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Adsorption Calorimetric Measurements and ^{27}Al DOR NMR Studies on the Molecular Sieve $\text{AlPO}_4\text{-18}$

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Highly crystalline samples of the chabazite-related aluminophosphate $\text{AlPO}_4\text{-18}$ (AEI) have been prepared and characterized by adsorption measurements as well as by ^{27}Al double rotation (DOR) NMR studies. Whereas the heat curves and isotherms of *n*-paraffins on AEI show the common feature for adsorption on nonpolar molecular sieves with a given pore dimension, methanol gives an unusual heat curve with a deep minimum for a loading >4 molecules per cavity. This corresponds to the extended low-pressure hysteresis loop of the isotherm which is absent in SAPO-34. In accordance with the structure determination and Rietveld refinement of the as-synthesized AEI, three crystallographically inequivalent Al positions including one pentacoordinated Al could be detected and assigned by ^{27}Al DOR NMR. Calcination as well as the adsorption of polar molecules results in a structure change. While water and ammonia generate octahedrally coordinated Al, methanol gives only Al^{V} as has been found for the template-containing sample. The methanol adsorption has been studied in more detail. It has been found that the formation of the Al^{V} requires more than one methanol molecule per Al_1 site. This process occurs for a loading between one and four molecules per cavity; it is isobaric and compares to a hydration process. Two additional molecules can be accommodated in the AEI cavity which seems to be related to the second step of the methanol isotherm and the extended low-pressure hysteresis loop which is absent in the isotherm of water. This is accompanied by another reversible structure change resulting in four NMR lines for the six different Al positions in the double 6-ring, the secondary building unit of the AEI.

Introduction

Aluminophosphate molecular sieves represent a new family of microporous adsorbents of broad structural diversity¹ which includes now 23 accepted structure types with 14 novel structures.² One of these new structures is the small-pore molecular sieve $\text{AlPO}_4\text{-18}$ (AEI), which recently has been characterized by synchrotron-based X-ray powder diffraction and Rietveld refinement as a chabazite-related three-dimensional 8-ring channel system. After calcination structural changes occur.³ In the as-synthesized form, it contains pentacoordinated Al caused by the presence of the tetraethylammonium hydroxide in its cavities. Therefore, some unusual adsorption properties, especially regarding polar molecules, can be expected as has been shown for other structures of this family such as VFI, AFI, AEL, ERI, and others using NMR or adsorption techniques.^{4–15} Very little, however, is known about the adsorption properties of AEI as only a few related studies have been carried out so far.¹⁶

In the present contribution the adsorption behavior of the pure aluminophosphate AEI has been investigated using adsorption calorimetry. To explain the unusual adsorption properties of this molecular sieve with regard to polar molecules, the ^{27}Al DOR (double rotation) NMR technique has been applied to samples with different loadings. For the first time a direct correlation of results of adsorption methods and DOR NMR data is made. For comparison, the chabazite isotypic structure SAPO-34 is included in this study.

Experimental Section

AEI and SAPO-34 (CHA) were synthesized according to the patent literature¹⁷ in a slightly modified procedure. The samples

were prepared in a hydrothermal system at 473 K for 20–60 h containing aluminum triisopropylate, phosphoric acid (85%), tetraethylammonium hydroxide (TEAOH, 20%), and silica sol (30%) as a silica source for the SAPO-34. No hydrochloric acid was added to the gel. The molar ratios of the synthesis mixture were $0.75(\text{TEA})_2\text{O}:\text{Al}_2\text{O}_3:1.4\text{P}_2\text{O}_5:50\text{H}_2\text{O}$ and $0.75(\text{TEA})_2\text{O}:\text{Al}_2\text{O}_3:\text{P}_2\text{O}_5 \geq 0.3\text{SiO}_2:60\text{H}_2\text{O}$. The products were centrifuged, washed with distilled water, and dried at 383 K. X-ray diffraction, IR, and adsorption measurements showed them to be highly crystalline and pure. The two AEI batches, $\text{AlPO}_4\text{-18/1}$ and $\text{AlPO}_4\text{-18/2}$, prepared in this study differ only slightly in their pore volumes (see Table I).

