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Sequential Steps of Ammoniation of the Microporous Silicoaluminophosphates H-SAPO-34 and H-SAPO-37 Investigated by In Situ CF MAS NMR Spectroscopy

A. Buchholz, W. Wang, M. Xu, A. Arnold, and M. Hunger*

Institute of Chemical Technology, University of Stuttgart, D-70550 Stuttgart, Germany

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By studying the ammoniation of the silicoaluminophosphate-type zeolites H-SAPO-34 and H-SAPO-37 by in situ ^1H and ^{27}Al MAS NMR under continuous-flow (CF) conditions, a two-step adsorption process was determined. The first ammoniation step consists of an adsorption of ammonia exclusively at Brønsted acidic bridging OH groups (SiOHAl), leading to the formation of ammonium ions (NH_4-form). The second ammoniation step, which occurs at a higher ammonia coverage, consists of a coordination of ammonia molecules to framework Al atoms in $\equiv P-O-Al\equiv$ bridges. This second adsorption step causes a change of the aluminum coordination from a tetrahedral coordination to an octahedral coordination. The ammonia coordination to Al atoms is reversible when the material is purged at 413 K. The hydration of NH_4-form silicoaluminophosphates (ammoniated bridging OH groups) causes a coordination of water molecules exclusively to Al atoms in $\equiv P-O-Al\equiv$ bridges, leading to a hydrolysis of the framework. Therefore, a hydrolysis of the silicoaluminophosphate framework is hindered if the bridging OH groups (SiOHAl), as well as the aluminophosphate framework ($\equiv P-O-Al\equiv$), is covered by ammonia. The latter may support the stabilizing effect of preloaded ammonia on H-form silicoaluminophosphates toward hydration and weak hydrothermal treatments, as recently observed for H-SAPO-34.

Introduction

During the past decade, the silicoaluminophosphate-type zeolites H-SAPO-34 (CHA) and H-SAPO-37 (FAU) have found an increasing interest as microporous solid acids in heterogeneous catalysis reactions, such as the conversion of methanol to olefins and the isomerization of decane.[1,2] The incorporation of Si atoms at P sites of the aluminophosphate framework (P → Si) leads to the formation of $\equiv Si-O-Al\equiv$ bridges, causing a negative charge at the tetrahedrally coordinated framework Al atom, which is compensated by a bridging hydroxyl proton. These Brønsted acidic bridging OH groups (SiOHAl) have a local structure that is similar to those occurring in aluminosilicate-type zeolites.[3] An incorporation of two Si atoms at neighboring Al and P sites (Al, P → Si, Si) causes the formation of $\equiv Si-O-Si\equiv$ bridges that are free of framework charges and can lead to the formation of siliceous islands. Via neutron diffraction and Fourier transform infrared (FTIR) spectroscopy, it could be shown that dehydrated H-SAPO-34 exhibits bridging OH groups located at O(2) and O(4) atoms in eight-membered rings of the chabasite structure, causing stretching vibrations at 3630 and 3610 cm^{-1}.[4] The bridging OH groups located in supercages and sodalite cages of the faujasite structure of dehydrated H-SAPO-37 are characterized by stretching vibrations at 3640 and 3575 cm^{-1}, respectively.[5]

Minchev et al.,[6] Briend et al.,[7] and Parlitz et al.[8] investigated the effect of water on the local structure of aluminum in the framework of silicoaluminophosphates. In the case of H-SAPO-

34, hydration of the calcined material has been observed to cause a significant decrease of the crystallinity, which is reversible after short durations and irreversible upon hydration on the order of weeks and months. In contrast, the hydration of calcined H-SAPO-37 causes immediate damage of the silicoaluminophosphate framework. Recently, in situ ^{1}H and ^{27}Al MAS NMR spectroscopic investigations were performed to study the hydration and dehydration of H-SAPO-34 and H-SAPO-37 in flowing nitrogen loaded with water and in a flow of dry nitrogen, respectively.[9] This study indicated that the hydration of H-SAPO-34 and H-SAPO-37 is a two-step process that starts with an adsorption of water molecules at Brønsted acidic bridging OH groups (SiOHAl) before a hydration of framework Al atoms occurs during the second hydration step at higher water coverages. In the case of H-SAPO-37, the second hydration step is responsible for an immediate hydrolysis of $\equiv$P$-$O$-$Al$\equiv$ bridges and damage of the silicoaluminophosphate framework.

As published by Vomscheid et al. and Peltre et al.,[10,11] the adsorption of ammonia on silicoaluminophosphates is accompanied by a transformation of tetrahedrally coordinated framework Al atoms into octahedrally coordinated aluminum species. Recently, Mees et al. found that the stability of the silicoaluminophosphate H-SAPO-34 toward hydration and hydrothermal treatments can be strongly improved by an adsorption of ammonia.[12] This finding was evidenced by investigating steamed (at 383 K) H-SAPO-34 samples without and after former loading of ammonia. Although the preloaded samples showed no significant decrease of the IR band of bridging OH groups and of the characteristic X-ray reflections, the unloaded sample was strongly damaged. The authors explained this stabilization of the SAPO-34 framework by a reversible ammoniation of the Brønsted acidic bridging OH groups (SiOHAl). In the case of hydrated samples of ammonium- and sodium-exchanged silicoaluminophosphates, Parlitz et al. observed more-severe structural damage than in the case of nonexchanged materials.[8] This finding was explained by a shift in the $\equiv$P$-$O$-$Al$\equiv$ hydrolysis equilibrium, which was due to the presence of NH_4^+ or Na^+ cations.

