

Enhanced Resolution of Aluminum and Proton Sites in the Molecular Sieve SAPO-37 by ^{27}Al Multiple Quantum Magic Angle Spinning and ^1H Spin Echo Editing NMR

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The aluminum coordination state of the molecular sieve SAPO-37 has been studied by ^{27}Al multiple quantum (MQ) magic angle spinning (MAS) NMR spectroscopy. Although the 1D ^{27}Al MAS NMR spectra of the aluminum sites show complex patterns, the 2D 3Q MAS NMR spectra of SAPO-37 samples, submitted to different treatments, lead to the detection of four distinct framework Al species in the as-synthesized sample, i.e., (i) tetrahedral Al sites with four phosphorus atoms, (ii) tetrahedral Al sites with one (or more) Si as nearest neighbors interacting with tetrapropylammonium (TPA), and Al coordinated with (iii) tetramethylammonium (TMA) or (iv) water. Also, the Al environments with or without Si neighbors are distinguished for the first time in calcined, template-free H-SAPO-37. By use of ^1H spin echo editing MAS NMR experiments, a new proton signal at 3.4 ppm is observed in the calcined H-SAPO-37. By $^1\text{H}\{^{27}\text{Al}\}$ and $^1\text{H}\{^{31}\text{P}\}$ spin echo double-resonance experiments, this new signal is assigned to a kind of framework Al–OH hydroxyls caused by partially broken Al–O bonds. These aluminum defect sites originate either from the attack by a residual small amount of water, generated during the burning out of templates at high temperature in SAPO-37, or from the initial stage of the dehydroxylation process during the calcination.

Introduction

SAPO-37, an isotype of the faujasite structure contains aluminum, silicon, and phosphorus atoms as framework tetrahedral sites. Si atoms can be introduced into the AlPO lattice via the synthesis mechanism SM1 (replacement of one Al by one Si), the mechanism SM2 (replacement of one P by one Si), and SM3 (replacement of one P together with one adjacent Al by two Si atoms simultaneously) to form isolated Si and Si islands.¹ The synthesis mechanism SM1 has been proved impossible because no P–O–Si connections were found in the SAPO framework. It has been shown that in the synthesized SAPO-37, the tetrapropylammonium (TPA) template cations are located in the supercages while the tetramethylammonium (TMA) cations are occluded in the sodalite cages.² By their location in the sodalite cages the TMA cations especially contribute to the thermal stability of the crystal structure.³

Depending on the specific type of Si incorporation, the framework aluminum atoms in SAPO-37 display several kinds of structural orderings, i.e., Al with four P as nearest neighbors (pure AlPO phase), Al with one Si neighbor (pure SAPO phase), and Al with even more Si neighbors at the edge of Si island domains. It has even been postulated that a zeolitic Si(4Al) phase may exist.¹ Furthermore, templates exerting a charge balance toward the framework may also distort the tetrahedral Al sites, thus making the Al environment more complex.

1D ^{27}Al magic angle spinning (MAS) NMR spectroscopy has been used to investigate the coordination state of Al in SAPO molecular sieves.^{2,4} However, owing to the complex coordinated states of Al, it is difficult to distinguish the different Al species. On the other hand, transferred-echo double-resonance (TEDOR) NMR provides direct information on the ^{27}Al – ^{31}P and ^{27}Al –

^{29}Si connections. This method has been applied in the structure study of the molecular sieve SAPO-37,⁵ but the coordinating effect of the templates in the as-synthesized sample was not taken into account; therefore, the assignments of the ^{27}Al NMR signals still remain ambiguous.

It has been shown that the recently developed 2D multiple quantum (MQ) MAS NMR method^{6,7} is able to refocus the second-order quadrupolar broadening effect of half-integer quadrupolar nuclei. By selecting the multiple quantum coherence and transferring them into a detectable single quantum coherence over 2 time domains, one obtains isotropic resolution. This method has been demonstrated to be a powerful technique to elucidate the structure of several AlPO₄ and SAPO molecular sieves,^{8–10} aluminosilicates, and glasses.¹¹

The templates in SAPO-37 can be burnt out by calcination in a flow of oxygen at 873 K, forming H-SAPO-37. The ^1H MAS NMR study of SAPO-37 reported three lines at 1.6, 3.8, and 4.3 ± 0.1 ppm,¹² corresponding to IR bands at 3746, 3639, 3572 cm^{-1} , respectively. The last two lines were assigned to Brönsted hydroxyls in supercages and sodalite cages, respectively, the other one to silanol groups.

