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A Combined NMR and XRD Study of AFI and AEL Type Molecular Sieves

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Calcined dehydrated AlPO₄-5 has been studied by X-ray powder diffraction, ³¹P MAS, and ²⁷Al MAS and double-rotation (DOR) NMR. The results indicate that three crystallographically different sites can be distinguished in the structure of dehydrated AlPO₄-5 in the ratio 1:1:1. The observed splitting of the NMR spectra is correlated to the line width of the XRD peaks between 29 = 19° and 29 = 23°. Simulations of ²⁷Al DOR (4.7, 9.4, and 11.7 T) and MAS spectra (7.0 and 9.4 T) yield the isotropic chemical shifts (δiso), quadrupolar coupling constants (CQ), and the asymmetry parameters (γ) of the different sites in dry AFI. The interaction of water, methanol, ammonia, and acetonitrile with AlPO₄-5 and AlPO₄-11 is studied by XRD and ²⁷Al DOR and MAS NMR. Both water and ammonia are able to coordinate to part of the framework aluminum, leading to five- and or six-coordinated aluminum. The relative amounts of five- and six-coordinated aluminum depend on the crystal structure and the interacting sorbate. Whereas water in AlPO₄-11 is interacting with one specific aluminum site (Al₂), the interaction of water with AlPO₄-5 occurs randomly. This leads to a broadening of the tetrahedral signals at higher water loading (above 10–12 wt %). At low MAS frequencies some dipolar broadening occurs, whereas at high spinning frequencies or 850–1000 Hz DOR the broadening is caused by site distribution. Methanol and acetonitrile do not interact with framework atoms. These molecules are too big to coordinate to framework aluminum in AFI and AEL type molecular sieves. The broadening of the spectral features observed after methanol adsorption is apparently due to an increase in chemical shift dispersion brought about by nonspecific interactions of methanol with the framework, thereby causing a larger spread in Al–O–P angles.

Introduction

AlPO₄-5 (AFI) and AlPO₄-11 (AEL) are two of a series of molecular sieves first synthesized by the Union Carbide Corporation. The structures are built of alternating AlO₄ and PO₄ tetrahedra, which are connected via bridging oxygen atoms to form a one-directional pore system with a diameter of 7.3 Å (12-membered rings) in the case of AFI and 3.9 × 6.4 Å (10-membered rings) in the case of AEL. On the basis of neutron diffraction,¹ it was concluded that the dehydrated AFI structure contains a unique T-site for both Al and P, while three crystallographically different sites can be distinguished in the dry AFI molecular sieve. Upon hydration of AEL a change of symmetry is observed, leading to five T-sites. The structure of AEL in relation with NMR and XRD was reported in a previous publication.²

Recently, the results of a ²⁷Al DOR NMR study of hydrated and dehydrated VPI-5 (VFI) and AFI were reported.³ For calcined (dehydrated) VFI two different peaks in the ratio 2:1 can be observed for the three different crystallographic sites, at least for some magnetic field strengths. Upon hydration of the sample, the line widths of the tetrahedral aluminum resonances do not increase and a signal at -15.5 ppm is formed, with a line width comparable to the signals of aluminum in the tetrahedral region. Separate resonances for all three crystallographic sites can be observed. The ²⁷Al DOR spectrum of calcined dehydrated AFI at 11.7 T consists of a single line at 36.1 ppm, which is consistent with the neutron diffraction study. However, the line width (at half-height) of the ²⁷Al DOR NMR signal of tetrahedrally coordinated aluminum in dehydrated AFI is more than twice as large as the line width of the (single) lines of dehydrated VFI, indicating that the observed signal might well be an envelope of signals. Upon water adsorption, the line width of the tetrahedral NMR signal (39.3 ppm) increases significantly, and the resonances of both five- and six-coordinated aluminum are observed at +5 and -14 ppm, respectively. The broadening of the signal is ascribed to either the formation of hydroxide defects or nonselective adsorption of water molecules in the relatively narrow channels of AFI. This would produce a large distribution of ²⁷Al environments leading to a spread of the NMR resonances over a large spectral range.