In the present work, solid-state NMR spectroscopy has been applied to study the ammoniation and deammoniation of H-SAPO-34 and H-SAPO-37 and the hydration of the ammoniated silicoaluminophosphates for the first time under in situ conditions. These investigations were performed by an injection of nitrogen gas loaded with ammonia or water or of dry nitrogen gas into an MAS NMR rotor that was filled with H-SAPO-34 or H-SAPO-37. Via this technique, simultaneous in situ ^{1}H and ^{27}Al MAS NMR investigations of the hydroxyl groups and of the local structure of Al atoms in silicoaluminophosphates during ammoniation, deammoniation and subsequent hydration were performed. The purpose of this study was to clarify the sequence of ammoniation of the surface sites in silicoaluminophosphates and investigate the stabilizing effect of ammonia on the framework of silicoaluminophosphates.

Experimental Section

SAPO-34 was prepared according to a recipe for the synthesis of Ni-SAPO-34, but omitting the nickel salt.[13] SAPO-37 was synthesized according to de Saldarriaga et al.[14] As determined by atomic emission spectroscopy, coupled with inductively coupled plasma spectroscopy (AES$-$ICP), the as-synthesized silicoaluminophosphates SAPO-34 and SAPO-37 have molar $n_{Si}/(n_{Si} + n_{Al} + n_P)$ ratios of 0.11 and 0.14, which respectively correspond to 1.45 and 1.77 mmol of Si atoms per gram of

silicoaluminophosphate. To remove the template, the materials were heated with 1 K/min to 823 K in dry nitrogen and calcined at this temperature for 6 h in synthetic air (60 L/h). After this calcination, the obtained H-SAPO-34 and H-SAPO-37 were sealed in glass ampules. If mentioned, the samples were additionally dehydrated under vacuum at a temperature of 673 K for 12 h before the NMR experiments. In the latter case, the dehydrated powder material was filled into the MAS NMR rotor under dry nitrogen, using a glovebox.

Powder X-ray diffraction (XRD) patterns were obtained on a Siemens model D5000 diffractometer (Cu Kα radiation). ^{1}H and ^{27}Al MAS NMR measurements were performed on a Bruker model MSL 400 spectrometer at resonance frequencies of 400.13 and 104.26 MHz, respectively. The in situ MAS NMR investigations were performed by applying a Bruker MAS NMR probe (4 mm in diameter) that had been modified with a gas injection system, as described by Hunger et al.[15] During these experiments, a glass tube with an outer diameter of 1 mm was inserted into a 4-mm MAS NMR rotor via a hole in the rotor cap. Using a special tool, ca. 50 mg of the powder material under study was pressed to a hollow cylinder inside the MAS NMR rotor. The in situ CF MAS NMR measurements were conducted with a sample spinning rate of 10 kHz, single pulse π/2 and π/12 excitation, repetition times of 10 s and 500 ms, and 64 and 1200 accumulations for ^{1}H and ^{27}Al nuclei, respectively. During the in situ CF MAS NMR experiments, a flow of nitrogen ($\dot{V}(N_2)$ = 25 mL/min) mixed with a flow of ammonia (ammoniation) ($\dot{V}(NH_3)$ = 0.2 mL/min) or of dry nitrogen (deammoniation) was injected into the spinning MAS NMR rotor. The in situ hydration experiments were performed with a flow of nitrogen ($\dot{V}(N_2)$ = 25 mL/min) loaded with water (at a pressure of p_{H_2O} = 2.3 kPa). The concentration of OH groups in the dehydrated materials and of ammonia and water molecules on partially ammoniated and hydrated samples was determined by comparing the ^{1}H MAS NMR intensities with that of an external intensity standard (dehydrated zeolite Na,H$-$Y with an exchange degree of 35%). The total ^{27}Al MAS NMR intensities (I_{27Al}), given on the right-hand side of Figures 2$-$5, were determined by an integration of the entire spectral range after Fourier transformation in the absolute intensity mode. Dehydrated H-SAPO-34 and H-SAPO-37 materials were used as external intensity standards, with I_{27Al} = 1.00.

