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^{129}Xe NMR SPECTROSCOPY ON MOLECULAR SIEVES SAPO-37, AlPO$_4$-5, SAPO-5 and SSZ-24

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Xe NMR spectroscopy is used to study SAPO-37, NaY, AlPO$_4$-5, SAPO-5, and SSZ-24. Of these samples, those with FAU topology show that the ^{129}Xe chemical shift is dependent upon framework composition while the materials with AFI topology do not. Values of the ^{129}Xe NMR chemical shifts at zero xenon pressure cannot be correlated with the size of the framework void space.

1. Introduction

The use of ^{129}Xe NMR spectroscopy in the study of molecular sieves has been receiving much attention. Claims have been made that this technique can probe physicochemical properties such as degree of crystallinity, structure defects, pore blocking, location of coke, location of various cations, size and location of metal particles, and distribution of chemisorbed species on supported metals [1–3]. More recently, this technique has been used to investigate alumina supported metal particles [4]. Thus, for the study of metal particles and chemisorbed species upon them, microporous structures are not necessary for successful application of the ^{129}Xe NMR technique. Here we are concerned only with the application of ^{129}Xe NMR to study the physicochemical properties of microporous materials.

While ^{129}Xe NMR spectra are readily obtained from microporous materials, it is our belief that the interpretation of these spectra is difficult. At this time, there is no *clear* interpretation of the relationship between the ^{129}Xe NMR shift and the physicochemical characteristics of microporous materials.

Fraissard and coworkers [5] have proposed that there is a correlation between the ^{129}Xe NMR chemical shift at zero Xe pressure, δ_s (xenon-wall collision), and

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the mean free path of a Xe atom in the void space of zeolites. This analysis is quite confusing since it is hard to believe that molecules residing within microporous environments act as rigid spheres with mean free paths and elastic collisions with the zeolite surface (wall). In fact, adsorbates are more likely behaving as if they are in a liquid solvent. The best example of "solid solvation" of adsorbates is given by Yoon and Kochi [6]. In keeping with the concept of a "solid solvent," Derouane and coworkers have proposed a model describing the interaction of a sorbed molecule with its surroundings in molecular sieve pores [7,8]. This model takes into account the polarizability of the adsorbate and the adsorbent and appears more realistic in view of data such as those of Yoon and Kochi [6].

Several years ago we were the first group to study the ^{129}Xe NMR of aluminophosphate ($AlPO_4$'s) and silicoaluminophosphate (SAPO's) molecular sieves [9]. We claimed that δ_s should decrease in magnitude in the order aluminosilicate, silicoaluminophosphate, and aluminophosphate, and thus indicate variations in adsorbate-adsorbent interactions. In fact, our ^{129}Xe NMR results showed the same trends as observed from heats of adsorption and are those expected from the models of Derouane et al. [10]. Recently, Chen et al. [11] have performed ^{129}Xe NMR on aluminophosphate and silicoaluminophosphate molecular sieves, and some of their results are in conflict with those reported previously by us [9] and others [12].

The purpose of our work is to investigate the effect of molecular sieve framework composition on ^{129}Xe NMR spectra. Two framework topologies are studied: FAU (NaY and SAPO-37), AFI ($AlPO_4$-5, SAPO-5, SSZ-24). Unfortunately, the $AlPO_4$ and pure silica analogs of FAU have not as yet been synthesized. Also, the aluminosilicate analog of AFI does not exist. However, the ^{129}Xe NMR chemical shift of NaY is the same as HY [1] so a comparison between NaY and SAPO-37 is valid. We will show that no consistent interpretation is possible for all molecular sieves. Thus, at this time a priori predictions of ^{129}Xe NMR spectra are not possible.

