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Adsorption effects in aluminophosphate molecular sieves studied by ^{27}Al double-rotation NMR

R. Jelinek, B.F. Chmelka [1], Y. Wu [2], M.E. Davis [3], J.G. Ulan [4], R. Gronsky [5]
and A. Pines *

Materials Sciences Division, Lawrence Berkeley Laboratory and Department of Chemistry,
University of California, Berkeley, CA 94720, USA

^{27} Al double rotation NMR (DOR) spectroscopy is used to investigate structural changes in the framework of several aluminophosphate molecular sieves upon adsorption of water. The shapes, widths, and positions of the spectral lines yield information on the aluminum environments, adsorption sites, and degree of structural disorder undergone upon water adsorption.

Keywords: NMR (DOR) spectroscopy; aluminophosphate; molecular sieves; aluminum environment; adsorption sites; structural disorder; water adsorption

1. Introduction

Aluminophosphate molecular sieves have attracted considerable interest since they were first synthesized a decade ago at Union Carbide Laboratories [1]. The uniform open-channel structure of these materials offers potential uses in catalysis, ion exchange and gas separations. Recently, aluminophosphate channels have been used for assemblies of organic molecules that feature non-linear optical effects [2].

In the absence of extraframework charge-balancing cations, such as found in zeolites [3], the aluminum atoms in the aluminophosphate framework play a crucial role in determining the adsorption properties of the materials. ^{27}Al NMR

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* To whom correspondence should be addressed.

[1] Department of Chemical and Nuclear Engineering, University of California, Santa Barbara, CA 93106, USA.

[2] Department of Physics, University of North Carolina, Chapel Hill, NC 27599, USA.

[3] Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA.

[4] Institute for Environmental Chemistry, National Research Council Canada.

[5] National Center of Electron Microscopy, Materials and Sciences Division, Lawrence Berkeley Laboratory, USA.

provides a useful probe of the microstructure of aluminum atoms in solids. However, ^{27}Al nuclei experience anisotropic quadrupolar interactions, that cannot be removed by magic angle spinning (MAS) or multiple-pulse NMR sequences alone, thus broadening spectral lines that render interpretation of NMR spectra difficult. By using the technique of double-rotation NMR (DOR) [4], one can remove spectral broadening from second-order quadrupolar effects, thus producing better resolved spectra which yield greater insight into local structural arrangements of quadrupolar nuclei. Recently, ^{27}Al DOR has been used to investigate aluminum environments and structural transformations in some aluminophosphate molecular sieves [5–8]. In this work we examine the effects of water adsorption on framework aluminum atoms of the aluminophosphate molecular sieves VPI-5, $AlPO_4$-5, and in particular $AlPO_4$-8.

2. Experimental

NMR experiments were carried out in an 11.7 T magnetic field, on a Chemagnetics CMX-500 spectrometer, using a home-built DOR probe whose features are described elsewhere [9]. Spinning speeds of 5 kHz for the inner rotor and 600–700 Hz for the outer one were used. Short, 30°, radio-frequency pulses were employed with 0.5 s delays. All spectra are referenced to 0.1 M $Al(NO)_3$, used as an external standard.

Dehydration of the materials was carried out at $\approx 10^{-4}$ Torr according to the procedures 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; the $AlPO_4$-8 sample was prepared initially by thermal decomposition of nascent VPI-5 at 373 K for 4 h, with subsequent dehydration carried out by room temperature evacuation for 48 h. The samples were packed into the DOR rotor in a dry glove-box under rigorous anaerobic conditions. Water content of partially hydrated samples was determined by comparing the weight of the partially hydrated sample, to the fully dehydrated material.