Results and Discussion

Crystallinity and Local Structure of Calcined, Ammoniated, and Partially Hydrated H-SAPO-34 and H-SAPO-37, Studied by X-ray Diffraction. The top portion of Figure 1 shows the XRD patterns of H-SAPO-34 and H-SAPO-37, recorded after calcination of the as-synthesized materials. According to our recent work,[9] there is no significant change of the XRD patterns as a result of the calcination of the as-synthesized materials. The aforementioned calcined materials correspond to those used in the present in situ CF MAS NMR experiments. After the calcined H-SAPO-34 and H-SAPO-37 are loaded with ca. 7 mmol of NH_3 per gram, a weak decrease and broadening of the reflections in the XRD pattern of SAPO-34 occurred, whereas the pattern of SAPO-37 is strongly changed (Figure 1, middle). Hence, the adsorption of ammonia on H-SAPO-34 has no influence on the crystallinity of this material, whereas the framework of SAPO-37 is significantly affected. In the bottom portion of Figure 1, the XRD patterns of the ammoniated SAPO-34 and SAPO-37 recorded after a hydration with ca. 3 mmol of H_2O per gram are shown. The XRD patterns of both samples show no changes, in comparison
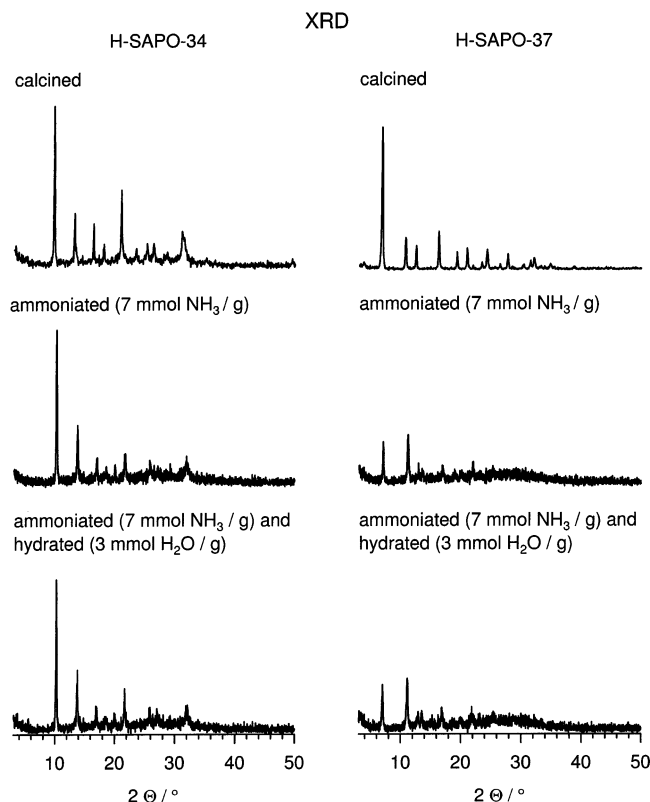
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Figure 1. X-ray patterns of calcined H-SAPO-34 (top, left) and H-SAPO-37 (top, right) after ammoniation with ca. 7 mmol of NH$_3$ per gram (middle) and an additional hydration with 3 mmol of water (H$_2$O) per gram (bottom).

Figure 2. ^{1}H (left) and ^{27}Al MAS NMR spectra (right) of H-SAPO-34 recorded during ammoniation of the dehydrated material in a flow of nitrogen gas loaded with ammonia: (a−c) adsorption of ammonia at Brønsted acidic bridging OH groups and (d, e) coordination of ammonia molecules to aluminum species. The values on the right-hand site give the relative ^{27}Al MAS NMR intensities (I_{27Al}), relative to the dehydrated sample (first line).

to the patterns shown in the middle portion of Figure 1. In agreement with Mees et al.,[12] this observation indicates that the ammoniation of SAPO-34 stabilizes the silicoaluminophosphate framework, which hinders hydrolysis upon hydration of the samples. In contrast, the framework of SAPO-37 is strongly affected already by the adsorption of ammonia. In the subsequent solid-state NMR investigations, similar treatments of SAPO-34 and SAPO-37 were performed to investigate the changes of the local framework structure that occurs upon ammoniation and hydration.

Ammoniation of H-SAPO-34 and H-SAPO-37. Detailed solid-state NMR spectroscopic investigations (see ref 9) of the calcined material indicated an intact local structure of the silicoaluminophosphates under study giving ^{31}P MAS NMR signals of P(4Al) species at −28 to −26 ppm and ^{27}Al MAS NMR signals of tetrahedrally coordinated Al atoms at 31 to 42 ppm with a weak high-field shoulder of pentacoordinated aluminum species at −13 to −11 ppm.[9] The ^{29}Si MAS NMR spectra of calcined H-SAPO-34 and H-SAPO-37 consist of single lines at −91 to −92 ppm that are due to Si(4Al) species.[9] By quantitative ^{1}H MAS NMR spectroscopy of the dehydrated samples, concentrations of bridging OH groups (SiOHAl groups at δ_{1H} = 3.7 to 4.7 ppm) of 1.5 mmol/g for H-SAPO-34 and 1.6 mmol/g for H-SAPO-37 were determined.[9] These values are evidence that all Si atoms are incorporated into the framework of H-SAPO-34 (1.45 mmol/g) and H-SAPO-37 (1.77 mmol/g) in an isolated manner, i.e., that each incorporated Si atom causes approximately one bridging OH group.

