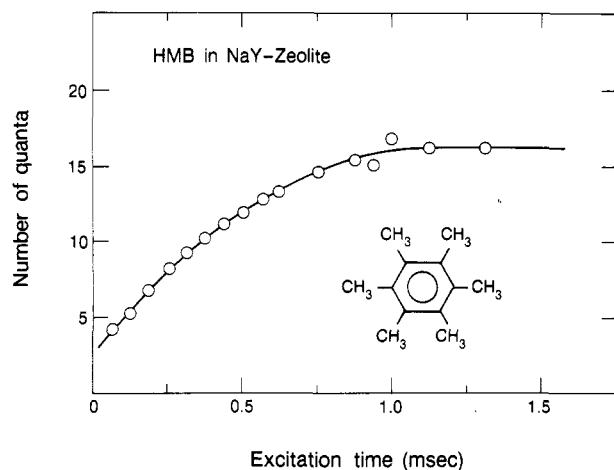

Chemical shift (ppm)

Figure 3. Effect of heat treatment on xenon-129 NMR spectra of xenon (pressure 300 Torr) adsorbed in Na–Y zeolite with an HMB loading corresponding to half the number of zeolite supercages: (A) sample heat treated at 523 K for 2 h, reproduced from Figure 1c; (B) the same sample heat treated at 573 K for 2 h.

line appears whose chemical shift, $\delta(Xe)$ 94, is intermediate between the previous two lines of Figure 1c, suggesting that the guest molecules are now homogeneously distributed among the zeolite cavities. The 573 K heat treatment temperature, to which the sample of Figure 3B was subjected, appears to induce diffusion of the HMB molecules throughout the zeolite cavities. The NMR spectrum in Figure 3B is consistent with the distributions shown in Figure 2B,C; both are macroscopically uniform in the zeolite

Figure 4. Proton multiple-quantum NMR results for HMB chemisorbed in Na-Y zeolite. Sample coverage corresponds to an average of 0.5 HMB per supercage, the same as that in Figure 3. The number of quanta reaches a maximum at about 16, corresponding to a cluster of 18 hydrogen atoms on a single HMB molecule.

particles and both would yield only one average xenon NMR line. The distributions in Figure 2B,C cannot be distinguished easily by xenon-129 NMR because the resonance signal is averaged by high xenon mobility, even at temperatures well below 298 K.

To differentiate between the two cases in Figure 2B,C for the heat-treated sample, we require a technique which is sensitive to clustering in the zeolite cavities. Multiple-quantum NMR is such a technique, providing a unique way of counting hydrogen clusters.[4,5] Multiple-quantum NMR allows the determination of the number of spins in a finite cluster by measuring the response of

coupled spins to pumping (excitation) by radio-frequency pulses[5] as a function of excitation time. The maximum number of correlated spins coupled by dipolar couplings (which corresponds to the maximum number of quanta at long excitation times) is limited by the number of spins in the cluster. Figure 4 shows the results of such an experiment on HMB chemisorbed in a Na-Y zeolite with a sample loading corresponding to Figure 1c, i.e., an average of 0.5 HMB per supercage. The asymptotic maximum of about 16 quanta is consistent with the picture in which only one HMB molecule (containing 18 hydrogens, maximum of 18 quanta) occupies each zeolite supercage. The results in Figure 4 thus resolve the situation in favor of the "uniform" distribution shown in Figure 2B. At higher HMB loadings, the multiple-quantum experiments indicate that cluster sizes extend to more than 30 quanta, consistent with two HMB molecules per cavity.[7] These experiments will be described in detail in a full paper.

Conclusions

In conclusion, the combination of xenon-129 and multiple-quantum NMR experiments provides a rather direct picture of how molecules are distributed amongst the cavities of zeolites and points out the importance of sample heat treatment in the preparation of uniform samples. At low loading, there is no indication in the present samples of any molecular clustering in the zeolite cavities.

Effects of Dilution on the Ultraviolet and Visible Absorptivity of CS₂ under Static and Shock Compression

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A comparison of diamond-anvil cell measurements with results of a time-resolved shock experiment provides the first quantitative evidence of large differences in the electronic processes occurring under conditions of static and dynamic compression. Samples consist of 1% solutions of CS_2 in hexane, and the measurements are of absorption spectra in the range 25 000 to 35 000 cm⁻¹. Static measurements of temperature coefficients show that the spectral differences cannot be due to temperature effects.

The state of matter undergoing shock loading is changed from that existing at ambient conditions to one of high pressure and temperature in a time which is commonly a fraction of a nanosecond. Because of the limitations of geometry in the laboratory, the duration of the compressed state seldom exceeds a few microseconds, and measurements are commonly made within a small fraction of a microsecond after the initial compression. The application of time-resolved spectroscopy in shock experiments is a relatively new development which offers opportunities for probing molecular properties of condensed matter. The macroscopic features which distinguish it from static compression are the temporal and temperature aspects mentioned above and, in addition, the constraint of strain to be uniaxial. This last condition

implies the existence of shear stresses, which may have important molecular consequences. A further consideration is the possibility that "temperature" may be anisotropic, first proposed by Band[1] and recently confirmed by Hoover et al.[2]

Given these differences between static and shock compression, it is somewhat surprising that shock compression experiments have contributed so largely to our knowledge of equilibrium material behavior at very high pressures, but that is the case, as evidenced by the amount of shock data on equations of state. But pressure

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