In contrast to the situation in zeolites, small polar molecules are able to coordinate to part of the framework aluminum atoms in aluminophosphates. The adsorption of small polar molecules in aluminophosphates has been the subject of many studies.⁴ Water is known to transform part of the aluminum of AFI type molecular sieves into five- and six-coordinated aluminum, while only four- and six-coordinated aluminum is found in the AEL type molecular sieves. Adsorption of ammonia leads to five- and six-coordination of part of the aluminum in AFI type molecular sieves, while methanol does not.⁴ Two possible explanations were given for the fact that methanol adsorption did not lead to a strong coordination to part of the aluminum: methanol is not as good a ligand as water, and ammonia or methanol is too large to coordinate to the aluminum.

Here, we report the results of a ²⁷Al DOR NMR study of a series of AFI molecular sieves obtained via three independent syntheses. The products are further characterized by ³¹P MAS NMR, XRD, and n-butane adsorption. The results indicate that three crystallographically different T-sites can be distinguished in the dry AFI molecular sieve.

The adsorption of small polar molecules on AFI and AEL type molecular sieves was studied with XRD and ²⁷Al DOR and MAS NMR. Water and ammonia transform part of the tetrahedrally coordinated aluminum into five- and/or six-coordinated aluminum. Adsorption of water and ammonia in AFI causes broadening of the spectral features in ²⁷Al NMR, eventually leading to a single broad signal for the tetrahedrally coordinated aluminum. Methanol and acetonitrile are too bulky to coordinate to the aluminum in AFI and AEL type molecular sieves.

Experimental Section

Syntheses. AFI, AEL, and CoAPO₄-5 samples were prepared by a method described in the patent literature.⁵ A gel with a molar composition of 1.02P₂O₅:Al₂O₃:y template:η=40–50 H₂O...
AFI and AEL Type Molecular Sieves

was prepared. Some Co(OAc)₂ ((Al/P)/Co = 4000) was added to the diluted phosphoric acid for the synthesis of CoAPO-5 molecular sieves. For the syntheses of AFI samples both tripropylamine (samples 1 and 2) and triethylamine (sample 3) were used as template (γ = 1.5), while for the CoAPO-5 samples triethylamine (γ = 1.5) was used. The template used for the crystallization of AEL was di-n-propylamine (γ = 1.0). Crystallization was performed by heating the gels in stainless steel Teflon-lined autoclaves at 423 K for 1–2 days. After quenching of the autoclaves, the crystalline product was separated from the mother liquor by sedimentation or centrifugation. After drying of the samples, calcination was performed by heating the samples in a flow of dry oxygen at a rate of 1 K min⁻¹ to 873 K and keeping them at the final temperature for 5 h.

**Characterization.** X-ray diffraction measurements were performed on a Philips PW 7200 diffractometer at room temperature. Spectra were recorded between 2θ = 5° and 2θ = 50° with a scanning rate of 1 deg min⁻¹.

Pore volumes were determined gravimetrically using n-butane adsorption on a Cahn 2000 electrobalance. This electrobalance was used to check the loading of sorbates on the aluminophosphates before and after the ⁷Al DOR NMR measurements. No significant changes in the loading of the samples were observed before and after the DOR NMR measurements.

²⁷Al DOR NMR spectra at different magnetic fields were measured on Bruker MSL spectrometers. The pulse length was varied between 1 and 3 μs, corresponding to a flip angle of approximately 20°. A recycle delay of 1 s was used. The outer rotor was spun at 850–1000 Hz with the inner rotor spinning at 4–5 kHz. Typically 800–1000 pulses were accumulated. Rotor synchronized pulsing was applied to suppress the odd numbered spinning sidebands. Rotation of the inner rotor cannot be monitored directly with the present equipment. However, a sudden stop of the inner rotor during the measurement invariably results in a frequency drop of 20–30 Hz of the outer rotor. Additionally, rotation of the inner rotor was checked when slowing down the outer rotor; after a crash, a restart was always quite easily audible.