In this paper, the ^{27}Al MQ NMR method is used to enhance the resolution of the aluminum sites in the silicoaluminophosphate molecular sieve SAPO-37. The spin echo editing NMR method has been widely used in the study of aluminum¹³ and protons¹⁴ in zeolites. Here in this paper, an unexpected resolution enhancement has been obtained in the study of the hydroxyls in the H-SAPO-37 by ^1H spin echo editing NMR and $^1\text{H}\{^{27}\text{Al}\}$ spin echo double-resonance NMR methods.

Experimental Section

Sample Preparation. The SAPO-37 sample with the composition of $[\text{Si}_{21}\text{Al}_{97}\text{P}_{74}\text{O}_{384}]/\text{TMA}_8/\text{TPA}_{12}/64\text{H}_2\text{O}$ as determined

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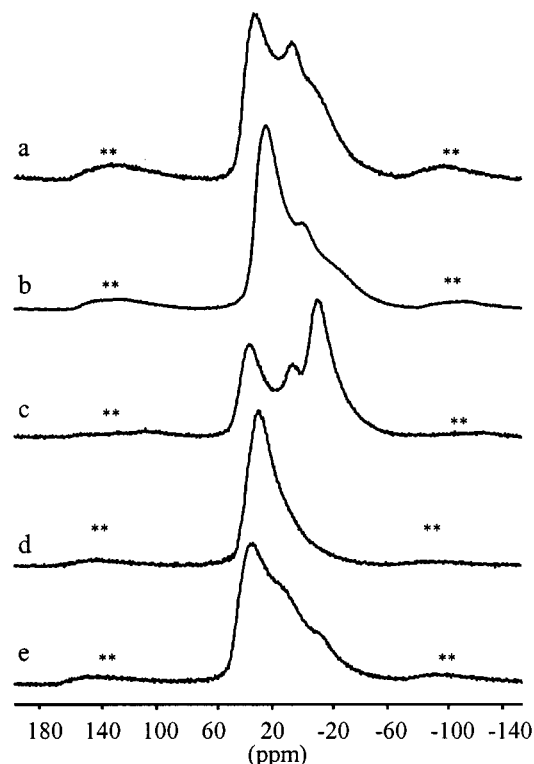


Figure 1. ^{27}Al MAS NMR spectra of SAPO-37: (a) as-synthesized; (b) dehydrated at 473 K; (c) TPA extracted by methanolic HCl and washed with water; (d) 873 K calcined; (e) after pyridine adsorption. Spinning sidebands are indicated by **.

by electron probe microanalysis and thermal analysis was synthesized according to the recipe described by Martens et al.¹ The XRD diffractogram demonstrates that the sample is highly crystalline (Figure 1S in Supporting Information). The ^{29}Si MAS NMR spectrum shows isolated Si (pure SAPO phase) as well as a small amount of Si islands in this sample (Figure 2S in Supporting Information).

The TPA-extracted sample was prepared according to ref 15, with a HCl–methanol solution, and washed with H_2O . The dehydrated sample was prepared by heating the powder in a quartz tube at 473 K for 10 h while evacuated at 10^{-2} Pa. The template-free sample was obtained by heating the as-synthesized sample at 873 K in a quartz tube in a flow of O_2 for 20 h, with a temperature increment of 1 K/min. Because H–SAPO-37 is very sensitive to water, after the thermal treatment the quartz tube was closed and the sample was transferred into a glovebox with dry N_2 where a 4 mm rotor was filled.