The differential molar heats of adsorption of *n*-pentane, *n*-hexane, and methanol were measured using a Calvet-type microcalorimeter (Setaram) at 303 K. Adsorption isotherms were determined simultaneously at the same temperature using a standard volumetric adsorption apparatus which was connected to the calorimeter. Additional isotherms were measured gravimetrically with a McBain isotherm facility in adsorption and desorption at the temperature of the NMR experiment (298 K) and with the same sample as used for NMR. The equilibrium pressure was estimated by a high-precision membrane manometer (MKS Baratron).

The ^{27}Al DOR NMR experiments were performed on Bruker spectrometers of the types MSL 400 and CXP 300 with spinning rates of approximately 4–5 kHz for the inner rotor and 850–1000 Hz for the outer one. Rotor synchronized pulsing was applied to suppress the odd-numbered spinning sidebands.¹⁸ A pulse length of 1 μs was used, corresponding to a flip angle of approximately 20° . The AEI samples for the NMR experiment were loaded on a vacuum line with well-defined amounts of methanol and kept in a sealed tube after preparation. The samples

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Figure 1. Adsorption isotherms of *n*-hexane at 298 K on $\text{AlPO}_4\text{-18.2}$ (■, adsorption; □, desorption) and SAPO-34 (●, adsorption; ○, desorption).

TABLE I: Adsorption Capacities of the Molecular Sieves Used Determined at Relative Pressure 0.5

sample	adsorption capacity, cm^3/g		
	<i>n</i> -hexane	<i>n</i> -pentane	methanol
$\text{AlPO}_4\text{-18/1}$	0.183	0.170	0.314
$\text{AlPO}_4\text{-18/2}$	0.190		0.328
SAPO-34	0.187		0.304
$\text{AlPO}_4\text{-5}$	0.124	0.136	0.157

were transferred into tightly closed rotors in a glovebox prior to the NMR measurements. It was checked that no changes in the sample compositions occurred during the measurements.

Results and Discussion

From measurements of the adsorption isotherms of *n*-pentane, *n*-hexane, and methanol, the adsorption capacities of AEI and SAPO-34 (relative pressure 0.5) were determined. They are listed in Table I together with those of AFI, for comparison. The values obtained for methanol on the AEI samples and SAPO-34 are very close to the value of the free volume of the chabazite structure ($0.32 \text{ cm}^3/\text{g}^{19}$), confirming the high purity of the samples. The adsorption of *n*-paraffins gave capacities of $0.19 \text{ cm}^3/\text{g}$ only, less than can be expected to fill the cavities considering the density of the liquid sorbate. Similar results have been reported for methanol and Ar adsorption on AEI¹⁶ as well as for polar and nonpolar sorbates on VFI.⁶ The apparent saturation capacities for *n*-hexane and for *n*-pentane are approximately one molecule per cavity. This is in agreement with two propane or two *n*-butane molecules per cage in H-chabazite reported by Barrer.²⁰

From Figures 1 and 2 it can be seen that there is another difference in the adsorption behavior of the polar methanol and *n*-hexane on AEI and the SAPO form of this molecular sieve. Whereas almost no difference is found between the *n*-hexane adsorptions on both materials (Figure 1), methanol gives a higher saturation capacity on AEI and a pronounced low-pressure hysteresis loop (Figure 2). Because of the low relative pressure (<0.2) and the absence of a pronounced hysteresis for the *n*-hexane adsorption, this methanol hysteresis should not be ascribed to capillary condensation. Probably a sorbate structure can be assumed as has been reported for the adsorption of benzene on silicalite.²¹ Second, the AEI exhibits an unusual isotherm shape. That is, little adsorption of methanol followed by an isobaric rise (phase transition like) and a step after adsorption of approximately four molecules per cavity. This isotherm is of type V whereas all other isotherms are of type I,²² which normally would be expected for microporous adsorbents. A type V isotherm has been found for the adsorption of water on many AlPO_4 -based

Figure 2. Adsorption isotherms of methanol at 298 K on $\text{AlPO}_4\text{-18/2}$ and SAPO-34 (denotation as in Figure 1).

Figure 3. Calorimetrically (at 303 K) measured differential molar heats of adsorption of *n*-hexane (■, ▽) and *n*-pentane (◆, ▲) on $\text{AlPO}_4\text{-18/1}$ (filled symbols) and $\text{AlPO}_4\text{-5}$.

Figure 4. Calorimetrically (at 303 K) measured differential molar heats of adsorption of methanol on $\text{AlPO}_4\text{-18/1}$ (■) and $\text{AlPO}_4\text{-5}$ (▲). The upper scale in molecules per cage is related to AEI.

molecular sieves such as AFI, AEL, AEI, ERI, SOD, and VFI^{5,6,8,9,16} but not for methanol.