³¹P and ⁷Al MAS NMR measurements were recorded on a Bruker MSL 400 spectrometer using a 4-mm double bearing MAS probe. A recycle delay of 60 s was found sufficiently long to record ³¹P MAS NMR spectra that were unaffected by further enlarging of the delay. A spinning rate of 10.0 kHz was used. ²⁷Al MAS NMR spectra were recorded using a pulse length of 1 μs, corresponding to a flip angle of approximately 20°. A recycle delay of 1 s was used. High-power proton decoupling was applied when appropriate.

**Results and Discussion**

The X-ray diffraction patterns of some calcined dehydrated AFI molecular sieves are given in Figure 1. It can be seen that all samples are highly crystalline and that only one sample (AFI-2) is contaminated with a small amount of amorphous material, probably trydimite. The ²⁷Al DOR NMR and ³¹P MAS NMR spectra, however, show some interesting differences (Figure 2). Two of the three synthesis procedures, AFI synthesized with tripropylamine (AFI-1 and AFI-2) and CoAPO-5 synthesized with triethylamine (not shown), yield samples of which both the ²⁷Al DOR NMR and ³¹P MAS NMR spectra show (at least) two signals. The total widths of these signals are not significantly larger than the widths of the single signal for the other samples. To the best of our knowledge there are, however, no indications in the literature which might indicate the existence of more than one crystallographically different site in this alumino-phosphate structure.

There is, however, one paper where two signals in the ³¹P MAS NMR spectra are observed if the Al/P ratio of the sample is much higher than unity. In that case the ³¹P MAS NMR spectrum shows two signals at -28.5 and -17.2 ppm, while the ⁷Al DOR NMR lines, AFI-1 and AFI-2, the sum of the line widths (at half-heights) amounts to 0.53° 2θ while for the sample where no splitting is observed the
line width is equal to 0.73° 2θ. An increased line width suggests a less ordered structure (more lattice defects) or very small crystallites. Since the size of the crystals is on the order of some microns (SEM), the last explanation does not apply here. The less ordered structure may possibly lead to less ordered local environments which can then conceal the existence of more than one crystallographically different T-site in NMR. The differences in intensities of the reflections are explained by the different morphologies of the crystals which causes some reflections to be more intense.

The possibility of an intergrowth to explain the splitting in the NMR spectra is very remote in view of the relative intensities of the 27Al DOR NMR signals. Simulations (see below) indicate that the relative contribution of the different lines are 33% each. From the 27Al DOR and 31P MAS NMR spectra we conclude that not all T-sites are equivalent but that there exist three different T-sites in dehydrated AFI molecular sieves. More details presumably have to await the complete Rietveld refinement of the XRD data. To the best of our knowledge, this is not available at this time. At the moment we are therefore not able to propose a new (presumably slightly altered) structure, based on XRD data.

27Al DOR NMR measurements on dry AFI-2 were performed at different magnetic fields to determine both the isotropic chemical shifts ($\delta_0$) and the quadrupolar parameters ($C_Q$ and $\eta$) of the different aluminum sites. The spectra are displayed in Figure 3; the low-field shoulder is caused by the presence of some dense phase material. At first sight, no significant increase of the resolution is obtained by measuring at magnetic field strengths of 4.7, 9.4, and 11.7 T. There is, however, a distinct change in the envelope pattern, due to overlap of the (three) separate lines; see Figure 3. Deconvolution of the DOR NMR spectra was performed using three signals with equal intensities. A plot of the DOR NMR line positions versus 100/(B₀)¹ is given in Figure 4. The slope of the line is related to the product of the quadrupolar coupling constant $C_Q$ and $\eta$ (see formula in Figure 4). Extrapolation of the lines to infinite magnetic fields yields the isotropic chemical shift. Spectral simulations were performed with three different tetrahedral sites with equal intensities. Figure 5 displays the results of the simulation of the DOR spectrum measured at 4.7 T. The quadrupolar parameters, derived from simulation of DOR and MAS NMR spectra at various magnetic fields, of the three different peaks observed in the calcined (dry) AFI-2 sample are given in Table I. All spectra could be simulated using a relative intensity of 33% for each aluminum site. This suggest that the 12-membered ring of AFI, which contains six aluminum atoms, has three crystallographically different sites. The fact that the quadrupolar coupling constants of two sites are practically the same is a strong indication that we are dealing with two T-sites with only slightly different environments. The third line has a much larger quadrupolar coupling constant and isotropic chemical shift.
applying high-power proton decoupling (Figure 7). The broad and featureless spectra obtained in these slow MAS experiments confirm the correctness of the DOR measurements. (After a stop of the inner rotor, in fact, MAS spectra would be recorded with a spinning frequency of 850–1000 Hz.) At high MAS frequencies spectra are obtained which are only slightly broader than the DOR spectra, independent of the application of high-power dipolar decoupling (Figure 7, traces 3 and 4). This is expected since MAS frequencies larger than the heteronuclear dipolar coupling constant will remove this interaction from the spectrum. From these results, together with the DOR experiments, it can be concluded that broadening of the spectral features is largely due to a dispersion in chemical shifts after hydration. A minor influence of the quadrupolar effect of $^{27}$Al environments can be deduced from the differences in line widths of MAS and DOR spectra. Noneselective hydration would produce a large distribution of $^{27}$Al environments, leading to a spread of the resonances over a large spectral range.