3. Results and discussion

Fig. 1 shows the ^{27}Al DOR spectra of dehydrated and hydrated VPI-5, and a schematic drawing of its dehydrated aluminophosphate structure. This molecular sieve, with 18-membered ring channels, has a large, 12 Å, pore diameter [10]. Two tetrahedrally coordinated framework aluminum sites are resolved, at 36.2 and 34.2 ppm, in the dehydrated sample, fig. 1b, while the peaks overlap completely, at 41.2 ppm, in the hydrated material, as shown in fig. 1c. The two aluminum resonances in the hydrated sample are not resolved in an 11.7 T

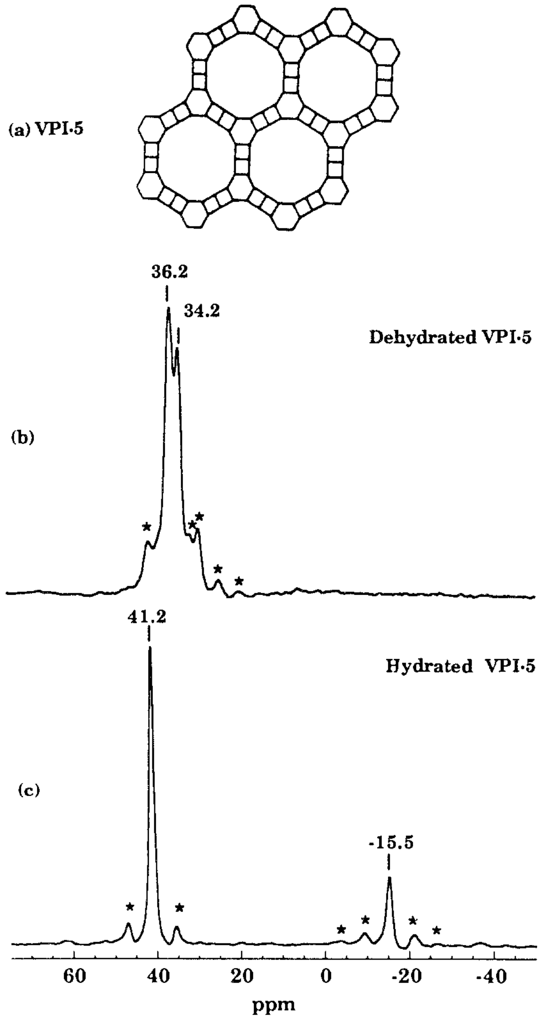

Fig. 1. Schematic diagram of the dehydrated structure of VPI-5 (a); and ^{27}Al DOR spectra of (b) dehydrated VPI-5; (c) hydrated VPI-5. The asterisks indicate spinning sidebands from the large outer rotor.

magnetic field, because they possess similar isotropic chemical shift values. The aluminum sites, however, have quite different quadrupolar parameters which enable the two ^{27}Al DOR resonances to be resolved in hydrated VPI-5 in a lower magnetic field strength [5,11]. A sharp peak, at -15.5 ppm, appears in the spectrum of the hydrated material, fig. 1c, that is assigned to an octahedral aluminum species, formed upon chemisorption of two water molecules at framework aluminum sites tetrahedrally coordinated to framework oxygen atoms. The DOR spectra are reproduced upon successive hydration/dehydration treatments, indicating that the water adsorption process is fully reversible.

The positions of the two tetrahedral ^{27}Al peaks in dehydrated VPI-5 shift upon water adsorption, as shown in fig. 1. This observation indicates that both the aluminum site located between the four- and six-membered rings in the VPI-5 framework (which corresponds to the signal at 36.2 ppm), as well as the aluminum site between the two four-membered rings (which gives rise to the ^{27}Al DOR signal at 34.2 ppm), are sensitive to the adsorption of water. The widths of the signals do not change appreciably upon the addition of water, indicating that the short-range ordering of the aluminum environments is retained throughout the adsorption process. The ordering is also evident in the octahedrally coordinated aluminum environments, as the width of the resonance at -15.5 ppm, fig. 1c, is comparable to the tetrahedral aluminum species.