NMR Experiments. The ^{27}Al NMR experiments were performed on a Bruker MSL-400 spectrometer at 104.26 MHz, with a 4 mm ZrO_2 rotor spinning at 12.5 kHz. The 1D ^{27}Al MAS NMR measurements were performed with a pulse length of 0.6 μs corresponding to a $\pi/18$ pulse length and a recycle delay of 0.1 s. A two-pulse 3Q MAS method⁷ was employed with pulse lengths of 2.7 and 0.8 μs , a radio frequency field of ca. 120 kHz, and a 0.5 s recycle time; 512 points were acquired in the t_1 dimension with increments of 2 μs or 6 μs ; 480 scans were recorded per free induction decay (FID). Chemical shifts are referenced to an $\text{Al}(\text{NO}_3)_3$ solution, the F_1 dimension was referenced to the $3\nu_0$ frequency.

The ^1H NMR measurements were performed on a Bruker AMX-300 spectrometer at 300.13 MHz, with a spin rate of 10 kHz and a 10 s recycle delay. A Hahn echo sequence ($\pi/2 - \tau - \pi - \tau$) was used, with a $\pi/2$ pulse length of 3.5 μs . The echo delay was set to multiples of the rotor period. The spin

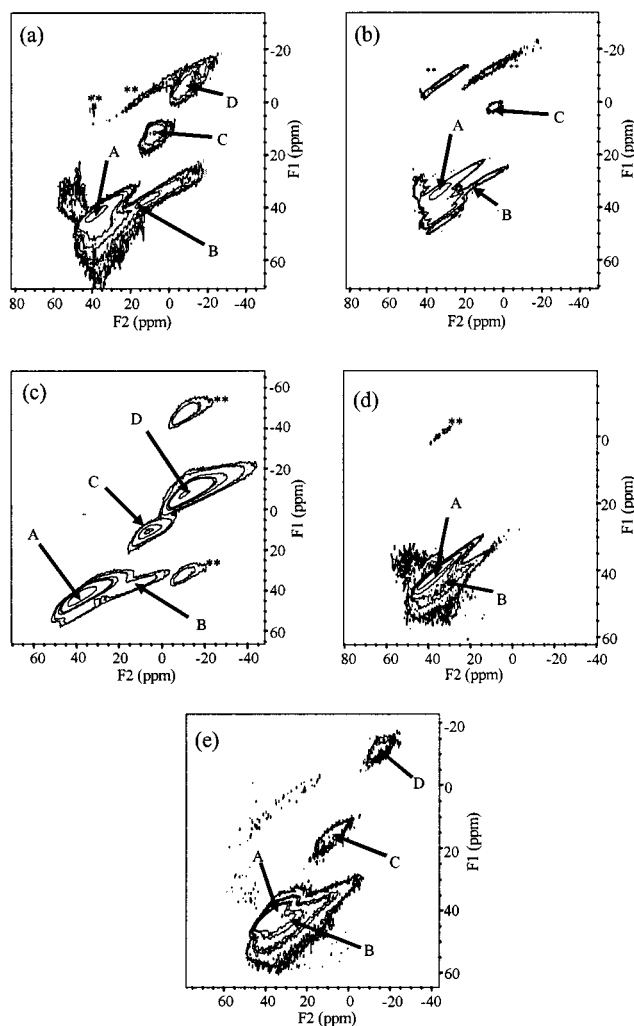


Figure 2. ^{27}Al 3QMAS NMR spectra of SAPO-37: (a) as-synthesized; (b) dehydrated at 473 K; (c) TPA extracted by methanolic HCl and washed with water; (d) 873 K calcined; (e) after pyridine adsorption. Spinning sidebands are indicated by **.

echo double-resonance experiments were performed according to Beck et al.¹⁶ The ^1H chemical shift was referenced to tetramethylsilane (TMS).