The formation of five-coordinated aluminum upon water adsorption was not observed for AEL samples. There, even at very low water loading octahedrally coordinated aluminum was formed. Up to 20% of the aluminum becomes octahedrally coordinated, and maximally four lines are observed in the region where the resonances of tetrahedrally coordinated aluminum occur (Figure 8). Combination of the quadrupolar coupling constants and the local symmetries derived from X-ray diffraction data enabled us to show that the A12 site of AEL becomes preferentially hydrated and to denote the observed $^{27}$Al DOR NMR resonances to the five different crystallographic sites. This assignment will be used here. The conclusion that the A12 site becomes preferentially hydrated can be reconciled with recent CP-DOR NMR measurements performed on fully hydrated AEL. In the CP-DOR experiment the octahedral signal is enhanced with respect to the signal of tetrahedrally coordinated aluminum. However, the signals of the tetrahedrally coordinated A13 (40.9 ppm), A4 (37.7 ppm), and A6 (33.6 ppm) sites are also visible, while the signal of A12 (23.4 ppm) is absent in the CP-DOR spectrum. The observed spectrum can be explained if the water molecules (in a cross section view of the AEL channel) are placed close to the A12 sites and two water molecules near the center of the pore (Figure 9). The water coordinating to an aluminum atom (A12) is 'bounded' to this position, while the water molecules in the center of the pore are physisorbed and mobile. It is clear that the signals previously assigned by us to the A1 and A1 sites...
Figure 8. $^{27}$Al DOR NMR spectra of fully hydrated AEL measured at different magnetic field strengths: $B_0 = 4.7$ T (trace 1), 7.0 (trace 2), 9.4 T (trace 3), and 11.7 (trace 4).

Figure 9. Cross section view of the AEL channel after complete saturation with water.

The relative positions (shifts) do is caused by symmetry changes of the lattice induced by water adsorption. In the dry state (three different T-sites) some of the aluminum resonances are (partially) overlapping, leading to broad envelope of signals. Upon hydration the number of different T-sites is increased to five. The originally overlapping signals are now split into separate resonances.

The amount of five- and six-coordinated aluminum as a function of the water content of AEL and AFI is plotted in Figure 10. In the AEL type molecular sieve all water adsorbed ($H_2O/Al < 0.55$) is interacting specifically with the Al$_{13}$ site, leading to octahedrally coordinated aluminum. Only at very low water loading ($H_2O/Al < 0.07$) no five- and/or six-coordinated aluminum could be observed. For the AFI type molecular sieves a somewhat different behavior is observed. At low water loading the amount of five- and six-coordinated aluminum is less than can be expected for specific interaction of water with an aluminum site (dashed line in Figure 10). Only above an $H_2O/Al$ ratio of 0.75 (11-12 wt %) is a strong increase in the amount of five- and six-coordinated aluminum observed, in the same region where a pronounced broadening of the tetrahedrally coordinated aluminum is observed. This is in agreement with the $^{27}$Al NMR study performed on this system by Goldfarb et al. There, no octahedrally coordinated aluminum was observed with $^{27}$Al MAS NMR at water loadings up to 5 wt %. Moreover, $^2$H NMR showed the existence of mobile water only.