2. Experimental

SYNTHESIS

The molecular sieves $AlPO_4$-5 and SAPO-5 were synthesized according to procedures outlined in examples 32 and 12, respectively, of the Union Carbide Patents [13]. Synthesis of the molecular sieve SSZ-24 was performed via a modification of examples 1, 3 and 10 in the Chevron Patent [14]. Briefly, the procedure was as follows: 1-adamantanamine was quaternized with methyl iodide according to a new peptide method [15]. The quaternary ammonium iodide salt was subsequently converted to the hydroxide form by using Dowex AG 1-X8 hydroxide anion exchange resin. Fumed silica (Cabosil Grade EH-5) and KOH were then added to the N,N,N, trimethyl-1-adamantammonium hydroxide solution. The final gel composition was: 0.14 1-$Ada^+ \cdot$ 0.16 $KOH \cdot SiO_2 \cdot$ 146 H_2O. The resulting gel was charged into Teflon-lined, stainless-steel autoclaves. The autoclaves were heated statically under autogenous pressure for 18 days at 150°C. The final product was collected by vacuum filtration.

ANALYSIS

The as-synthesized materials were characterized by X-ray powder diffraction with a Siemens I2 diffractometer using CuKα radiation. Thermogravimetric analysis was performed on a DuPont 951 thermogravimetric analyzer. The templating agents were removed by calcination in air for 10 hours at 550°C. By TG analysis of the calcined materials, it was shown that the templating agents were completely removed. The calcined materials were further characterized by X-ray powder diffraction and argon adsorption.

Powder diffraction data used for unit cell determination were collected between 3 and 50 degrees 2θ. A step width and step time of 0.01 degrees 2θ and 10 seconds, respectively, were used. A well-characterized $MgAl_2O_4$ spinel, which contained distinct reflections at 2.3659 Å, 1.4839 Å and 1.2846 Å, was used as an internal standard. Miller indices were assigned to the molecular sieve reflections according to those reported for a simulated powder pattern of $AlPO_4$-5 [16]. The indexed data were then refined using least-squares analysis.

Argon adsorption isotherms were collected for each material, at liquid argon temperatures, using an Omnisorp 100 analyzer.

^{129}Xe NMR

Xenon adsorption isotherms were collected at 22°C using a McBain-Bakr balance.

In preparing a sample for Xe NMR spectroscopy, a given molecular sieve sample was loaded into a specially modified 10 mm NMR tube. A valve was connected to the top of the NMR tube and the sample was heated under vacuum (10^{-3} Torr) to 350°C. By TG analysis, this treatment was sufficient to remove water. The NMR tube, while under vacuum, was transferred to the Omnisorp 100 instrument. Here, the sample was dosed with a known pressure of high purity xenon gas (99.998%, Matheson Gas Products, Inc.). (Pressure readings were made via a pressure transducer. The transducer was calibrated at 0.6 Torr using a McLeod gauge and at 700 Torr using a home-made silicone oil U-tube manometer.) After dosing the sample with xenon gas, the valve was closed and NMR tube removed from the Omnisorp 100. The NMR tube was then permanently sealed just below the valve. The sealing procedure was checked by sealing a modified, blank NMR tube at 120 Torr xenon gas while it was connected to a pressure transducer. *No change in pressure* and *no leaks* were observed after the sealing process.

^{129}Xe NMR spectra were recorded on a Bruker WP-200 spectrometer at 55.36 MHz. A pulse width of 25 μs and a 1-second relaxation delay were used. The number of scans was dependent upon the xenon concentration and varied from 392 to 41709 scans. All samples were referenced relative to xenon gas at 679 Torr. Jameson and co-workers [17] have shown that the chemical shift of xenon gas is a linear function of xenon density (except at high pressures of xenon) and have fit a curve to this data. Based on the resulting least-squares polynominal, a value of -0.434 ppm was assigned to the gas-phase xenon peak at 679 Torr.

Several of the sealed samples were analyzed by another laboratory (Mobil Central Research Laboratory) for verification of chemical shifts.

