CHEMISTRY OF MATERIALS

VOLUME 12, NUMBER 5 MAY 2000

Communications

Continuous Flow NMR with Hyperpolarized Xenon for the Characterization of Materials and Processes[†]

Igor L. Moudrakovski,[‡] Andrej Nossov,[‡,§]
Stephen Lang,[‡,§] Steven R. Breeze,[‡,§]
Christopher I. Ratcliffe,[‡] Benoit Simard,[‡]
Giles Santyr,[§] and John A. Ripmeester*,[‡]

Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6, and Department of Medical Physics, Carleton University, Ottawa, Ontario, Canada K1S 5B6

Received December 28, 1999
Revised Manuscript Received February 29, 2000

Because of the great sensitivity of the ^{129}Xe chemical shift to the local environment,^{129}Xe NMR spectroscopy has become a popular method for the study of microporous solids.[1–3] Information can be obtained on the structure and statistics of filling of the void space, intersite and interparticle exchange, metal particle distribution in catalysts, and so on. From a fundamental point of view, the interpretation of shifts in terms of interatomic potentials and dynamics has been put on a firm theoretical basis by the work of Jameson et al.[4] The general applicability of ^{129}Xe NMR spectroscopy to materials has been hampered by low sensitivity, requiring long data acquisition times, especially on materials with low surface areas. Progress toward a general solution to the problem has come from the development of optical pumping techniques for the production of hyperpolarized xenon,[5] increasing the general sensitivity by factors of up to 10^4. This has been used to good advantage in the development of HP xenon imaging for clinical applications, especially lung imaging.[6] Recent advances include examples of HP Xe delivery into MAS probes,[7] and a recirculating continuous flow system that offers prospects for the recording of Xe spectra of materials in a closed system.[8–10] In this communication we report application of a simple flow system of general utility that produces HP Xe at low partial pressure and high polarization that can be integrated easily into existing probe technology. Spectra can be obtained at very low partial pressure of HP Xe and thus are characteristic of the framework or surface. We also illustrate the monitoring of adsorption and desorption processes in zeolites in real time.

The experimental details are given below.[11] Figure 1 shows the ^{129}Xe NMR spectra of xenon adsorbed in the one-dimensional channels of two different molecular

---

* Author for correspondence.

[†] Issued as NRCC no. 43831.

[‡] Steacie Institute for Molecular Sciences.

[§] Carleton University.

(1) Ito, T.; Fraissard, J. *J. Chem. Phys.* **1982**, *76*, 5225.

(2) Ripmeester, J. *J. Am. Chem. Soc.* **1982**, *104*, 289

(3) (a)Ratcliffe, C. I. *Ann. Rep. NMR Spectrosc.* **1998**, *36*, 124. (b) Raftery, D.; Chmelka, B. F. *NMR Basic Principles Prog.* **1994**, *30*, 111. (c)Barrie, P. J.; Klinowski, J. *Prog. NMR Spectrosc.* **1992**, *24*, 91.

(4) (a) Jameson, C. J.; Jameson, A. K.; Baello, B. I.; Lim, H.-M. *J. Chem. Phys.* **1994**, *100*, 5965. (b) Jameson, C. J.; Jameson, A. K.; Lim, H.-M.; Baello, B. I. *J. Chem. Phys.* **1994**, *100*, 5977. (c) Jameson, C. J.; Jameson, A. K.; Lim, H.-M. *J. Chem. Phys.* **1996**, *104*, 1709.

(5) (a) Grover, B. C. *Phys. Rev. Lett.* **1978**, *40*, 391. (b) Happer, W.; Miron, E.; Schaefer, S.; Schreiber, D.; van Wingaarden, W. A.; Zeng, X. *Phys. Rev. A* **1984**, *29*, 3092.

(6) (a) Albert, M. S.; Cates, G. D.; Driehuys, B.; Happer, W.; Saam, B.; Springer, C. S.; Wishnia, A. *Nature* **1994**, *370*, 188. (b) Mugler, J., III.; Driehuys, B.; Brookeman, J.; et al. *Magn. Res. Med.* **1997**, *37*, 809.

(7) Raftery, D.; MacNamara, E.; Fisher, G.; Rice, C. V.; Smith, J. *J. Am. Chem. Soc.* **1997**, *119*, 8746.

(8) Haake, M.; Pines, A.; Reimer, J. A.; Seydoux, R. *J. Am. Chem. Soc.* **1997**, *119*, 11711.