In Figure 2a, the ^{1}H and ^{27}Al MAS NMR spectra of dehydrated H-SAPO-34 recorded before the in situ ammoniation experiment began are shown. The ^{1}H MAS NMR signal that occurs at 3.6 ppm is due to bridging OH groups. A weak high-field shoulder at ca. 2 ppm indicates a small number of defect
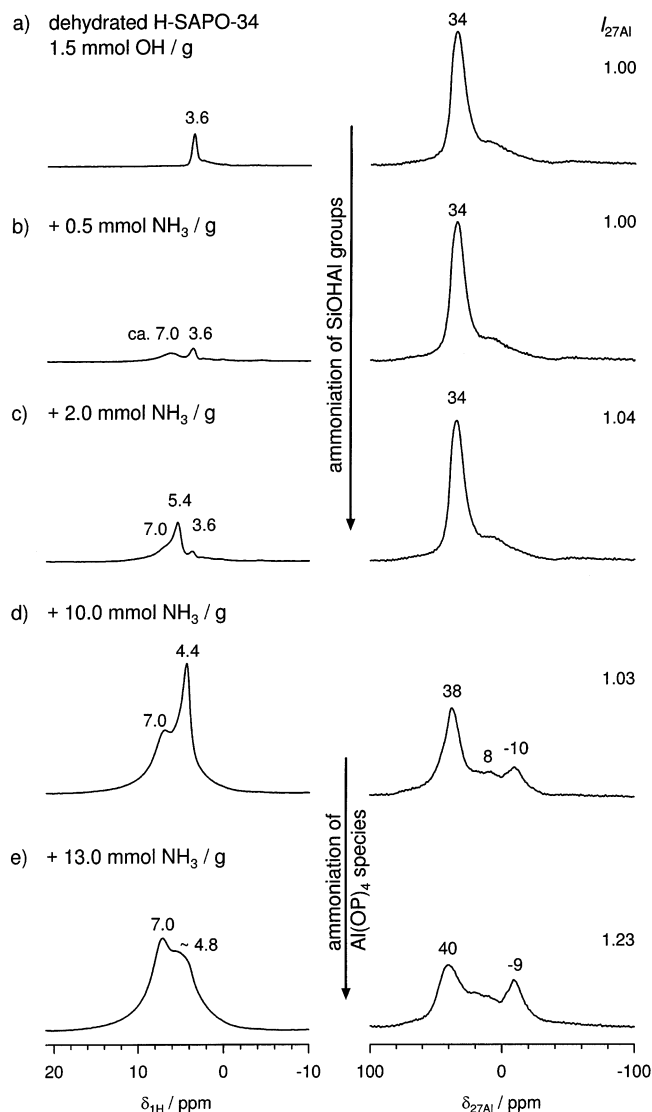
SiOH groups. The ^{27}Al MAS NMR spectrum is dominated by the signal of the tetrahedrally coordinated framework Al at 34 ppm, which is accompanied by a high-field shoulder of pentacoordinated aluminum species. After an adsorption of 0.5 mmol of NH$_3$ per gram (Figure 2b), a broad ^{1}H MAS NMR signal occurred at 7.0 ppm, indicating the formation of NH$_4^+$ ions at former bridging OH groups. A similar signal was observed for NH$_4^+$ ions in zeolite Y.[16,17] Simultaneously, the signal of the bridging OH groups at 3.6 ppm was significantly decreased. An adsorption of 2.0 mmol of NH$_3$ per gram caused a further decrease of the signal of the bridging OH groups at 3.6 ppm and the occurrence of a new signal at 5.4 ppm. The latter line can be explained by a rapid chemical exchange of NH$_4^+$ ions and weakly physisorbed or gaseous NH$_3$ molecules. According to the literature,[16,17] this signal indicates that more than one NH$_3$ molecule is adsorbed at one bridging OH group. Up to a coverage of ca. 2.0 mmol of NH$_3$ per gram of H-SAPO-34, no change was observed in the ^{27}Al MAS NMR spectra of the dehydrated H-SAPO-34 (see right-hand side of Figures 2b

and 2c). Hence, the loading of the NH_3 molecules on H-SAPO-34 starts with an adsorption exclusively at bridging OH groups, leading to the formation of NH_4^+ ions. This first adsorption step does not influence the local structure of framework Al atoms in the H-SAPO-34 under study.

After 10.0 mmol of NH_3 per gram of H-SAPO-34 had been adsorbed, a ^{27}Al MAS NMR signal appeared at -10 ppm (Figure 2d, right). This signal hints to a transformation of tetrahedrally coordinated framework Al atoms (38 ppm) into octahedrally coordinated Al species (-10 ppm), which is caused by a coordination of NH_3 molecules to these framework atoms. After a further increase in the number of NH_3 molecules adsorbed, the relative intensity of the signal of octahedrally coordinated Al species increased up to 35%, whereas the signal of tetrahedrally coordinated framework Al atoms decreased (Figure 2e, right). The increase of the total ^{27}Al MAS NMR intensity to a value of $I_{27Al} = 1.23$ indicates that this coordination change is accompanied by a decrease of the strength of quadrupolar interactions of the ^{27}Al nuclei that have a spin of $I = ^5/_2$. Until now, only a few solid-state NMR investigations of Al atoms in silicoaluminophosphates have been published.[18−22] Most of these works were performed on hydrated materials. Through ^{27}Al 3Q MAS NMR spectroscopy of the hydrated H-SAPO-34, Yan et al.[21] determined second-order quadrupolar effect (SOQE) parameters of 3.9 MHz for tetrahedrally coordinated framework Al atoms bound to four P atoms at *T*-sites and 8.2 MHz for tetrahedrally coordinated framework Al atoms bound to one Si and three P atoms at *T*-sites. However, in the dehydrated state of silicoaluminophosphates, it must be expected that the latter type of framework Al atoms is characterized by an SOQE value of ca. 16 MHz, as found for Al atoms in the local structure of Brønsted acidic bridging OH groups in dehydrated aluminosilicate-type zeolites.[22] On the other hand, octahedrally coordinated Al atoms are involved in weak quadrupolar interactions that correspond to SOQE values on the order of 1 MHz.[20] According to Massiot et al.,[23] a decrease of the quadrupolar interaction is accompanied by an increase of the NMR intensity that occurs in the central line of an MAS NMR signal and vice versa.

The ^1H MAS NMR spectrum of H-SAPO-34 recorded upon adsorption of 10.0 mmol of NH_3 per gram consists of a small signal at 7.0 ppm that is due to NH_4^+ ions and a signal at 4.4 ppm (Figure 2d, left). The resonance position of the narrow high-field signal at 4.4 ppm corresponds to a rapid exchange of ca. 0.8 mmol of NH_3 molecules ($\delta_{1H} = 0.8$ ppm)[16,17] and ca. 1.2 mmol of NH_4^+ ions ($\delta_{1H} = 7.0$ ppm) per gram. Assuming that each octahedrally coordinated Al atom that exists in the high-field ^{27}Al MAS NMR signal in the right-hand side of Figure 2d coordinates three NH_3 molecules, the residual NH_3 molecules are bound at the framework. These NH_3 molecules cause a broad ^1H MAS NMR signal in the background.