Results and Discussion

^{27}Al MAS NMR and ^{27}Al MQ MAS NMR. 1. As-Synthesized Sample. The ^{27}Al MAS NMR spectrum of the as-synthesized SAPO-37 sample, shown in Figure 1a, contains two peaks at 34 and 9 ppm, as well as a broad hump at around 0 ppm. The peak at 34 ppm has been assigned to tetrahedrally coordinated aluminum. By the TEDOR method, Fyfe et al. ascribed this peak to $\text{Al}(4\text{P})$ and $\text{Al}(4\text{Si})$ framework configurations.⁵ The 9 ppm peak was regarded by some authors as framework Al coordinated to TMA,³ while in contrast this line was assigned to octahedral extraframework Al.⁵ In the 1D spectrum of our sample, this 9 ppm peak was not as intense as that in Fyfe's sample,⁵ which contains more than 50 atom % aluminum, implying that some extraframework aluminum may exist. Although the peak of residual pseudoboehmite used in the synthesis can appear at this position in the spectrum,^{1,2} it does not necessarily mean that the signal at this position corresponds only to extraframework aluminum. Indeed it was verified that in the SAPO-37 sample after calcination at 673 K this 9 ppm peak would disappear, while the signal of pseudo-

TABLE 1: Chemical Shift and SOQE Parameters of the As-Synthesized Sample from the 2D MQ MAS Experiment

signal	δ_2 (ppm)	δ_1 (ppm)	δ_{iso} (ppm)	SOQE (MHz)
A	37.8	42.7	44.3	3.4
B	22.2	40.0	45.9	6.6
C	7.8	11.2	12.3	2.9
D	-5.8	-5.3	-5.1	1.1

boehmite remained after the same treatment.³ The broad hump around 0 ppm in the 1D ^{27}Al spectrum (Figure 1a) was overlooked by some authors because of the low magnetic field or low spinning rate used in their ^{27}Al MAS NMR measurements.^{2,17} This broad line was assigned by Fyfe et al.⁵ to framework Al with one, two, or three Si as nearest neighbors, possessing strong quadrupolar effects due to the asymmetric coordination of these Al sites, but the effect of templates was not taken into account in their study.

The 2D 3Q MAS spectrum of the as-synthesized SAPO-37 (Figure 2a) exhibits a more resolved pattern than the 1D MAS experiment. At least four species of Al could be distinguished, marked as A, B, C, and D. The isotropic chemical shift δ_{iso} as well as the second-order quadrupolar effect (SOQE) can be deduced from the position of the signals in the 2D 3Q spectrum by⁹

$$\delta_{\text{iso}} = \frac{4}{3}\delta_1 - \frac{1}{3}\delta_2 \quad (1)$$

$$\text{SOQE}^2 = C_q^2(1 + \eta/3) = (\delta_{\text{iso}} - \delta_2)\nu_0^2/6000 \quad (2)$$

with δ_1 and δ_2 being the centers of gravity of the signals in the F_1 and F_2 dimensions, respectively. C_q , the quadrupolar coupling constant, and η , the asymmetry parameter, cannot be determined independently. The different values are listed in Table 1. From the combined results of the 2D 3QMAS and the 1D MAS spectra of the as-synthesized sample, signal A (Figure 2a) can be assigned to a tetrahedral site. Taking into account the relative strong intensity of signal A and its SOQE value (Table 1), it is reasonable to assign this signal to the Al(4P) species.

Signal B, with a relatively low intensity, lies along the anisotropic axis and displays the strongest quadrupolar interaction of all the Al species in this sample. From the position of signal B and its SOQE value, this signal has to be attributed to tetrahedrally coordinated Al species with a quadrupolar effect stronger than the ones giving signal A (Table 1). It corresponds to the broad hump in the 1D spectrum, which has been proven to be caused by strong quadrupolar coupled Al species, as shown by ^{27}Al MAS NMR experiments at different magnetic fields.¹⁸ This signal B could correspond to Al sites with one Si as the nearest neighbor. There are also some Al sites with two or three Si as nearest neighbors because of the presence of silicon patches in our sample; the signals of these Al atoms with different Si neighbors cannot be distinguished in our experiments because of both their small quantity and the stronger quadrupolar effect of their asymmetric environments. It should be pointed out that in the fully calcined, template-free sample (see below), these kinds of Al-Si environments must also exist, but neither the 1D MAS nor the 2D 3QMAS spectra (Figures 1d and 2d) of the template-free sample display the broad hump as that of the synthesized sample. This implies that in the as-synthesized sample not only the Si neighbor(s) can distort the Al environment but the templates also play a role in the Al environments.