(9) Seydoux, R.; Pines, A.; Haake, M.; Reimer, J. A. *J. Phys. Chem. B* **1999**, *103*, 4629.

(10) Brunner, E.; Haake, M.; Kaiser, L.; Pines, A.; Reimer, J. A. *J. Magn. Res.* **1999**, *138*, 155.

10.1021/cm9908015 CCC: $19.00 Published 2000 by the American Chemical Society

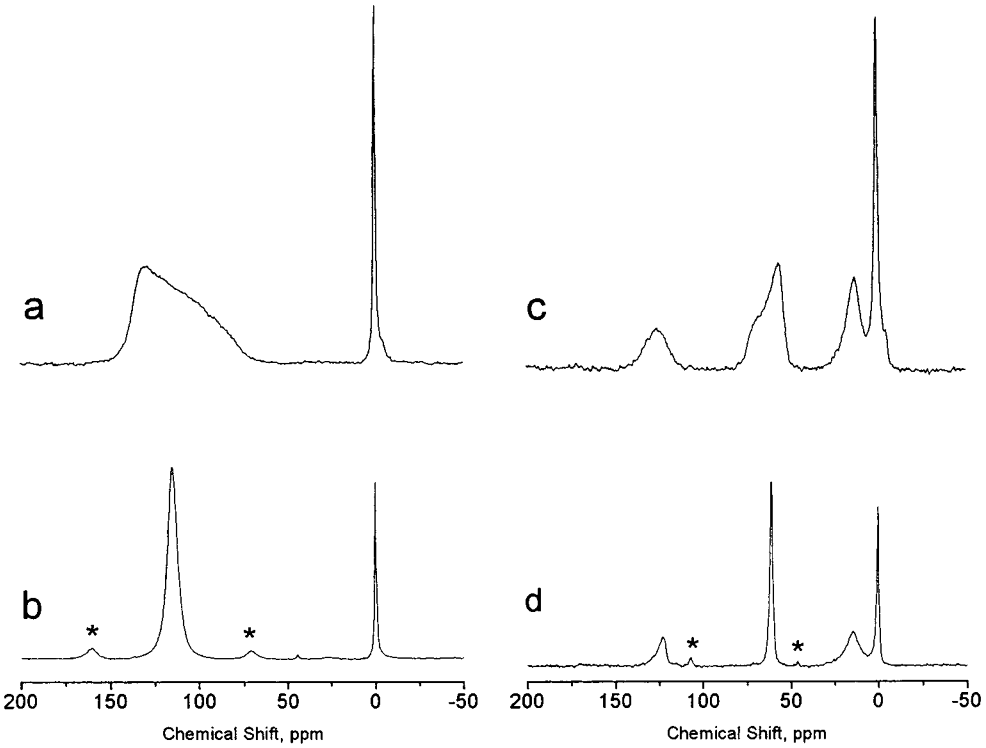

Figure 1. ^{129}Xe NMR spectra at 293 K of HP xenon adsorbed on powder samples of AlPO-11 (a, static; b, MAS) and SSZ-24 (c, static; and d, MAS). The total pressure in the Xe/N_2/He mixture in the area of detection was 1020−1050 mbar, the flow rate 300 cm^3/min (* indicates spinning sidebands).

sieves: the aluminophosphate AlPO-11[14] and highly siliceous zeolite SSZ-24.[15] The reduced dimensionality of the void space causes the anisotropy of the chemical shift in these static spectra (Figure 1a,c), which is effectively reduced by fast magic angle spinning (MAS) (Figure 1b,d). It is generally accepted that the chemical shift of xenon adsorbed in nanopores correlates with the size and geometry of voids. To exclude contributions from Xe−Xe interactions to the observed chemical shift, measurements need to be done at the lowest possible loading, but for reasons of sensitivity this often is replaced by extrapolation of the experimental data to zero loading. The very low partial pressure of xenon in the flowing mixture (1% at total pressure of about 1000 mbar, or ~10 mbar) corresponds to an extremely low loading of xenon, thus obviating the need for extrapolation. For thermally polarized xenon, measuring spectra at such low equilibrium pressures requires extremely long accumulation times and for this reason is rarely performed. With hyperpolarized (HP) xenon these experiments can be done *in a single scan*. Instead of tens of hours of accumulation required to get decent signal-to-noise in the spectrum of xenon in AlPO-11 at the lowest pressure in equilibrium conditions,[16] only a few seconds were necessary to obtain the spectra on Figure 1. The parameters of the spectrum in Figure 1a are essentially the same as those reported in ref 16, whereas the continuous flow (CF) MAS spectrum of Figure 1b provides an accurate value for the isotropic shift of 115.4 ppm, cf. the extrapolated value of 114.4 ppm from ref 16. We note that the other components in the gas mixture, He and N_2, do not affect either the Xe adsorption processes or the Xe chemical shifts (within a fraction of a part per million) in the gas phase under the conditions used in our experiments. The low levels of Xe also provide the additional benefit of allowing the observation of xenon adsorbed in sites which have very low concentration that are essentially invisible at higher Xe pressures as they would be masked by much stronger signals from more abundant sites. For the spectra shown in Figure 1c and 1d, only the signal with axial anisotropy belongs to xenon in the one-dimensional channels of SSZ-24,[15] whereas those at ~15 and 123.5 ppm originate from the xenon atoms strongly bound to a small number of defect sites. This is confirmed by the fact that the relative intensities of these lines decrease when the xenon pressure increases (not shown), as all of the defect sites already are completely populated even at low pressure. Both signals are barely visible in a spectrum recorded at high equilibrium pressure. Since both these lines are observed separately and their

