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Title:
PROBING ZEOLITE INTERNAL STRUCTURES USING VERY LOW TEMPERATURE ^{129}XE NMR

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ABSTRACT

In recent years, probing pore structure with ^{129}Xe NMR has received a bad reputation. This is due to the fact that the method is more complex than was originally suggested so the data is somewhat difficult to interpret. We find that the use of a wide temperature range (40-350 K) allows us to interpret ^{129}Xe chemical shifts in terms of van der Waals attraction between the xenon atom and oxygen in zeolite walls. Using rather simple models from the literature, we can extract useful pore size information as well as the van der Waals potential energy.

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INTRODUCTION

In 1981 and 82[1,2], ^{129}Xe NMR was proposed as a method for measuring pore sizes and structures in porous materials in general and zeolites in particular. Unfortunately the technique has not proven to be as generally applicable or as useful as originally promulgated. Ripmeester and coworkers have pointed out some of the problems with ^{129}Xe NMR[3,4] and there is a general belief that the technique is not useful for structural studies of porous materials, particularly zeolites. There is definite rationale for this belief, ^{129}Xe NMR has proven to be much less useful for unknown materials than proposed. However there are particular applications and methods of use of ^{129}Xe NMR that can be very useful when applied correctly.

Cheung published a little known (or little appreciated) paper which discusses models for xenon-pore wall interactions[5]. The fundamental model is a van der Waals attraction between xenon atoms and framework oxygens in the zeolite pores. He starts with a complete model that uses Lennard-Jones potentials however, to make the mathematics tractable he resorts to a simplified square well potential with minimum potential when the xenon is at a van der Waals contact from the wall, a higher potential when the xenon is in the center of a pore (not in contact with wall oxygens), and infinite potential when the xenon atom intersects the wall. He also assumes cylindrical pores. In spite of the simplicity of the model, Cheung is able to fit low temperature ^{129}Xe NMR data for a few zeolites. Cheung only has experimental data at two temperatures, room temperature and 144 K. We have made ^{129}Xe chemical shift measurements in zeolite Y as a function of temperature from room temperature to 40 K at several different xenon loadings.

Raftery, et al, use another model which is applicable to xenon at low pressures[6]. They simply use a standard NMR two site chemical exchange model with the sites being: xenon in the gas (center of the pore) and in contact with the wall. They assign different chemical shifts to these two sites and are able to describe the variable temperature shifts for xenon adsorbed on poly(acrylic acid).

EXPERIMENTAL

The zeolite used for these experiments is a commercial zeolite Y obtained from Grace Chemical Company. We have characterized it extensively with powder x-ray diffraction (XRD), ^{29}Si MAS NMR, elemental analysis, and scanning electron microscopy (SEM). The XRD pattern is characteristic of zeolite Y with no crystalline impurities and no indications of significant amorphous material. The ^{29}Si NMR spectrum has very little intensity in the silanol region, indicating high crystallinity. From the ratios of the Si(1Al), Si(2Al), etc. peaks we calculate the Si:Al ratio to be 2.6. The SEM photographs show very regular cubes with dimensions approximately 0.5 µm on a side. The elemental analysis agrees with the spectroscopic data but with an iron impurity level of about 200 ppm (wt %). Overall this is a very good zeolite Y although the iron level is somewhat high for some NMR measurements.

Samples were prepared for ^{129}Xe NMR by carefully weighing the zeolite into an 8mm (outside diameter) glass tube which was mounted on a vacuum system and carefully dried by slow heating to 723 K and held at that temperature for 12 hours. The zeolite was then cooled and natural abundance xenon gas was measured into the tube, volumetrically and the tube was flame sealed. We have prepared many samples in this fashion, the sample reported in this communication contained approximately 1 xenon atom for every 0.4 supercages of the zeolite Y. The sample was also prepared with approximately 20 torr of He gas to facilitate thermal equilibrium in the variable temperature experiments.

NMR measurements were made on a Varian Unity-400 NMR spectrometer with a 9.4 T magnet and a nominal resonance frequency of 110.6 MHz for ^{129}Xe. Variable temperature was accomplished with an Oxford model CF 1200 cryostat and a homebuilt transmission line probe[7]. Sample temperature was measured with a Lakeshore Cryogenics calibrated carbon-glass resistor close to the NMR sample. Chemical shifts were measured relative to an external standard.

RESULTS AND DISCUSSION

Without going through the derivation of the equations, the chemical shift using Cheung's model is:

$$\delta(\mathrm{T}) = \frac{\mathrm{c}\varepsilon}{\left(1 + \mathrm{F}\exp\left(\frac{-\varepsilon}{\mathrm{k_B T}}\right)\right)}$$

Where ε is the depth of the square well potential, c is a phenomenological constant, and F is a geometrical term given by :

$$\mathrm{F} = (\mathrm{L} - 2\mathrm{a}_{\mathrm{Xe}}) / 2\mathrm{lm} - 1.$$

a_{Xe} is the van der Waals radius of the xenon atom and m is 1, 2, or 3 for one-, two-, or three-dimensional pores. The potential well has a width of l and a value of -ε inside the well and zero on the outside. It becomes infinite when the distance between Xe and O atoms is smaller than the sum of their Van der Walls radii. The quantity, L, expresses the mean 'free' pore size which is related to the xenon mean-free path (λ), *i.e.*, $L = a_{xe} + 2\lambda$.