Signal C (Figure 2a) corresponds to the relatively sharp line at 9 ppm in the 1D spectrum (Figure 1a), and signal D (Figure

2a), detected in the 3Q experiment, could be masked by the broad hump signal in the 1D spectrum (Figure 1a). According to its chemical shift position, it is obvious that signal D corresponds to six-coordinated Al species, and it is reasonable to assign signal C by its position to five-coordinated Al species.

In the 2D 3Q spectrum of the sample dehydrated at 473 K (Figure 2b), all the signals remain except signal D. The 1D ^{27}Al spectrum of the dehydrated sample (Figure 1b) also indicates an increase of the tetrahedral site intensity, leading to a less pronounced 9 ppm peak. This means that, owing to the dehydration, some six-coordinated Al species change back to a tetrahedral coordination. So signal D can be assigned to framework Al coordinated with two water molecules, to be six-coordinated. The quantity of this D species should be small because in the as-synthesized sample there is hardly any space left for water in the cages containing the templates. On the other hand, the quadrupolar-broadened hump still remains in the 1D spectrum of the dehydrated sample.

2. TPA-Extracted Sample. Most of the TPA molecules occluded in the supercages can be extracted by a methanol-HCl treatment while the TMA molecules in the sodalite cages remain intact.¹³ In the 1D ^{27}Al MAS NMR spectrum of this sample (Figure 1c) the 9 ppm peak is still present after the treatment. Also in the 2D spectrum (Figure 2c) the signal C remains. If this peak were caused by extraframework Al, it would not have been present because extraction of the extraframework Al by this treatment is expected. In contrast, the broad hump around 0 ppm disappears in the 1D spectrum and is replaced by a six-coordinated Al line at -10 ppm, owing to a water/methanol-Al coordination in supercages when the TPA molecules are extracted. In the 2D 3Q spectrum of the TPA extracted sample (Figure 2c), the former strong quadrupolar-coupled signal B in Figure 2a is now replaced by a different tetrahedral signal B close to signal A, indicating a smaller quadrupolar coupling constant than that of signal B in Figure 2a. This implies that the Al species corresponding to signal B in Figure 2a of the as-synthesized sample are strongly distorted by the interaction with the charge-compensating TPA^+ template ion. By their position in the 2D MQ spectrum, they remain tetrahedrally coordinated.

3. 873 K Calcined, Template-Free Sample. When the sample is calcined at 873 K in oxygen for 20 h, all the templates are removed; thus, the influence of templates on the Al environment will not be considered. The 1D spectrum of this sample shows an asymmetric quadrupolar-broadened peak (Figure 1d); no broad hump signal is present anymore. If, as stated by Fyfe et al.,⁵ the broad hump in the 1D ^{27}Al spectrum of the as-synthesized sample (Figure 1a) was *only* caused by Al with Si neighbors, it should have remained in the spectrum of the template-free sample. But it is not the case here. From a quantification study of the 1D ^{27}Al NMR spectra, no intensity loss was found after the 873 K calcination compared with the as-synthesized sample, which means that the absence of the broad hump in the ^{27}Al spectrum (Figure 1d) must correlate with the loss of the templates by the calcination.

The resolution of aluminum sites is increased by the 2D 3Q MAS method. In Figure 2d, two signals are left, corresponding to two kinds of tetrahedral Al sites (signals A and B), and should be assigned to Al(4P) and Al(3P,1Si; 2P,2Si; and 1P,3Si) environments, respectively. Owing to the calcination, the template ions are extracted and Brønsted acid sites emerge, causing a reduction of the distortion of the tetrahedral Al sites with Si neighbor(s). This can be seen from signal B in the 2D 3Q spectra of the fully calcined sample (Figure 2d), showing a

