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B. F. CHMELKA, Y. WU, R. JELINEK, M. E. DAVIS, AND A. PINES

Materials Sciences Division, Lawrence Berkeley Laboratory and

Department of Chemistry, University of California, Berkeley

Berkeley, California 94720

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Framework Ordering in Aluminophosphate Molecular Sieves Studied by ^{27}Al Double Rotation NMR

B.F. Chmelka, Y. Wu, R. Jelinek, M.E. Davis†, and A. Pines

Materials Sciences Division, Lawrence Berkeley Laboratory and Department of Chemistry, University of California. Berkeley, California 94720 U.S.A.

†Chemical Engineering, California Institute of Technology, Pasadena, California 91125 U.S.A.

Abstract

Aluminum-27 Double Rotation NMR spectroscopy (DOR) has been used to investigate framework ordering in the aluminophosphate molecular sieves VPI-5, $AlPO_4$-5, and $AlPO_4$-8. Well-resolved peaks in the ^{27}Al DOR spectra of both hydrated and dehydrated VPI-5 allow isotropic shifts to be correlated with local framework structure. More distorted aluminum environments are reflected by broader lines in ^{27}Al DOR spectra of $AlPO_4$-5 and $AlPO_4$-8.

1. Introduction

Framework aluminum atoms play a crucial role in establishing the adsorption and reaction properties of zeolite and aluminophosphate molecular sieves. It is, consequently, important to understand how molecular sieve structure correlates with the locations and interactions of guest-molecules adsorbed at lattice sites within porous aluminosilicate or aluminophosphate matrices. While ^{27}Al NMR is known to be a sensitive probe of solid microstructure [1-5], it has previously experienced limited application to the study of framework ordering in molecular sieves, largely because of troublesome broadening from anisotropic second-order quadrupolar interactions that dominate the NMR spectra of ^{27}Al species in many polycrystalline solids. By using the technique of Double Rotation NMR (DOR) [6,7], however, this broadening can be eliminated completely to provide new insight into bonding arrangements of framework atoms in molecular sieves. High-resolution ^{27}Al DOR can, thus, be used to examine subtle structural changes in molecular sieves produced by adsorption of guest molecules or by thermal treatment at elevated temperatures. We have previously published a preliminary report on interactions between the porous aluminophosphate VPI-5 and adsorbed water [8]. We focus here on the

different framework ordering properties of closely related VPI-5, $AlPO_4$-5, and $AlPO_4$-8 molecular sieve structures.

2. Experimental

Dehydration of 0.30 g each of hydrophilic aluminophosphates VPI-5, $AlPO_4$-5, and $AlPO_4$-8 was carried out at $\sim 10^{-4}$ torr as described below: VPI-5 was evacuated at room-temperature for 72 h; $AlPO_4$-5 was evacuated at room-temperature for 48 h, followed by 5 h at 473 K; $AlPO_4$-8 was evacuated at room-temperature for 48 h. The $AlPO_4$-8 sample was prepared initially by thermal decomposition of nascent VPI-5 at 373 K for 4 h. Schematic diagrams of the dehydrated framework structures for VPI-5 [9,10], $AlPO_4$-5 [11,12], and $AlPO_4$-8 [13,14] are shown in Figure 1. X-ray diffraction data confirmed that all samples were highly crystalline with no impurity phases present. The dehydrated samples were transferred in a dry nitrogen glove box to air-tight sample spinners for use in the DOR experiments. After DOR experiments were performed on the dehydrated materials, the samples were rehydrated in air overnight, after which DOR experiments were again performed.

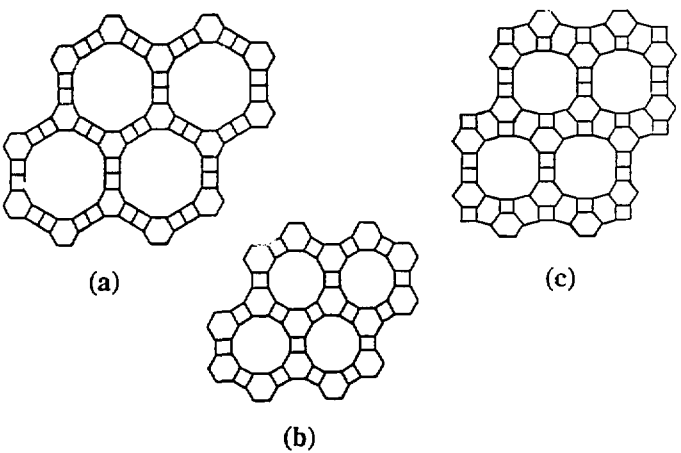

Figure 1: Diagrams of the dehydrated framework structures of large pore aluminophosphates (a) VPI-5, (b) $AlPO_4$-5, and (c) $AlPO_4$-8. The lines represent bridging oxygen atoms bonded to aluminum and phosphorus atoms which alternate at the vertices.