A further increase of the number of adsorbed NH_3 molecules (Figure 2e, left) causes a strong broadening of the high-field signal. This observation can be explained by a restriction of the mobility of the adsorbed NH_3 molecules, especially of those that are coordinated to Al atoms. In this case, the strong dipolar interactions between the H atoms of the coordinated NH_3 molecules cannot be averaged by an isotropic reorientation. Hence, the second step of the adsorption process of NH_3 on H-SAPO-34 consists of the coordination of NH_3 molecules to framework Al atoms in $\equiv P-O-Al\equiv$ bridges.

The ^1H MAS NMR spectrum of dehydrated H-SAPO-37 consists of two signals of bridging OH groups located in the supercages (3.6 ppm) and in the small sodalite cages (4.2 ppm)
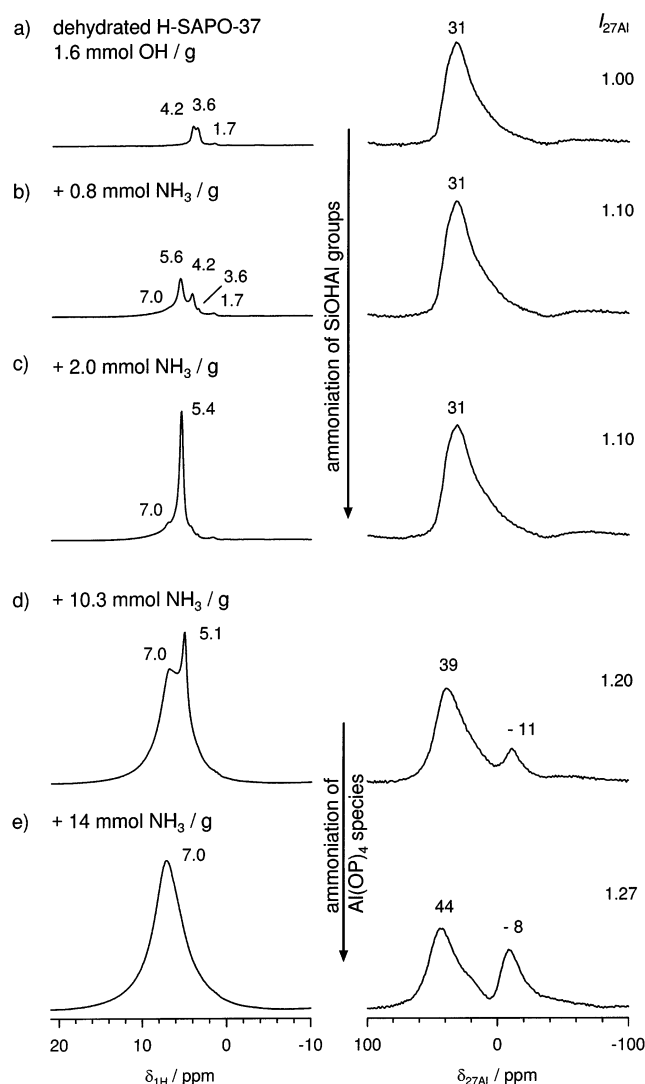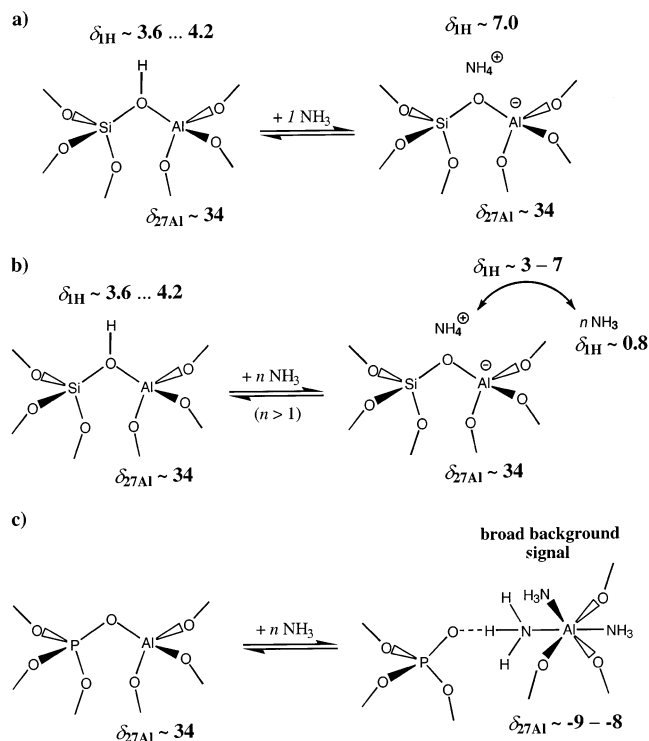

Figure 3. ^1H (left) and ^{27}Al MAS NMR spectra (right) of H-SAPO-37 recorded during ammoniation of the dehydrated material in a flow of nitrogen loaded with water: (a−c) adsorption of water at Brønsted acidic bridging OH groups and (d, e) coordination of ammonia molecules to Al species. Values on the right-hand side give the relative ^{27}Al MAS NMR intensities I_{27Al}, relative to the dehydrated sample (first line).