Different results are obtained for $AlPO_4$-5, an aluminophosphate molecular sieve with significantly narrower channels formed by 12-membered rings, having diameters of ≈ 7 Å [12]. Fig. 2 shows the ^{27}Al DOR spectra of dehydrated and hydrated $AlPO_4$-5, and a schematic drawing of the dehydrated structure. The framework of the dehydrated material contains a single tetrahedral aluminum environment, which gives rise to the single sharp Gaussian peak at 36.1 ppm in fig. 2b. The spectrum of the hydrated material, shown in fig. 2c, features two prominent signals, at around 39 and -14 ppm, respectively. Both are substantially broader than the resonance observed in the ^{27}Al DOR spectrum of the dehydrated material in fig. 2b. The downfield peak, at around 39 ppm, is ascribed to tetrahedrally coordinated aluminum species, while the peak that emerges around -15 ppm corresponds to octahedral aluminum environments. The small hump observed in the vicinity of 0 ppm probably arises from aluminum sites with intermediate coordinations, most likely (nominally) 5-coordinated Al species, which have been observed to produce ^{27}Al DOR resonances in this spectral region [6].

The broad spectral lines in the ^{27}Al DOR spectrum of hydrated $AlPO_4$-5, fig. 2c, indicate diminished structural ordering, compared in particular to the highly ordered VPI-5 framework, which yields the narrow peaks in fig. 1c following adsorption of water. Previous studies have hypothesized the formation of hydroxide defect sites within $AlPO_4$-5 framework upon water adsorption [13], which might lead to broadening of the spectral lines. In addition, adsorption of water molecules non-selectively at sites within the relatively narrow channels of $AlPO_4$-5 may also contribute to the broad, featureless signals observed in the ^{27}Al DOR spectrum of the hydrated material, fig. 2c. Non-selective adsorption might consequently produce a large distribution of ^{27}Al environments that would spread the NMR frequencies over a large spectral range.

As discussed above, the channel sizes of the various aluminophosphate molecular sieves are expected to influence the adsorption properties of the materials. In order to pursue this assumption we examined the water adsorption process within $AlPO_4$-8. The framework of this aluminophosphate, which is produced upon structural transformation of VPI-5 under thermal treatment [14],

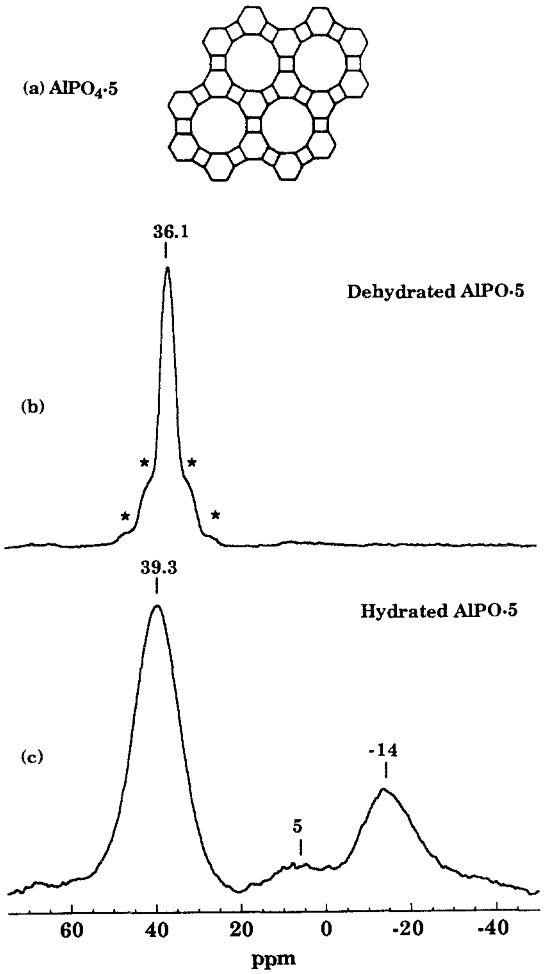

Fig. 2. Schematic diagram of the dehydrated structure of $AlPO_4$-5 (a); and ^{27}Al DOR spectra of (b) dehydrated $AlPO_4$-5; (c) hydrated $AlPO_4$-5. The asterisks indicate spinning sidebands from the large outer rotor.

contains 14-membered ring channels with diameters of 8.7 Å [15]. The ^{27}Al DOR spectra of $AlPO_4$-8 containing different amounts of adsorbed water are shown in fig. 3. The DOR spectrum of dehydrated $AlPO_4$-8, fig. 3b, is not resolved into specific ^{27}Al sites because of overlapping signals from the five distinct aluminum sites in the dehydrated material. In addition, a relatively high degree of aluminum disorder likely accounts for the unresolved ^{27}Al signals, though X-ray diffraction experiments show the material to be highly crystalline [15].