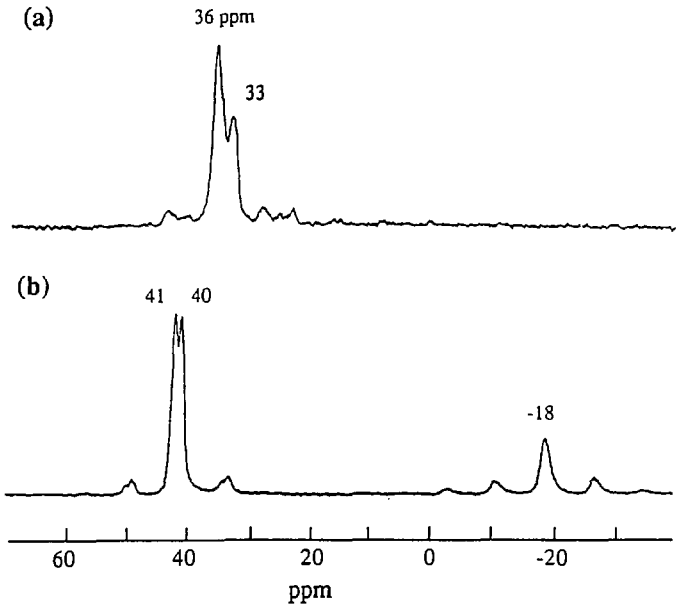

Figure 2: ^{27}Al DOR spectra at 9.4 T of (a) dehydrated and (b) hydrated VPI-5. Spinning sidebands are present on each side of the centerbands at integer multiples of the spinning frequency (800 Hz) of the large outer rotor used in the DOR experiments.

All DOR experiments were performed at room temperature on pulsed NMR spectrometers operating at either 104.23 MHz or 130.29 MHz, using home-built DOR probes that have been described elsewhere [15]. DOR spinning speeds of 5 kHz for the inner rotor and 800 Hz for the outer rotor were obtained routinely. Spectra were obtained using a 1-s delay between 45° pulses with 1000-2000 acquisitions. All isotropic ^{27}Al shifts have been referenced to $Al(NO_3)_3$ in aqueous solution.

3. Results and Discussion

AlO_4 and PO_4 tetrahedra in VPI-5 are arranged with a high degree of order, so that under conditions of double rotation, high-resolution ^{27}Al NMR spectra are obtained for both the dehydrated and hydrated materials. As shown in Figure 2(a), the ^{27}Al DOR spectrum of dehydrated VPI-5 at 9.4 T contains two peaks, at 36 ppm and 33 ppm, that are attributed to different tetrahedrally-coordinated ^{27}Al species. The linewidths of the peaks are approximately 200 Hz. Based on the dehydrated structure for VPI-5 in Figure 1(a), the 2:1 intensity ratio of the ^{27}Al signals permits assignment of the peak at 36 ppm to tetrahedral aluminum sites in the six-membered oxygen rings and the peak at 33 ppm to tetrahedral sites in the center of the double four-membered rings [8]. Addition of adsorbed water dramatically alters the aluminum microstructure of VPI-5, as reflected by the markedly different ^{27}Al DOR spectra for the hydrated and dehydrated materials in Figure 2. The peaks at 36 ppm and 33 ppm in Figure 2(a) have disappeared completely in Figure 2(b), as the presence of adsorbed water imparts a new microstructural configuration to framework aluminum atoms, which nonetheless retain a high degree of order. Two partially resolved peaks associated with tetrahedral ^{27}Al environments are present at 41 ppm and 40 ppm (100 Hz linewidths) in Figure 2(b), together with a somewhat broader upfield peak at -18 ppm in the range ascribed to octahedral ^{27}Al sites [1]. The integrated intensities of the three peaks in Figure 2(b) occur in a 1:1:1 ratio. Certain aluminum atoms in the framework, thus, acquire octahedral coordination in the presence of chemisorbed water molecules, while others retain modified tetrahedral configurations [8]. High-resolution ^{27}Al DOR spectra reveal ordered aluminum microstructures in both dehydrated and hydrated forms of VPI-5.