3. Results and discussions

In our original work [9] we were interested in proving that SAPO-37 (silicoaluminophosphate with the FAU topology) was a homogeneous molecular sieve. Variable-temperature ^{129}Xe NMR spectra revealed only a single resonance consistent with the premise that our sample of SAPO-37 was homogeneous. This result was in accord with our previous conclusions obtained via a variety of physicochemical properties [18]. We noticed the chemical shift at zero Xe pressure, δ_s, for SAPO-37 was not the same as that for NaY, and this result led us to study other $AlPO_4$ and SAPO molecular sieves. In that work we used a NaY obtained from Strem Chemical Company as the standard for determining Xe chemical shifts. Specifically, we loaded NaY with Xe and matched its ^{129}Xe NMR spectra against those reported by Fraissard and co-workers. Upon recent reexamination, we have shown that the sample used was not pure as determined by physical adsorption. NaY samples synthesized in our laboratory show the expected adsorption capacities. Because of this problem, our previous ^{129}Xe chemical shifts are low by 13.5 ppm. Here, we collected a gas phase ^{129}Xe NMR spectrum and used it as the reference. Thus, the correct value of δ_s for our SAPO-37 is 52.7 ppm, and is consistent with the recent work of others [11,12]. Table 1 shows δ_s for various samples of SAPO-37 and NaY. It is clear from these results that there is a difference in δ_s between SAPO-37 with Si contents below 20

Table 1
Data for SAPO-37 and NaY

Sample	Bulk composition	δ_s	Reference
SAPO-37 (A)	$(Si_{0.22}Al_{0.45}P_{0.33})O_2$	60	[11]
SAPO-37 (B)	$(Si_{0.16}Al_{0.48}P_{0.36})O_2$	56	[11]
SAPO-37 (C)	$(Si_{0.15}Al_{0.45}P_{0.40})O_2$	56	[11]
NaY (A)	$\sim (Si_{0.7}Al_{0.3})O_2$	60	[11]
SAPO-37 (D)	$(Si_{0.10}Al_{0.50}P_{0.40})O_2$	57	[12]
NaY (B)	$\sim (Si_{0.7}Al_{0.3})O_2$	64	[12]
SAPO-37 (E)	$(Si_{0.15}Al_{0.50}P_{0.35})O_2$	53	this work

wt% and NaY. As the silicon content of the SAPO-37 increases (SAPO-37A), δ_s shifts to values that more closely approach those of NaY. Unfortunately, there is no aluminophosphate with the FAU topology. This type of sample would be useful in verifying that increasing silicon contents in SAPO-37 increase the value of δ_s. Thus, the FAU Materials (SAPO-37, NaY) do show the trends in δ_s with framework composition as we first reported [9].

To test further the idea of the relationship between framework composition and δ_s we synthesized a series of molecular sieves in which the topology remained the same, i.e., AFI, while the composition changed from $AlPO_4$ ($AlPO_4$-5) to SAPO (SAPO-5) and ended with a phosphate free sample (SSZ-24). This series of materials is the only one that spans the complete compositional region from $AlPO_4$ to silica with micropores sufficiently large to allow the adsorption of xenon. Fig. 1 shows the X-ray powder diffraction patterns for the $AlPO_4$-5, SAPO-5, and SSZ-24 used here. All three patterns show that these materials are highly crystalline and that no other phases are present. Fig. 2 gives the argon adsorption isotherms for the three AFI structures. Notice that SSZ-24 reveals a slightly different isotherm than $AlPO_4$-5 and SAPO-5 but is well within the limits of the isotherm expected for the AFI topology [13]. Table 2 shows the composition, unit cell parameters, and micropore filling adsorption volume for $AlPO_4$-5, SAPO-5, and SSZ-24. These data along with the X-ray powder diffraction patterns conclusively show that these materials are pure. It is critical that the