and a weak high-field signal (1.7 ppm), which are due to defect SiOH groups (Figure 3a, left).[3] The adsorption of 0.8 mmol of NH_3 per gram causes a significant decrease of the ^1H MAS NMR signal at 3.7 ppm and the occurrence of a strong signal at 5.6 ppm with a low-field shoulder at 7.0 ppm (Figure 3b, left). This finding indicates a preferred formation of NH_4^+ ions in the supercages. The signal at 5.6 ppm is due to NH_4^+ ions that are involved in a rapid exchange with gaseous NH_3 molecules (0.8 ppm),[16,17] whereas the low-field shoulder at 7.0 ppm suggests the presence of isolated NH_4^+ ions. After an adsorption of 2.0 mmol of NH_3 per gram of H-SAPO-37, almost all bridging OH groups are involved in the formation of NH_4^+ ions (Figure 3c, left). The weak signal of bridging OH groups located in the small sodalite cages indicates a hindered migration of NH_3 molecules into these structural units. As observed for dehydrated H-SAPO-34 (see Figure 2), during this first step of the ammoniation of dehydrated H-SAPO-37, no change of the local structure of Al atoms was observed by ^{27}Al MAS NMR spectroscopy (see the right-hand side of Figures 3b and 3c). The ^{27}Al MAS NMR spectra of the corresponding samples are

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SCHEME 1

Figure 4. ^1H (left) and ^{27}Al MAS NMR spectra (right) of (a,b) ammoniated H-SAPO-34 and (c, d) H-SAPO-37, recorded during purging with dry nitrogen at 295 and 413 K. The values on the right-hand side give the relative ^{27}Al MAS NMR intensities I_{27Al}, relative to the dehydrated H-SAPO-34 and H-SAPO-37 in Figures 2 and 3 (first line), respectively.

dominated by the signal from tetrahedrally coordinated framework Al atoms at 31 ppm, which have a broad high-field shoulder due to pentacoordinated aluminum species.

After the adsorption of a number of ammonia molecules that is significantly higher than the concentration of bridging OH groups in dehydrated H-SAPO-37, the ^{27}Al MAS NMR spectra shown on the right-hand side of Figure 3d and 3e indicate a coordination of NH_3 molecules at Al atoms. In these spectra, a signal of octahedrally coordinated Al species occurs at -11 ppm, with a relative intensity of up to 30%. As in the case of H-SAPO-34, this change of the aluminum coordination, from tetrahedrally to octahedrally coordinated species, is accompanied by an increase of the total ^{27}Al MAS NMR intensities, I_{27Al}, (right-hand side) which corresponds to a decrease of the quadrupolar interactions of the Al atoms involved. In the simultaneously recorded ^1H MAS NMR spectra, a strong broadening of the low-field signals occurred, indicating restricted mobility of the NH_3 molecules coordinated at an Al species.

The in situ ^1H and ^{27}Al CF MAS NMR studies of the ammoniation of dehydrated H-SAPO-34 and H-SAPO-37 have shown that this process can be separated in two subsequent steps. The first step consists of an ammoniation of Brønsted acidic bridging OH groups leading to the formation of NH_4^+ ions (Scheme 1a). During this ammoniation step, no framework Al atoms are affected by NH_3 molecules. If the number of adsorbed NH_3 molecules is slightly higher than the number of bridging OH groups, a rapid chemical exchange between the NH_4^+ ions formed at former bridging OH groups and gaseous ammonia molecules occurs (Scheme 1b). Further ammonia adsorption causes a coordination of NH_3 molecules to framework Al atoms in $\equiv P-O-Al\equiv$ bridges. This second ammoniation step is accompanied by a transformation of tetrahedrally coordinated framework Al atoms into octahedrally coordinated Al species, which could occur according to Scheme 1c, as proposed by Vomscheid et al.[10] The two-step ammoniation of the silicoaluminophosphates under study is similar to the two-step hydration process investigated in our recently published work.[9]
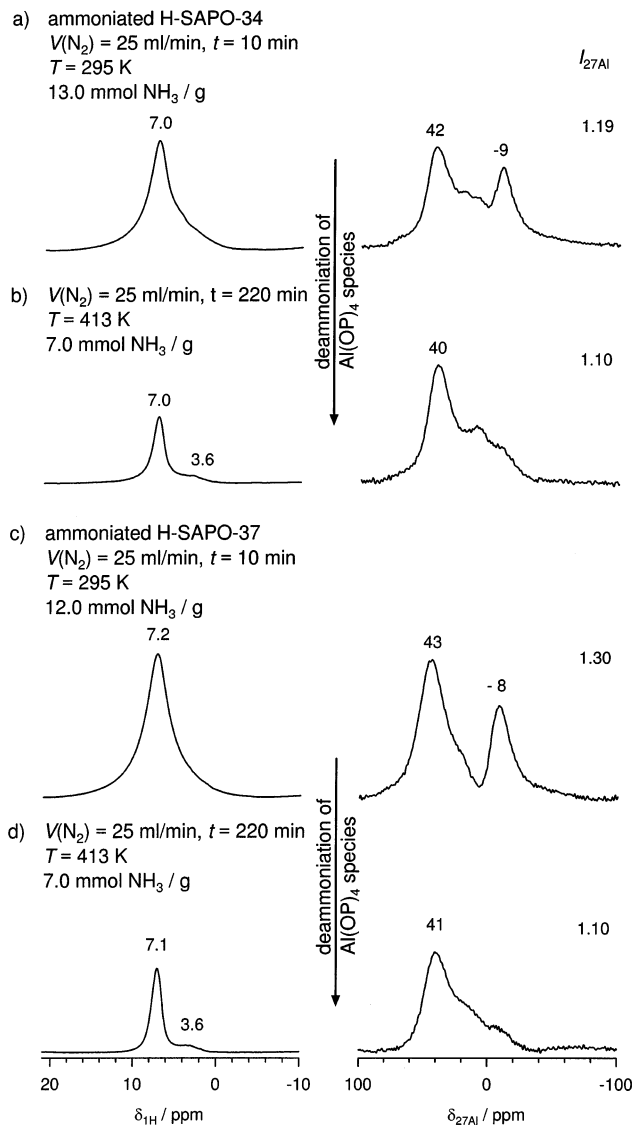
Also, the hydration of silicoaluminophosphates begins with an adsorption of water molecules at Brønsted acidic bridging OH groups before, in a second adsorption step, water molecules coordinate to Al atoms in $\equiv P-O-Al\equiv$ bridges.