---

(11) All NMR experiments were carried out on Bruker AMX-300 spectrometer (magnetic field 7.04 T, ^{129}Xe resonance frequency 83.03 MHz). A commercial 7 mm Bruker MAS probe was modified according to a design proposed by Hunger at al.[12] Samples of montmorillonite and silicalite were used as received and were heated at 373 K in situ under He flow to remove adsorbed water. Benzene was entrained in a helium stream and combined with the flow of polarized xenon. Optical polarization of xenon was achieved with an apparatus similar to that described in ref 13, with the optical pumping cell in the fringe field of the spectrometer magnet. The gas mixture with polarization of ^{129}Xe up to several percent was delivered at a flow rate 50−400 cm^3/min into the detection region via plastic tubing. Delivery of the mixture of HP Xe in buffer gas (1% N_2, 98% He) was facilitated by expansion to a pressure close to atmospheric (1050−1100 mbar) immediately after the pumping cell.

(12) Hunger, M.; Horvath, T. *J. Chem. Soc. Chem. Commun.* **1995**, 1423.

(13) Driehuys, B.; Cates, G. D.; Miron, E.; Sauer, K.; Walter, D. K.; Happer, W. *Appl. Phys. Lett.* **1996**, *69*, 1668.

(14) Bennett, J. M.; Richardson, J. W. Jr.; Pluth, J. J.; Smith, J. V. *Zeolites* **1987**, *7*, 160.

(15) Zones, S. I. U.S. Patent 4665110, 1987.

(16) Ripmeester, J. A.; Ratcliffe, C. I. *J. Phys. Chem.* **1995**, *99*, 619.

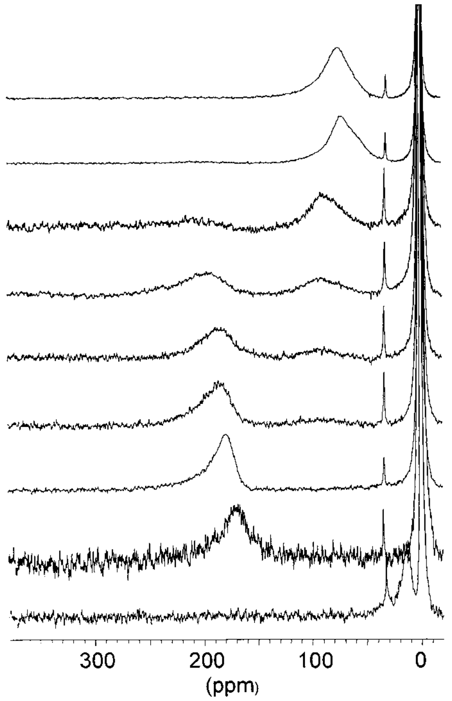

Figure 2. Variable-temperature ^{129}Xe NMR MAS spectra of HP xenon adsorbed in montmorillonite pillared with pyridinium ions. The Xe/N_2/He mixture flow rate is 300 cm^3/min. The signal at ~30 ppm was shown to be a spinning sideband of the gas line by its dependence on spinning speed.

chemical shifts are independent of pressure, we conclude that there is no appreciable exchange with xenon adsorbed in the channels. This could be an indication of a relatively high adsorption energy for these sites. With this flow system it is relatively easy to add nonpolarized xenon to the stream after the polarizing cell if other partial pressures of Xe are desired.