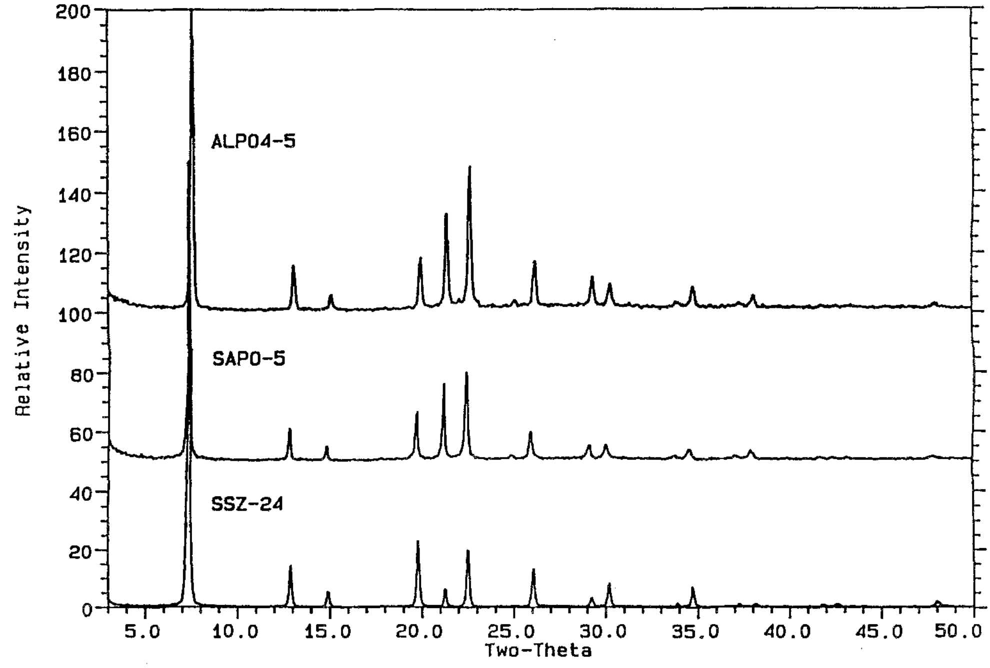

Fig. 1. Experimental X-ray powder patterns of $AlPO_4$-5, SAPO-5 and SSZ-24.

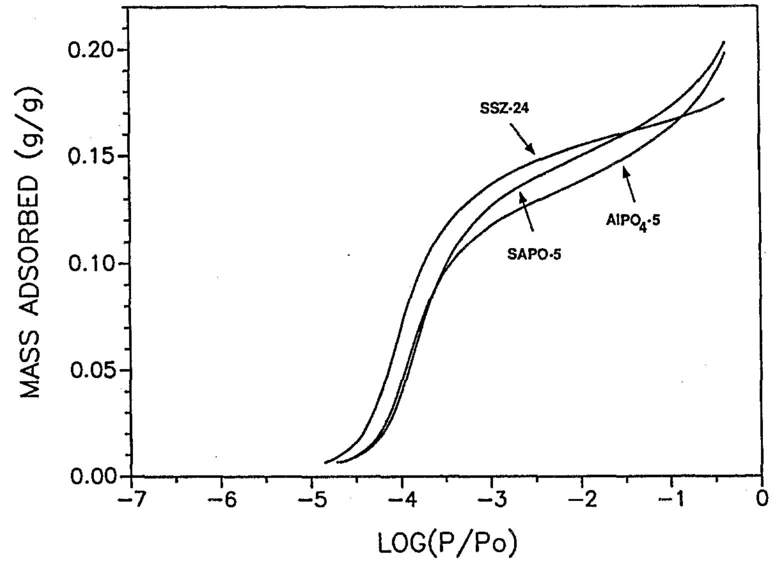

Fig. 2. Argon adsorption isotherms of $AlPO_4$-5, SAPO-5 and SSZ-24 recorded at liquid argon temperatures.

samples be well characterized. Small differences in purity can lead to large variations in δ as we have observed with zeolite Y samples (vide supra).

Fig. 3 illustrates the Xe adsorption isotherms for the AFI materials. The isotherms for $AlPO_4$-5 and SAPO-5 compare well to those reported by Chen et al. [11]. Notice that the uptake of Xe is higher for SSZ-24 than either $AlPO_4$-5 or SAPO-5. The reason for this difference is unknown to us at this time. Fig. 4 shows the ^{129}Xe NMR chemical shift data as a function of the number of Xe