Deammoniation of H-SAPO-34 and H-SAPO-37. To study the reversibility of the coordination change of Al atoms during the second ammoniation step, fully ammoniated silicoaluminophosphates were purged in a flow of dry nitrogen and investigated by in situ CF MAS NMR spectroscopy. Figure 4 shows the ^1H and ^{27}Al MAS NMR spectra of H-SAPO-34 (panels a and b) and H-SAPO-37 (panels c and d) recorded during purging at 295 (panels a and c) and 413 K (panels b and d). Purging at 295 K affects only the ^1H MAS NMR spectra of H-SAPO-34 and H-SAPO-37 (see left-hand side of Figures 4a and 4c). The weak decrease and narrowing of the signal at 7.0 ppm indicates that NH_3 molecules were desorbed. However, this ammonia desorption has no influence on the simultaneously recorded ^{27}Al MAS NMR spectra (right-hand side of Figures 4a and 4c). First, after increasing the temperature to 413 K, a significant decrease of the ^{27}Al MAS NMR signal of octahe-

drally coordinated aluminum species at −9 to −8 ppm occurs (see right-hand side of Figures 4b and 4d). The simultaneously recorded ^1H MAS NMR spectra of these samples are dominated by narrow signals of NH_4^+ ions at 7.0 ppm with a high-field shoulder at ca. 3.6 ppm that is due to a small number of bridging OH groups. Note that no signal from defect OH groups appeared at ca. 2 ppm, which indicates that the desorption of NH_3 molecules from the former octahedrally coordinated Al species is not accompanied by damage of ≡P−O−Al≡ bridges.[9]

The influence of the quadrupolar interactions of ^{27}Al nuclei on the ^{27}Al MAS NMR intensities of the experimentally observed signals hinders the decision of whether the deammoniation of silicoaluminophosphates conducted at 413 K leads to a fully reversible change of the aluminum coordination from an octahedral coordination to a tetrahedral coordination. In both cases of H-SAPO-34 and H-SAPO-37, the deammoniation performed at 413 K leads to a significant decrease of the total ^{27}Al MAS NMR intensities $I_{27_{Al}}$, given on the right-hand side of Figure 4. In both cases of H-SAPO-34 and H-SAPO-37, the desorption-induced disappearance of the ^{27}Al MAS NMR signal at −9 to −8 ppm is accompanied by a decrease of the total ^{27}Al MAS NMR intensity to a value which differs by 10% only from the values of the parent samples. Hence, most of the octahedrally coordinated Al species are transformed back to tetrahedrally coordinated Al atoms and not in extraframework species that are not visible in the ^{27}Al MAS NMR spectroscopy of dehydrated samples. This reversible coordination change occurs before the deammoniation of the Brønsted acidic bridging OH groups starts. This finding indicates that also the deammoniation of silicoaluminophosphates is a two-step process. In comparison with NH_3 molecules that have been chemisorbed at bridging OH groups, the NH_3 molecules coordinated to Al atoms of ≡P−O−Al≡ bridges are physisorbed only.

Hydration of H-SAPO-34 and H-SAPO-37 Loaded with Ammonia. Before the in situ hydration experiments were started, the silicoaluminophosphates under study were saturated with ammonia under flow conditions and subsequently purged with dry nitrogen at 413 K. The ^1H and ^{27}Al MAS NMR spectra of the resulting materials agree with those shown in Figures 4b and 4d. In these silicoaluminophosphates, all bridging OH groups are covered by at least one NH_3 molecule, leading to the formation of ammonium ions (NH_4-form), whereas only a very small number of octahedrally coordinated Al species occurred in the ^{27}Al MAS NMR spectra.

After the flow of nitrogen loaded with water began, a weak increase of the signals of octahedrally coordinated Al species was observed in the simultaneously recorded ^{27}Al MAS NMR spectra (right-hand side of Figures 5a and 5c). Interestingly, the resonance position of these signals (−12 ppm) shows a weak high-field shift, in comparison with those of octahedrally coordinated Al species formed upon the coordination of NH_3 to the Al species (−9 to −8 ppm). After a strong hydration of preammoniated (NH_4-form) silicoaluminophosphates, the ^{27}Al MAS NMR signals of octahedrally coordinated aluminum species attain relative intensities of 40% and 35% for H-SAPO-34 and H-SAPO-37, respectively (see right-hand side of Figures 5b and 5d).