The model used by Raftery, et al, results in somewhat simpler equations:

$$\delta = \delta_s P_s + \delta_g P_g$$

Where δ_g is the shift associated with xenon in the gas phase and δ_s on the inner surface and P_s and P_g are the probabilities of finding a xenon at each site. Then they define the probability of xenon on the surface in terms of a sticking time, τ_s, and the reciprocal of the collision rate with the surface, τ_v.

$$P_s = \tau_s / (\tau_s + \tau_v).$$

The average sticking time at the surface can be given by the Arrhenius relationship. After straightforward mathematical manipulations, the measured chemical shift can be plotted as a function of temperature and compared to both models as seen in figure 1.

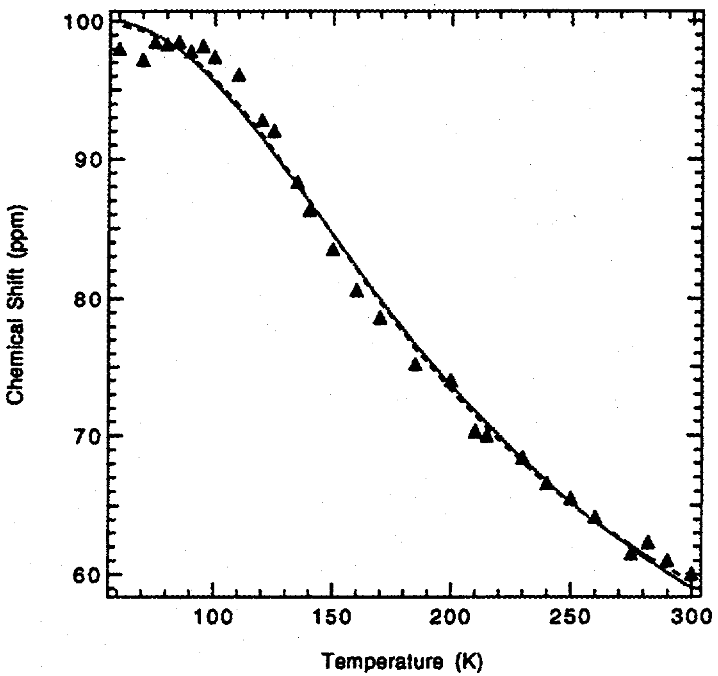

FIGURE 1: A plot of the measured ^{129}Xe chemical shift vs temperature for xenon on Na-Y.

The solid curve is a least squares fit to Cheung's model and the dashed curve to Raftery's. It is clear that there are enough fitting parameters in each of these models that a good fit can be obtained in either case. It is very reassuring that the experimental data reproduces the low temperature flattening in chemical shift predicted by both models. The parameters obtained from the fit to Cheung's equation are: $\varepsilon = 3.3$ kJ/mol, for the depth of the van der Waals potential, and a free pore size, L = 15.0 A. These are reasonably close to expectations for computed van der Waals potentials for Xe-O of 1.5 kJ/mol[8] given that the computed potential is a simple two body potential and in the measured case a xenon may interact with more than one oxygen in the pore. The free pore size agrees with the dimensions of the supercage of zeolite Y. From the fit to Raftery's model, similar parameters can be obtained. ε = 4.1 kJ/mol, $\tau_0 = 7.0 \times 10^{-11}$ s, and $\delta_s \approx 100$ ppm. The sticking potential is relatively close to the computed van der Waals potential and the sticking time, τ_0, is reasonable.

Overall, these results are particularly satisfying given the simplifying assumptions in the models used. Although the models start from somewhat different points, basically they both result in a similar description of the xenon atom in a pore: there is a van der Walls interaction between the xenon atom and oxygen atoms in the zeolite structure. Xenon in the "center" of the pore behaves like a gas. Xenon atoms jump between positions where they are stuck to the wall through this gas phase state. Neither model takes into account the detailed shape of the pore nor the presence of cations or other species in the pores. It is unlikely that these simple models can include detailed pore shape but we are working on including xenon-cation and xenon-metal cluster interactions in our work.

CONCLUSIONS

Early and very simplified models of ^{129}Xe NMR in pores have proven to be less useful than hoped. However, the large size and polarizability of xenon make it an extremely sensitive chemical shift probe for studying porous materials. Using very simple models and variable temperature ^{129}Xe NMR over an extended temperature range allow us to measure quantities such as the van der Waals interactions in the pores and average free pore dimensions. One of the reasons for inconsistent ^{129}Xe NMR results in the literature is that not all of the zeolite parameters (impurities, crystallite size, etc.) are accounted for in the chemical shift models and frequently these dominate the small shift effects measured.

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