Table 2
Structural and adsorption data for the AFI-type materials

Material	Bulk Composition	Unit Cell Parameters		Ref.	Ar Pore-filling capacity (g/g) **
		Experimental *	Literature		
$AlPO_4$-5	$(Al_{0.5}P_{0.5})O_2$	$a = 13.69$ Å, $c = 8.41$ Å, $V = 1365$ Å^3,	$a = 13.77$ $c = 8.41$ $V = 1376$	[19]	0.14 ± 0.01
SAPO-5	$(Si_{0.05}Al_{0.5}P_{0.45})O_2$	$a = 13.71$ Å, $c = 8.34$ Å, $V = 1357$ Å^3,			0.14
SSZ-24	essentially pure SiO_2	$a = 13.62$ Å, $c = 8.31$ Å, $V = 1335$ Å^3	$a = 13.62$ $c = 8.32$ $V = 1337$	[20]	0.15

* error on a and c values is ±0.01 Å.
** From data given in fig. 2.

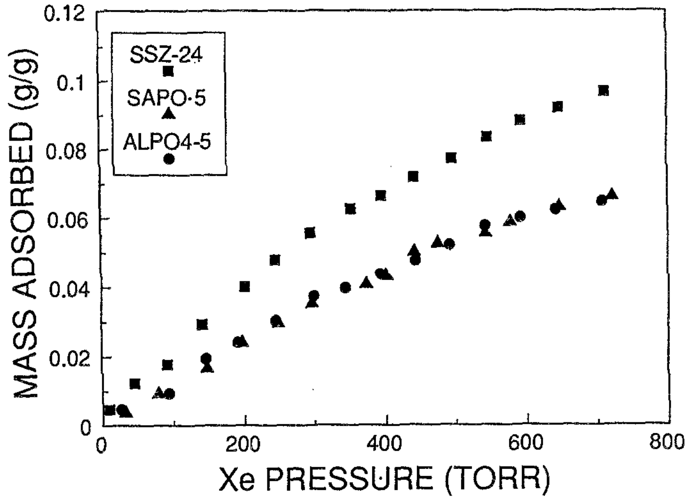

Fig. 3. Xenon adsorption isotherms of $AlPO_4$-5, SAPO-5 and SSZ-24 recorded at 22°C.

atoms adsorbed per unit cell of molecular sieve. The data from $AlPO_4$-5 and SAPO-5 agree with those of Chen et al. [11]. Our results indicate that there is no trend in δ_s with framework composition over the complete composition range from aluminophosphate to pure silica. Thus, in contrast to SAPO-37/NaY, the AFI series do not show a relationship between δ_s and framework composition. Notice also that the value of δ_s for AFI is similar to that of SAPO-37. Since the channels of AFI are ~ 8 Å while the supercages of SAPO-37 are ~ 13 Å, the AFI structures totally violate the proposed relationship between δ_s and mean free path of Xe in the void spaces as proposed by Fraissard and co-workers [5]. Chen et al. [11] observed the same trend with $AlPO_4$-5 and SAPO-5 but were unable to

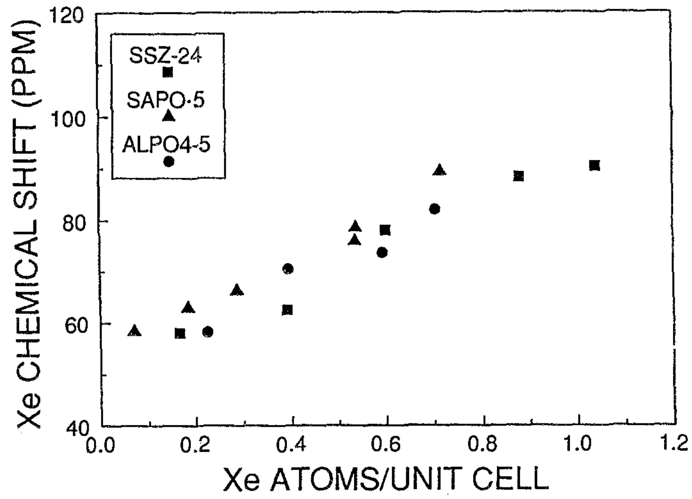

Fig. 4. ^{129}Xe NMR chemical shift as a function of Xe atoms per unit cell of molecular sieve for $AlPO_4$-5, SAPO-5 and SSZ-24.

explain the value of δ_s. Recently, Seo and Ryoo [21] observed that upon modification of H-ZSM-5 with diammonium hydrogen phosphate which is expected to reduce the effective pore size, the Xe chemical shift decreased. Again, the proposed relationship between δ_s and mean free path is violated. Seo and Ryoo attribute this behavior to a modified xenon-polarizing ability of the phosphorus containing sample, i.e., adsorbent-adsorbate interactions.