Corresponding results can be obtained from the adsorption calorimetric measurements. In Figures 3 and 4 the heat curves of *n*-pentane and *n*-hexane as well as those of methanol on AEI and AFI are depicted. Whereas the heat curves of the *n*-paraffins on the AEI show the common feature for adsorption on nonpolar molecular sieves with a given pore diameter, methanol gives an unusual heat curve with an extended linear part followed by a deep minimum at a loading of 5.5 mmol/g , which corresponds

TABLE II: Characteristic Heats of Adsorption of *n*-Hexane and Methanol on AlPO's

sample	pore dimension (nm)	FD ^a (T/nm ³)	<i>Q</i> (kJ/mol)	
			<i>n</i> -hexane	methanol
VFI	1.21	14.2	42.5	78
AEI	0.7 ^b	14.8	58.0	66
AFI	0.73	17.3	59.0	58
AEL	0.63 × 0.39	19.1	74.5	62
MFI(SiO ₂)	0.55	18.0	75.4	48

^a Framework density. ^b Diameter of a pear-shaped cavity with approximately 0.9-nm length.

again to four molecules per cage. This minimum coincides with the extended low-pressure hysteresis loop of the isotherm which is absent in SAPO-34.

Table II lists the initial heats of adsorption for *n*-hexane and some characteristic heats of adsorption of methanol on different AlPO₄ molecular sieves and silicalite (MFI). From Figure 3 and Table II it can be concluded that the heat of adsorption for the *n*-paraffin follows the pore diameter^{23,24} if the AEI cavity is approximated by a pear-shaped ellipsoid of 0.7-nm diameter and 0.9-nm length. The diameter of that cavity is then close to the pore diameter of AFI, which can explain the similar adsorption heat values connected with *n*-paraffin adsorption on both molecular sieves. This is generally in line with the confinement theory.²⁵ However, because of the existence of cavities in AEI instead of channels in the AFI, one should expect a somewhat higher heat for AEI. But if the low framework density and the open structure of AEI are taken into account, the heat of adsorption could be reduced again.²⁶ The only slightly increasing heat curves of AEI in Figure 3 as well as the saturation capacity of approximately one molecule per cavity lead to the presumption that *n*-hexane and *n*-pentane are occluded in the cavities separately with almost no sorbate-sorbate interaction.

In contrast, the heats of adsorption of methanol do not fit the pore dimension or the framework density approximation. Methanol in AEI follows (in Table II, column 5) the situation in VFI, which shows the highest strength of specific interaction with framework Al as has been proved by NMR and adsorption calorimetric measurements.⁶ AEL and AFI exhibit a lower value for the adsorption heat. This is, however, still 10 kJ/mol higher than for the small pore molecular sieve silicalite. (For further discussion see below.)

In the next part the results of the ²⁷Al DOR NMR are discussed. According to Meier et al.,³ one of the three crystallographically inequivalent T positions in the as-synthesized form, the Al₁, is additionally coordinated by the OH⁻ of the template molecule. Every unit cell contains four cages with two Al₁ per cage. Each of the cages includes one TEOH. The OH⁻ is attached to both Al₁ sites of the cavity to turn them into pentacoordination. This can be seen from spectra a and b in Figure 5. In the as-synthesized form two well-resolved lines at 37.8 and 44.3 ppm of comparable intensities are found as well as a third line at 6.4 ppm, which represents this Al^V. The ratios of these three lines amount to 1:1:1, including the contribution of the spinning sidebands. The ³¹P MAS spectrum shows also three lines confirming three inequivalent T positions for the phosphorus.

As can be seen from spectrum c in Figure 5, the spectrum of the unloaded calcined sample consists only of two signals with chemical shifts of 31.3 and 32.8 ppm, which are slightly better resolved at lower field (7.0 T, 25.6 and 27.9 ppm). The ratio of their intensities amounts to approximately 1:2, which is generally in agreement with the proposed structure having three inequivalent T positions. However, two of them cannot be distinguished by ²⁷Al DOR NMR, not even by using a different field (7.0 T). Moreover, the ³¹P spectrum shows only one line demonstrating a quite similar shielding of the three different crystallographic positions.