Figs. 3c–3f feature ^{27}Al DOR spectra of partially hydrated $AlPO_4$-8. The weight percentage of water adsorbed was determined after exposing the dehydrated material in the DOR rotor to atmospheric conditions for short time

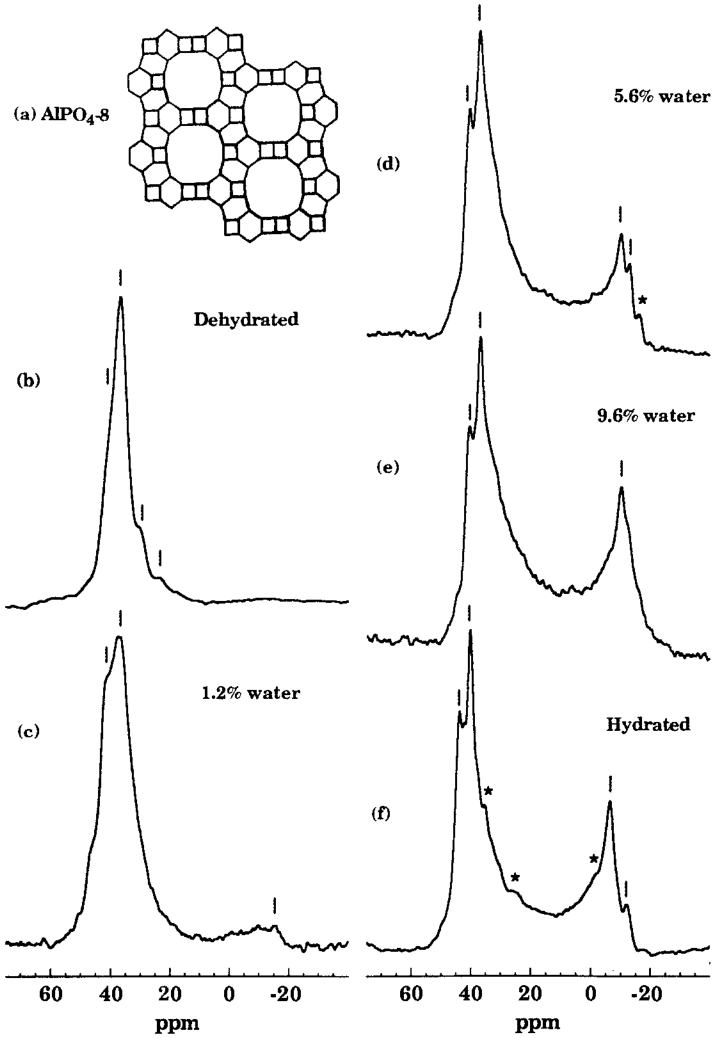

Fig. 3. Schematic diagram of the dehydrated structure of $AlPO_4$-8 (a); and ^{27}Al DOR spectra for various water loadings: (b) dehydrated $AlPO_4$-8; (c) 1.2 wt% water; (d) 5.6 wt% water; (e) 9.6 wt% water; (f) fully hydrated $AlPO_4$-8. The asterisks indicate spinning sidebands from the large outer rotor.

periods. From fig. 3, it is apparent that structural changes occur both in the tetrahedral aluminum sites, detected in the NMR spectra at around 40 ppm, as well as in the octahedral environments, which appear further upfield at around −15 ppm. Specifically, one can detect narrowing of the two downfield peaks, at 40 and 43.5 ppm, as a greater amount of water is adsorbed onto the $AlPO_4$-8 framework. Similarly, the octahedral aluminum environments exhibit significant sensitivity to water adsorption; one detects at least two sites at around −15 ppm, with the positions shifting somewhat as the water content is increased.