### Table II: Typical Line Widths of the $^{27}$Al DOR NMR Signals of Tetrahedrally Coordinated Aluminum (Hz) at Half-Height of the AFI and AEL Samples Measured at 9.4 T, in the As-Synthesized, Calcined Dehydrated, and Several Equilibrated States (with Adsorbed Methanol, Ammonia, Water, and Acetonitrile)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dry</th>
<th>$H_2O$</th>
<th>$CH_3OH$</th>
<th>$CH_3CN$</th>
<th>$NH_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFI</td>
<td>1170</td>
<td>590</td>
<td>1210 (23.8)</td>
<td>1150 (14.3)</td>
<td>650 (16.6)</td>
</tr>
<tr>
<td>AEL</td>
<td>960</td>
<td>390</td>
<td>240 (15.0)</td>
<td>650 (7.7)</td>
<td>430 (7.0)</td>
</tr>
</tbody>
</table>

* Numbers in parentheses are weight percent.
Considerable changes are observed in the XRD patterns after water adsorption. For AEL the reflections at low 2θ angles decrease strongly in intensity, which is ascribed to the interaction of water with a part of the T-atoms. The position of several lines in the diffractogram changes due to the deformation of the pores by water adsorption; the pores become more elliptical after water adsorption.15

A decrease of the intensities at low 2θ angles was also observed for the AFI samples. The observation that water coordinates to part of the aluminum atoms is in line with the above-mentioned explanation. However, no significant change of peak positions is observed after water adsorption, indicating that the symmetry and pore structure of the AFI system do not change after water adsorption.

**Methanol Adsorption.** The adsorption of methanol in AFI and AEL does not lead to the formation of five- and/or six-coordinated aluminum. However, significant broadening of the resonances attributed to tetrahedrally coordinated aluminum is observed. For AFI the line width increases from 400 to approximately 650 Hz for 850 Hz DOR (outer rotor) measured at 9.4 T, for AFI this increase is even more drastic, 600-1200 Hz. MAS measurements performed at 10.0 kHz with dipolar decoupling yield a line width of 1700 Hz for the AFI sample and a line width of 770 Hz for the AEL sample. Clearly, some second-order quadrupolar broadening is apparent in the MAS spectra, leading to slightly broader lines than in DOR spectra. However, the major cause of the broadening of the spectral features in fast MAS and in DOR spectra upon methanol adsorption stems from chemical shift dispersion, which in turn indicates changes in the framework geometry (i.e., Al−O−P angles) brought about by the adsorbed methanol. The line width of the as-synthesized sample, with the template in the pores, is also broadened in the presence of the template.

XRD measurements performed on these samples indicate that methanol adsorption leads to some small but significant changes in the observed pattern for AEL, while the diffraction pattern of AFI seems unaffected. No decrease in intensities of reflections at low 2θ angles was observed, suggesting no specific interaction of methanol with the T-atoms in AFI and AEL type molecular sieves, in line with the absence of five- and/or six-coordinated aluminum in the 27Al DOR NMR spectra.

**Acetonitrile Adsorption.** The absence of five- and/or six-coordinated aluminum after methanol adsorption can be due to sterical constraints and/or the dipole moment of the molecule. To distinguish between these parameters, acetonitrile and ammonia adsorptions were studied. Acetonitrile is bulkier than methanol but has a much larger dipole moment (3.92 D instead of 1.70 D), while ammonia is smaller but has a smaller dipole moment (1.3 D). The 27Al DOR NMR spectra after acetonitrile adsorption give no indication of five- or six-coordinated aluminum. It therefore seems that sterical constraints play a major role in controlling the interaction of polar molecules with aluminum in this type of molecular sieve.

Moreover, the adsorption of acetonitrile has only minor influences on the line widths of the 27Al DOR NMR resonances. The intensity of the spinning sidebands is, however, slightly increased (increased chemical shift anisotropy). The XRD patterns before and after acetonitrile adsorption are identical.