Figure 5. ²⁷Al DOR NMR spectra of AlPO₄-18/2: (a) as-synthesized, outer rotor spinning rate 850 Hz; (b) as-synthesized, 1000 Hz; (c) calcined, 1000 Hz; (d) *n*-hexane saturated, 850 Hz. Dots indicate spinning sidebands.

It is interesting to mention that in the ²⁷Al spectrum of the calcined AEI the low-field line (at 32.8 ppm) can already be influenced by *n*-hexane adsorption. As can be seen from spectrum d in Figure 5, this signal is slightly shifted by 0.7 ppm toward lower field. The other part of the 1:2 feature stays exactly at the same position. This small change can perhaps explain why the *n*-hexane isotherm is also not completely reversible even at low relative pressure.

From measurements at different fields²⁷ the isotropic chemical shift (δ_{iso}^{CS}) and the quadrupolar coupling constant (C_Q) for the different Al positions of the as-synthesized and the calcined AEI as well as of the methanol-saturated sample have been determined using the QNMR program.²⁸ The results are summarized in Table III. Because of the known structure parameters of the first two mentioned samples, the shear strain parameter ($|\psi|$) for the three Al positions could be calculated. It describes quantitatively the AlO₄ distortion from ideal tetrahedra and can be related to C_Q .²⁹ According to this, the lines of the as-synthesized AEI (spectra a and b, Figure 5) could be assigned to the corresponding Al lattice positions as shown in Table III. However, for the calcined AEI the C_Q and the $|\psi|$ values are rather close to each other ($|\psi|$ amounts for Al₁ to 0.224, for Al₂ to 0.182, and for Al₃ to 0.148), and this makes the assignment difficult. Therefore, a direct relation would yield little extra information.

As in the template-containing AEI, pentacoordinated Al has been found also after adsorption of methanol. Figure 6 shows

TABLE III: Isotropic Chemical Shifts ($\delta_{\text{iso}}^{\text{CS}}$), Quadrupolar Coupling Constants (C_Q) and Shear Strain Parameters ($|\eta|$) of As-Synthesized, Calcined, and Methanol-Saturated AEI (in the Calculation $\eta = 0.5$ Was Used)

sample		$\delta_{\text{iso}}^{\text{CS}}$ (ppm)	relat area (%)	C_Q (MHz)	$ \eta $
as-synthesized	Al_3	46.0	35 ^a	1.67	0.511
	Al_2	41.8	35	2.58	0.731
	Al_1	19.0	30	4.59	1.538
calcined	Al^{A}	39.1	36	3.24	
	Al^{B}	38.6	64	3.5	
CH_3OH -saturated	Al^{A}	46.5	20 ^b	2.66	
	Al^{B}	41.5	40	2.62	
	Al^{C}	32.0	20	2.02	
	Al^{D}	15.0	40	4.61	

^a Relative area estimated by peak deconvolution and integration.^b Relative area taken from the spectrum simulation with QNMR.

a set of spectra with increasing loadings of approximately 0, 1, 2, 2.8, 4.9, 6, and, after some desorption, 4.9 molecules of sorbate per cavity. Spectra e and g represent the same loading (4.9 molecules per cage or 6.5 mmol/g) but correspond to the different branches of the isotherm in Figure 2. As with the as-synthesized sample, a signal at 1.4 ppm starts to appear after adsorption of one molecule per cavity. Parallel to that the original, approximately 1:2 feature changes to a new approximately 1:1 ratio signal toward lower field (37.1 and 38.3 ppm).

Saturation with methanol causes a structural change which gives a completely different spectrum. Even after desorption toward the loading of spectrum e (Figure 6) in the range of the hysteresis, this change persists. It should be mentioned that in spectrum g two lines for Al^{V} have been found at 2.9 and 8.3 ppm. Spectra f and g can no longer be approximated by three crystallographically inequivalent sites. Quite obviously the symmetry properties have changed. Four lines with a ratio of 1:2:1:2 (see Table III) have been found which are due to six different Al in the double 6-ring, the secondary building unit of the AEI. The line Al^{D} for the pentacoordinated Al splits into two if one methanol of the six per cage is removed. After complete desorption, the spectrum of the calcined sample has been obtained again due to a reversible process.