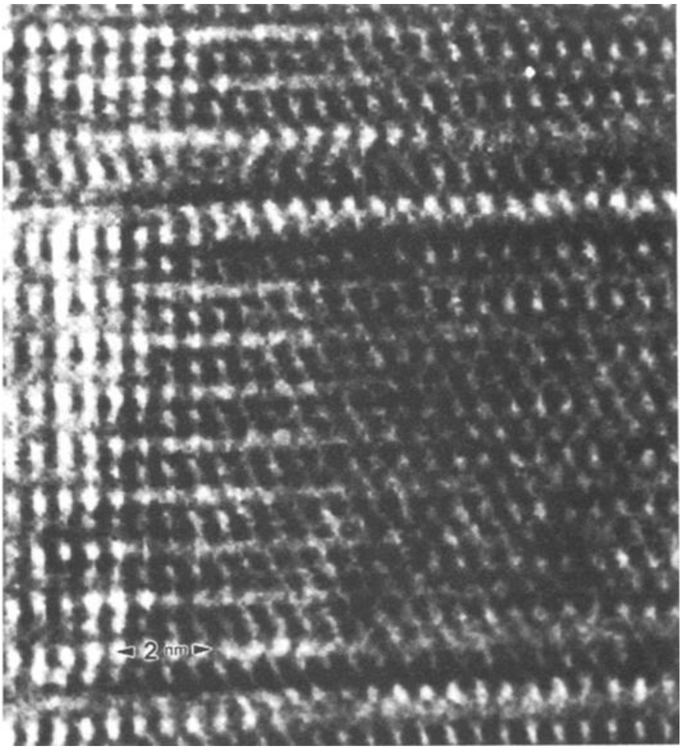

Fig. 4. TEM image of dehydrated $AlPO_4$-8. The image was recorded in JEOL JEM 200 CX transmission electron microscope at 200 kV accelerating potential.

The ^{27}Al DOR results obtained for $AlPO_4$-8 indicate that distinct hydration sites probably exist within the framework; these sites give rise to the sharp tetrahedral, and octahedral ^{27}Al peaks that emerge in the spectra upon adsorption of water. A recent ^{27}Al quadrupolar nutation analysis, combined with ^{1}H–^{27}Al cross-polarization experiments [17], has indeed indicated the appearance of specific hydration sites within the $AlPO_4$-8 framework. The broad ^{27}Al signal observed between the two prominent resonance regions in the spectra of the partially, and fully hydrated materials, figs. 3c–3f, indicates an essentially continuous distribution of ^{27}Al environments between the relatively ordered four- and six-coordinated Al species formed upon adsorption of water molecules.

High resolution transmission electron microscopy (HRTEM) experiments were conducted to determine the extent of structural ordering of $AlPO_4$-8 [16]. The TEM image of $AlPO_4$-8, shown in fig. 4, indicates an abundance of stacking faults perpendicular to the long axis of the crystalline $AlPO_4$-8. This observation might is consistent with the local aluminum disorder in dehydrated $AlPO_4$-8, manifested by the broad lines in the ^{27}Al DOR spectrum shown in fig. 3b. The appearance of stacking disorder throughout the aluminophosphate material could produce a large distribution of aluminum environments, that would broaden the ^{27}Al spectral lines observed in dehydrated $AlPO_4$-8, as well as for $AlPO_4$-8 in a state of incipient hydration, fig. 3c. These stacking orders may additionally contribute to the broad distribution of the aluminum environments between 0 and 20 ppm, figs. 3c–3f.

4. Conclusions

^{27}Al DOR provides useful information on water adsorption processes in aluminophosphate molecular sieves. The sensitivity of different sites to the addition of water molecules is examined through the positions of the ^{27}Al resonances, with the shapes and widths of the peaks providing insight in local ordering of framework aluminum sites. Different adsorption properties are detected at a molecular level for VPI-5, $AlPO_4$-5, and $AlPO_4$-8 reflecting a likely connection between sieve channel dimensions and both local and macroscopic adsorption characteristics.

Acknowledgement

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