**Ammonia Adsorption.** Ammonia is a small molecule with a small dipole moment (1.3 D). Goldfarb et al. reported 27Al MAS NMR spectra of AFI with adsorbed ammonia. Upon adsorption five- and six-coordinated aluminum was formed. Here, ammonia adsorption on AFI (18.6 wt %) and AEL (13.3 wt %) was studied with 27Al DOR NMR and XRD. Ammonia adsorption on the two types of molecular sieves resulted in the formation of five- and six-coordinated aluminum in both cases. The relative amounts are, however, somewhat different for the two types of molecular sieves (Figure 11). The part of the aluminum which remains

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**Figure 11.** 27Al MAS and DOR NMR spectra of AFI (traces 1–4) and AEL (traces 5–8) molecular sieves with adsorbed ammonia (9.4 T): MAS, 1.0 kHz (traces 1, 5); DOR, 1.0 kHz, high-power decoupling (traces 2, 6); MAS, 10.0 (traces 3, 7); DOR, 1000 Hz (traces 4, 8). The motion of about 50% of the ammonia was limited to a threelfold jump; this is probably the ammonia bounded to the aluminum site. The motion of the other 50% (physiosorbed ammonia) was not limited. This is in good agreement with the 27Al DOR NMR measurements.

MAS spectra were recorded to find out the reason for the broad resonances observed in the DOR spectra. At low MAS frequencies (1.0 kHz) broad spectra are obtained (Figure 11, traces 1 and 5) which become narrower after applying high-power proton decoupling (Figure 11, traces 2 and 6), indicating the presence of dipolar interactions. MAS spectra recorded at different spinning frequencies indicated that the dipolar interaction is removed from the spectrum at 6–7 kHz. The spectra recorded at a MAS frequency of 10.0 kHz (Figure 11, traces 3 and 7), with or without decoupling, are just slightly broader than the DOR spectra recorded with a spinning frequency of 1000 Hz (traces 4 and 8). Again, the main reason for broadening of the DOR spectra stems from chemical shift dispersion, although minor influences of quadrupolar interactions play a role in the MAS spectra. MAS spectra recorded with high-power decoupling at different MAS frequencies indicated that the CSA is removed from the spectrum at approximately 3 kHz.

In the case of AEL the amount of five-coordinated aluminum (20%) is slightly less than the amount of octahedrally coordinated aluminum (28%), whereas the amount of five-coordinated aluminum (14%) is much less than the amount of octahedrally coordinated aluminum (40%) in the case of AFI. The higher amount of five-coordinated aluminum in the AEL type molecular sieves, with respect to the AFI type molecular sieves, might be
explained by the small pores of AEL. The space is too limited to get octahedral coordination of all interacting aluminum atoms.

Only minor changes are observed in the XRD patterns of AFI after ammonia adsorption. The intensities of some reflections decrease, but the position of the reflections remains unchanged. For AEL a somewhat different behavior is observed. A slight decrease of intensity is observed, which is recovered after ammonia desorption and a shift of the most intense reflection to lower 2θ values. This shift is opposite to the shift observed after water adsorption. It is, however, clear that ammonia behaves quite differently than water (Figure 12).

Conclusions

$^{27}$Al DOR and $^{31}$P MAS NMR performed on AFI samples indicate that three crystallographically different T-sites can be distinguished in the structure of dehydrated AFI. Spectral simulations of the DOR and MAS spectra at different magnetic field elucidate that the three different T-sites exist in a 1:1:1 ratio. The quadrupolar parameters and isotropic chemical shifts of these sites were determined by spectral simulations of the DOR and MAS spectra.

The interactions of water, methanol, acetonitrile, and ammonia with framework aluminum atoms in AFI and AEL were studied. Water and ammonia are able to transform part of the tetrahedrally coordinated aluminum atoms into five- and/or six-coordinated aluminum. Methanol and acetonitrile are too bulky to coordinate to the aluminum atoms in AFI and AEL type molecular sieves.

Hydration of AEL occurs in a selective way. The aluminum site becomes octahedrally coordinated. This is confirmed by recent CP-DOR experiments performed on the same sample. Partial hydration of AFI showed that broadening of the $^{27}$Al DOR NMR signal occurs above $\approx$11–12 wt % water adsorption. Unlike in AEL, this interaction seems to occur in a random fashion.

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References and Notes