As the hysteresis of the isotherm and the deep minimum of the heat curve accompanied the structural change, the growing Al^{V} signal corresponds to the linear part of the isotherm and to the heat curve between one and four molecules per cavity. Up to an adsorbed amount of one molecule, which would be enough methanol to act like the OH^- of the template, as described above, very little Al^{V} occurs. From measurements of the mobility of water and ammonia in AFI,¹² it is known that up to 20% of the saturation capacity water adsorption did not affect the ^{27}Al and ^{31}P spectra, and rather mobile water was found (by ^2H NMR). Only for higher loadings up to saturation Al^{VI} and "bound" water (or ammonia) were detected. A similar behavior can be assumed for the AEI/methanol system which would correlate with the small uptake of methanol at the beginning of the isotherm and the first minimum of the heat curve (Figures 2 and 4).

From this it can be concluded that formation of Al^{V} requires the presence of more than one methanol molecule per cavity. Probably, a sorbate structure, as has been shown for water absorption on VPI-5,³⁰ is formed which leads to an inhomogeneous distribution of the sorbate molecules with empty and occupied cavities. This would be in line with the presence of a "mixed structure" of reacted and unreacted AEI represented by spectra b–d in Figure 6. The coordinative adsorption of the methanol on the Al_1 site and the sorbate structure, probably by hydrogen bonds (cooperative interaction), appears to be the reason for the unusual shape of the isotherm and the heat curve. It also could explain their straight parts between the loading of one and four molecules per cavity. Furthermore, this (weak) specific inter-

Figure 6. ^{27}Al DOR NMR spectra of $\text{AlPO}_4\text{-18/2}$: (a) calcined; (b) with methanol, 1 molecule/cavity; (c) 2 molecules/cavity; (d) 2.8 molecules/cavity; (e) 4.9 molecules/cavity; (f) saturated, 6 molecules/cavity; (g) after saturation desorbed up to 4.9 molecules/cavity. Dots indicate spinning sidebands.

action should be the reason for the comparatively high adsorption heat (see silicalite Table II) as discussed for other AlPO_4 's in ref 6.

Figure 7 shows DOR spectra of the as-synthesized AEI (spectrum a) as well as of samples saturated with methanol (b), ammonia (c), and water (d). Striking is that ammonia and water create octahedrally coordinated Al (bands at approximately -15 ppm). NMR measurements on a sample with a low loading of water also give only Al^{VI} , confirming the shape of the water isotherm in ref 16 which is rising vertically without any secondary step. The comparable positions of the remaining signals in the ^{27}Al spectra of samples with ammonia (38.1 and 43.1 ppm) and water (37.4 and 42.7 ppm), which are rather close to those of the as-synthesized sample, lead to the conclusion that the lattice geometries are not very different. That supports the assumption that adsorption of methanol influences the structure in a different way than the template, water, or ammonia does. The Al^{V}

Figure 7. ^{27}Al DOR NMR spectra of $\text{AlPO}_4\text{-18/2}$: (a) as-synthesized, (b) methanol-saturated, (c) ammonia-saturated, (d) saturated with water. Dots indicate spinning sidebands.

formation, however, is seen in the presence of the methanol as well as the template molecules.

Conclusions

If silicon is left out of the gel for preparation of SAPO-34, as described above a new chabazite-related structure is formed. Such material shows, in contrast to nonpolar sorbates, unusual adsorption properties regarding polar molecules as have been found for other AlPO_4 molecular sieves. In accordance with the Rietveld refinement of the as-synthesized AEI, three different Al positions including one Al^{IV} could be detected by ^{27}Al DOR NMR. After calcination the structure changes and shows a completely different spectrum without Al^{IV} . While water and ammonia generate after adsorption octahedrally coordinated Al, methanol gives only Al^{IV} , similar to the template-containing sample. As could be expected, the adsorption of *n*-hexane does not influence the structure very much; however, the position of one of the Al sites is somewhat different due to the presence of the *n*-hexane in the cavities.

From both the NMR and the adsorption calorimetric measurements, it can be concluded that methanol starts forming Al^{IV}

only after a certain amount is adsorbed which corresponds to approximately one molecule per cavity and which would be already sufficient to turn all Al^{I} into Al^{IV} . Between one and four molecules per cavity, the signal of the Al^{IV} grows which corresponds to the isobaric rise of the isotherm and the horizontal linear part in the heat curve. Two additional molecules can be accommodated per cavity, which results in a step and low-pressure hysteresis of the isotherm and a minimum of the heat curve at that loading as well as a second reversible structure change.

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