The ^1H MAS NMR spectra of the weakly hydrated NH_4-form silicoaluminophosphates are dominated by a signal of NH_4^+ ions at 7.0 ppm, which is superposed by a broad background (see left-hand side of Figures 5a and 5c). This background signal indicates the presence of nonmobile water molecules that are probably bound to octahedrally coordinated Al species. After a strong hydration, a broad ^1H MAS NMR
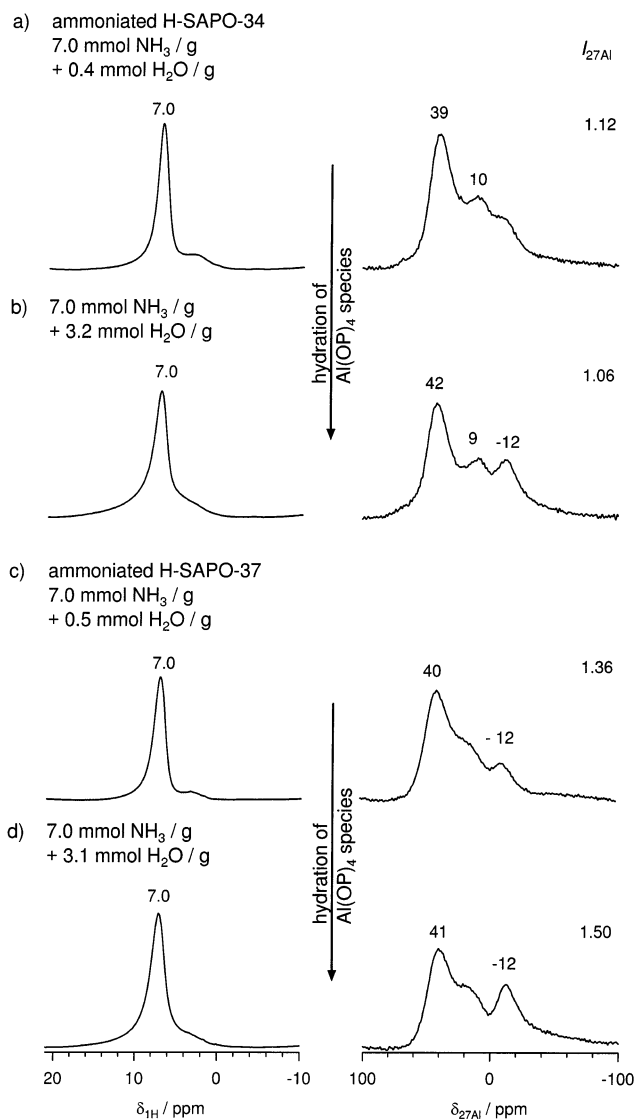

Figure 5. ^1H (left) and ^{27}Al MAS NMR spectra (right) of preammoniated (a, b) H-SAPO-34 and (c, d) H-SAPO-37, recorded during hydration in a flow of nitrogen loaded with water. Values on the right-hand side give the relative ^{27}Al MAS NMR intensities $I_{27_{Al}}$, relative to the dehydrated H-SAPO-34 and H-SAPO-37 in Figures 2 and 3 (first line), respectively.

signal appears at ca. 5.0 ppm, which is attributed to physisorbed water molecules.[24,25] The fact that, upon hydration, the ^1H MAS NMR spectra are dominated by signals of NH_4^+ ions (7.0 ppm) indicates a preferred coordination of water molecules to Al atoms in ≡P−O−Al≡ bridges. No water adsorption occurs at bridging OH groups, which can be explained by the higher base strength of NH_3 molecules, in comparison with that of water molecules.

As shown by the in situ MAS NMR spectroscopy, the formation of NH_4^+ ions at the former bridging OH groups does not hinder hydration of the aluminophosphate framework, which leads to a hydrolysis of ≡P−O−Al≡ bridges. However, if the Al atoms of the ≡P−O−Al≡ bridges are covered by NH_3 molecules, no hydrolysis of the aluminophosphate framework can occur. Therefore, as found by Mees et al.,[12] a strong preloading of NH_3 on silicoaluminophosphates hinders damage of the framework upon hydration and weak hydrothermal treatments at temperatures of <413 K. On the other hand, an ammoniation of bridging OH groups only, resulting in NH_4-form silicoaluminophosphates, leads to a preferred hydration

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of the $\equiv P-O-Al\equiv$ bridges and to a shift of the hydrolysis equilibrium, which cause preferred damage of the aluminophosphate framework.

Conclusions

The ammoniation, deammoniation, and hydration of the silicoaluminophosphates H-SAPO-34 and H-SAPO-37 were investigated simultaneously by ^{1}H and ^{27}Al MAS NMR spectroscopy and, for the first time, under in situ conditions. During the solid-state NMR measurements, the silicoaluminophosphates were purged by gaseous nitrogen loaded with ammonia and by dry nitrogen, respectively. Applying this experimental technique to study the successive ammoniation of dehydrated H-SAPO-34 and H-SAPO-37, a two-step ammonia adsorption was determined, starting with an ammoniation of Brønsted acidic bridging OH groups as the first step and a coordination of ammonia to framework Al atoms in $\equiv P-O-Al\equiv$ bridges as the second step. While the first adsorption step is a chemisorption of ammonia molecules on surface OH groups which has no influence on the local structure of framework Al atoms, the second ammoniation step is a weak physisorption that is accompanied by a transformation of tetrahedrally coordinated framework Al atoms to octahedrally coordinated Al species. By purging strongly ammoniated H-SAPO-34 and H-SAPO-37 with dry nitrogen at 413 K, it could be shown that the second ammoniation step is a reversible process.

In situ ^{1}H and ^{27}Al MAS NMR studies of the hydration behavior of NH$_4$-form silicoaluminophosphates indicate that this adsorption process leads to a preferred coordination of water molecules to framework Al atoms of $\equiv P-O-Al\equiv$ bridges. In strongly ammoniated silicoaluminophosphates, however, the Al atoms of $\equiv P-O-Al\equiv$ bridges are covered by NH$_3$ molecules which hinders an additional coordination of water molecules. Therefore, the ammoniation of $\equiv P-O-Al\equiv$ bridges may support the stabilization of silicoaluminophosphate frameworks by a preloading of ammonia as described by Mees et al. for H-SAPO-34.[12]

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