Because it is so easy to work with the open flow system, applications of HP xenon as a tracer become possible for such processes as the modification of void space, or the adsorption and diffusion of sorbents in real time. Figure 2 shows variable-temperature MAS NMR spectra of xenon in montmorillonite pillared with pyridinium. At 293K, the spectrum exhibits peaks at 0 ppm for the gas, and 15 ppm for Xe in the interparticle space of the hydrated montmorillonite. After heating the sample in situ at 373 K for 3 h in the flow of He, the spectrum is a broad asymmetric signal at 170 ppm, characteristic of the xenon in the interlamellar space that becomes by far the most preferred site for adsorption. The line shifts to lower field with decreasing temperature and this is thought to accompany the condensation of xenon into micropores. On cooling below ~283 K, the line shifts further downfield and weakens (vanishing below 243 K) as a new signal grows at ~90 ppm. This can be taken to mean that the interlamellar pore space becomes inaccessible to xenon because of its condensation, and instead the xenon is adsorbed into the mesopore void space.[17] This illustrates how the behavior of a porous material toward a potential sorbent can be followed during activation and changes in temperature in a very efficient manner, either for pure xenon or sorbents containing xenon as a tracer.

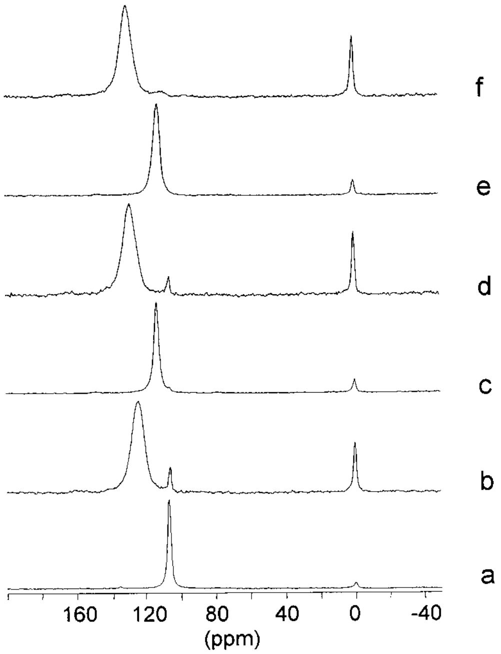

Figure 3. Evolution of the ^{129}Xe NMR MAS spectrum during benzene adsorption and equilibration at 293 K: (a) HP xenon adsorbed on a fresh sample of silicalite, (b) immediately after a pulse of benzene vapor ($\sim 2 \times 10^{20}$ molecules), (c) 1.5 h later, (d) immediately after the second pulse of benzene ($\sim 2 \times 10^{20}$ molecules), (e) 1.5 h later, and (f) immediately after the third pulse of benzene ($\sim 2 \times 10^{20}$ molecules).

The ^{129}Xe NMR MAS spectra of xenon adsorbed on silicalite, Figure 3, shows xenon gas and a signal at 103 ppm (Figure 3a). Immediately after a short exposure of the sample to a flow of 1.3% benzene vapor in helium ($\sim 2 \times 10^{20}$ molecules of benzene were passed through the sample) the initial signal shifts to 105.7 ppm and is largely replaced by a broader line at 123.8 ppm (Figure 3b), whose shift and line width decrease with time (Figure 3c). Further benzene pulses result in reproducible spectral changes. The Xe chemical shift decreases with time after the benzene pulses, as the benzene concentration decreases (at a rate of ~10%/h as monitored by proton NMR), and due to redistribution of benzene within the zeolite layer. Potentially these changes in the spectra can be analyzed using the approach developed in ref 18 and information concerning the diffusion properties of adsorbed molecules can be extracted.

The utility of CF HP Xe for a variety of applications to materials, either as a pure material or as a tracer along with other sorbents, is quite clear. By employing a relatively straightforward incorporation of the continuous flow system into largely existing probe technology, HP Xe has been made much more amenable, paving the way for more routine and widespread use.

CM9908015

---

(17) These assignments were checked with conventional ^{129}Xe NMR; BET analysis of the montmorillonite confirmed the presence of both nanopores (1.4 nm) and mesopores (3.6 nm).

(18) Magalhaes, F. D.; Laurence, R. L.; Curtis Conner, W.; Springuel-Huet, M.-A.; Nosov, A.; Fraissard, J. *J. Phys. Chem. B* **1997**, *101*, 2277.