The structure of $AlPO_4$-5 [Fig. 1(b)] is closely related to that of VPI-5, though the six-membered oxygen rings of the former are separated by single (instead of double) four-membered rings, resulting in smaller main channel dimensions. The ^{27}Al DOR spectrum of dehydrated $AlPO_4$-5 in Figure 3(a) contains a single peak at 36 ppm with a linewidth of approximately 200 Hz. The narrow linewidth indicates ordered framework aluminum positions within the dehydrated $AlPO_4$-5 lattice and is consistent with the lone tetrahedral aluminum environment expected from the structural configuration in Figure 1(b).

Adsorption of water molecules, however, has a much different effect on aluminum ordering in $AlPO_4$-5 than in VPI-5. The high degree of framework order in hydrated VPI-5, as measured by the well-resolved ^{27}Al peaks in Figure 2(b), is in contrast to significantly less-ordered aluminum environments in hydrated $AlPO_4$-5. The ^{27}Al DOR spectrum of hydrated $AlPO_4$-5 in Figure 3(b) has features that can be attributed to tetrahedral and octahedral ^{27}Al species at 39 ppm and -14 ppm, respectively, similar to DOR results for hydrated VPI-5. However, after eliminating

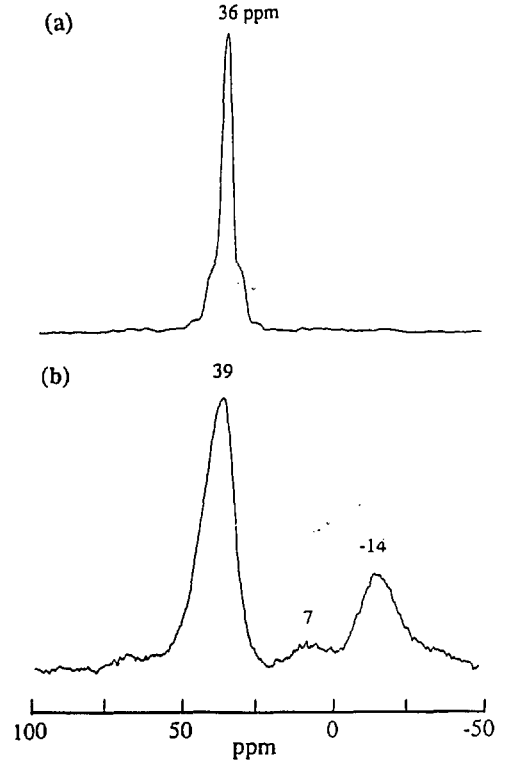

Figure 3: ^{27}Al DOR spectra at 11.7 T of (a) dehydrated and (b) hydrated $AlPO_4$-5. The shoulders in (a) are spinning sidebands which occur at integer multiples of the spinning frequency (800 Hz) of the large outer DOR rotor.

broadening contributions from first- and second-order interactions, including chemical shift anisotropy, dipole-dipole effects, and second-order quadrupolar effects, these peaks remain significantly broader than those observed in the ^{27}Al DOR spectrum of hydrated VPI-5 [Fig. 2(b)]. A small, broad feature is additionally

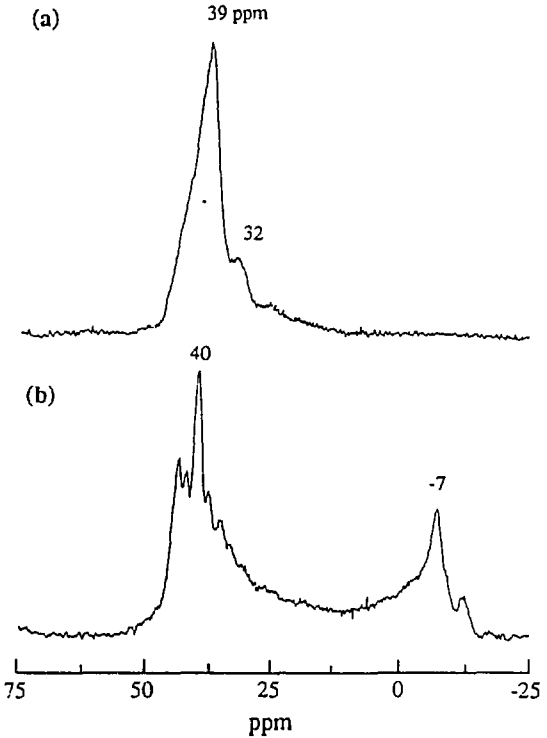

Figure 4: ^{27}Al DOR spectra at 11.7 T of (a) dehydrated and (b) hydrated $AlPO_4$-8.