The results obtained from the FAU (refs. [11,12, and this work]) materials and ZSM-5 [21] which has been reacted with phosphorus containing species show that δ is sensitive to the chemical composition of the framework while the data from the AFI (ref. [11 and this work]) materials do not. Also, the ZSM-5 and AFI data are in conflict with the proposed relationship between δ and the size of the void space. Thus, no consistent interpretation of the ^{129}Xe NMR chemical shift is currently possible and leaves one with no confidence in knowing a priori how a molecular sieve will interact with Xe.

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References

[1] J. Fraissard, T. Ito and M. A. Springuel-Huet, J. Chim. Phys. 62 (1988) 747; and references therein.
[2] L.C. de Menorval, J.P. Fraissard and T. Ito, J. Chem. Soc., Faraday Trans. 1, 78 (1962) 403.
[3] T. Ito, J.L. Bonardet, J. Fraissard, J.B. Nagy, C. André, Z. Gabelica and E.G. Derouane, Appl. Catal. 43 (1988) L5.
[4] M. Boudart, L.C. de Menorval, J. Fraissard and G.P. Valenca, J. Phys. Chem. 92 (1988) 4033.
[5] J. Dermarquay and J. Fraissard, Chem. Phys. Lett. 136 (1987) 314.
[6] K.B. Yoon and J.K. Kochi, J. Am. Chem. Soc. 110 (1988) 6586.
[7] E.G. Derouane, Chem. Phys. Lett. 142 (1987) 200.
[8] E.G. Derouane, J.M. André and A.A. Lucas, J. Catal. 110 (1988) 58.
[9] M.E. Davis, C. Saldarriaga, C. Montes and B.E. Hanson, J. Phys. Chem. 92 (1988) 2557.
[10] E.G. Derouane and M.E. Davis, J. Mol. Catal. 48 (1988) 37.
[11] Q.J. Chen, M.A. Springuel-Huet and J. Fraissard, J. Chem. Phys. Lett. 159 (1989) 117.
[12] N. Dumont, T. Ito and E.G. Derouane, Appl. Catal. 54 (1989) L1.
[13] a. S.T. Wilson, B.M. Lok, E.M. Flanigen, U.S. Patent 4310440, (1982);
b. B.M. Lok, C.A. Messina, C.A. Patton, R.T. Gajek, T.R. Cannan, E.M. Flanigen, U.S. Patent 4440871 (1984). (Here, pseudo-boemite was used as the alumina source.)
[14] S.I. Zones, U.S. Patent 4665110 (1987).

[15] F.C.M. Chen and N.L. Benoiton, Can. J. Chem. 54 (1976) 3310.

[16] R. von Ballmoos, *Collection of Simulated Powder Patterns for Zeolites*, (Butterworth Scientific Limited, Surrey, UK, 1984) 8.

[17] A.K. Jameson, C.J. Jameson and H.S. Gutowsky, J. Chem. Phys. 53 (1970) 2310.

[18] L. Sierra de Saldarraiga, C. Saldarriaga and M.E. Davis, J. Am. Chem. Soc. 109 (1987) 2686.

[19] J.W. Richardson, Jr., J.J. Pluth and J.V. Smith, Acta Cryst. C43 (1987) 1469.

[20] R.A. Van Nordstrand, D.S. Santilli and S.I. Zones, *Perspectives in Molecular Sieve Science*, ACS Symposium Series 368 (American Chemical Society: Washington, D.C., 1988) 236.

[21] G. Seo and R. Ryoo, J. Catal. 124 (1990) 224.