present near 7 ppm in a region of the spectrum where lines from penta-coordinated aluminum species have been observed in the aluminophosphate $AlPO_4$-21 [16]. These observations reflect a distribution of aluminum environments in hydrated $AlPO_4$-5, consistent with a highly strained framework configuration or a random distribution of water molecules adsorbed within the sieve channels. The presence of *double* four-membered oxygen rings apparently allows the VPI-5/H_2O system to adopt an ordered configuration which is not possible in $AlPO_4$-5. The absence of

such double four-membered rings in the $AlPO_4$-5 lattice, where only *single* four-membered oxygen rings separate the hexagonal six-rings [Fig. 1(b)], produces a hydrated aluminum microstructure that is much less ordered than in VPI-5. Similar hydration effects have been observed in the aluminophosphate sieve $AlPO_4$-25, which also possesses a structure containing single four-membered rings positioned between hexagonal six-rings [17]. The features in the ^{27}Al DOR spectrum of hydrated $AlPO_4$-25 at 11.7 T [16] are essentially identical to those present in the DOR spectrum of hydrated $AlPO_4$-5 shown in Figure 3(b).

Changes in aluminophosphate sieve structure produced by treatments at elevated temperatures can similarly be followed by ^{27}Al DOR. For example, thermal treatment of VPI-5 at 373 K dramatically alters the aluminophosphate framework, inducing an irreversible phase transformation to $AlPO_4$-8, a material containing five crystallographically distinct tetrahedral Al sites in its dehydrated form [Fig. 1(c)]. The ^{27}Al DOR spectra of $AlPO_4$-8 in Figure 4 are significantly different from those of VPI-5 in Figure 2, reflecting major modification of the VPI-5 structure after heating. Moreover, the broad ^{27}Al lines in Figure 4(a) indicate substantial disorder in the aluminum environments of the dehydrated $AlPO_4$-8 framework, especially when compared with the well-resolved ^{27}Al peaks of dehydrated VPI-5 [Fig. 2(a)] and dehydrated $AlPO_4$-5 [Fig. 3(a)]. This behavior is not unexpected, since $AlPO_4$-8 formed from thermal transformation of VPI-5 contains a high degree of stacking disorder [18]. Upon rehydration, sharpened peaks appear at 40 and -7 ppm in Figure 4(b), reflecting a more ordered aluminum arrangement in $AlPO_4$-8 with both tetrahedrally- and octahedrally-coordinated Al species present. Nevertheless, the broad feature connecting these two peaks indicates a continuous distribution of aluminum environments spanning the range between these two relatively ordered sites. The sharp subsidiary peaks on either side of the peak at 40 ppm and also upfield of the peak at -7 ppm appear not to be spinning sidebands and may reflect additional ordering of the $AlPO_4$-8 lattice. Adsorption of water, thus, imparts an additional degree of order to aluminum sites in the $AlPO_4$-8 framework.

4. Conclusions

Resolution of peaks from distinct aluminum sites in ^{27}Al DOR spectra of VPI-5 and dehydrated $AlPO_4$-5 permits isotropic shifts of the various framework ^{27}Al species to be determined. This allows local nuclear structure to be correlated with perturbations of the molecular sieve lattice induced either by adsorption of guest molecules or by thermal modification. Highly ordered aluminum environments in both hydrated and dehydrated VPI-5 suggest intriguing adsorbate interactions with the host framework. In the case of $AlPO_4$-5, the highly ordered framework of the dehydrated material is replaced by disordered aluminum environments following incorporation of water into the pore spaces. In contrast, the disordered aluminum

microstructure of dehydrated $AlPO_4$-8 is modified by adsorption of water molecules at framework sites, which apparently imparts additional order to the sieve structure. It is clear that ordering of framework aluminum atoms is highly dependent on local symmetry and bonding characteristics of the aluminophosphate matrix, both of which can be modified appreciably by interaction with adsorbed molecular guests. In circumstances where guest-induced changes in local lattice structure are significant, perturbations of the aluminophosphate framework are likely to have a substantial impact on the macroscopic adsorption and reaction properties of these materials.

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