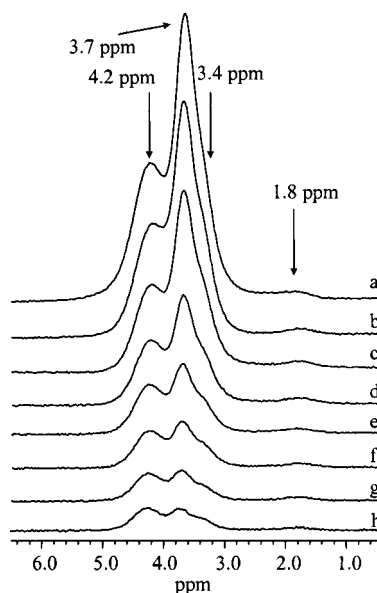


Figure 3. ^1H MAS spin echo NMR of H-SAPO-37, with a τ delay of (a) 100 μs , (b) 2 ms, (c) 5 ms, (d) 10 ms, (e) 15 ms, (f) 20 ms, (g) 25 ms, and (h) 30 ms.

reduced quadrupolar coupling constant, compared to signal B of the synthesized sample (Figure 2a).

4. Pyridine-Adsorbed Sample. It is clearly indicated by the 2D 3Q MAS spectrum that five- and six-coordinated Al exist in the pyridine-adsorbed sample (Figure 2e, signals C and D), providing direct evidence to the statement of Derewinski et al.⁴ that pyridine coordinates with framework Al sites to form different coordinated species. It should be noted that the pyridine may act like the templates TMA and TPA, coordinating with Al, to form the five- and six-coordinated Al.

^1H Spin Echo NMR and ^1H Spin Echo Double-Resonance NMR. The ^1H spin echo spectra of a calcined SAPO-37 sample (at 873 K for 20 h in oxygen) with different τ delays are shown in Figure 3. Three signals can be distinguished, in agreement with the results of the IR and NMR study,¹² i.e., a 1.8 ppm silanol band, a 3.7 ppm signal, and a 4.2 ppm signal attributed to Brönsted acid hydroxyls pointing into the supercages and sodalite cages. With the increment of the delay time τ , an unexpected new signal gradually develops at around 3.4 ppm and is well separated when the τ delay is 5 ms or longer. Though the spin echo method can refocus the inhomogeneity of the magnetic field and thus narrow the line width, to our knowledge, it is the first report on this new proton signal resolved in molecular sieves by this method. It is clear from the spin echo experiments that the spin-spin relaxation behavior of the 3.4 ppm signal is different from that of the 3.7 ppm signal; thus, it can be distinguished as a shoulder from the 3.7 ppm peak by the method.

In the ^1H NMR study of SAPO-17,¹² a signal at 3.3 ppm appeared, which was assigned to hydroxyls attached to phosphorus (POH). To check whether this 3.4 ppm peak in SAPO-37 is due to the POH species, a $^1\text{H}\{^{31}\text{P}\}$ spin echo double-resonance experiment was performed (data not shown here). The spectrum with a ^{31}P channel double resonance displays no difference compared with that without double resonance, so the 3.4 ppm line could not be suppressed by this $^1\text{H}\{^{31}\text{P}\}$ double resonance, implying this signal is not related to POH groups.

$^1\text{H}\{^{27}\text{Al}\}$ double-resonance experiments (Figure 4) are also performed to test whether the proton line at 3.4 ppm is linked to aluminum. At relatively strong ^{27}Al radio frequency power

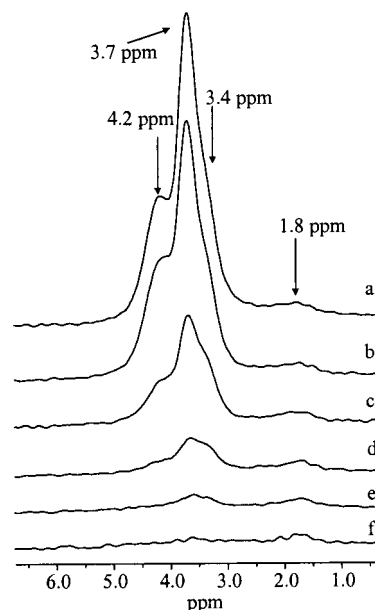


Figure 4. $^1\text{H}\{^{27}\text{Al}\}$ spin echo double-resonance NMR of H-SAPO-37, with a τ delay of 2 ms: (a) no irradiation; (b) with irradiation radio frequency strength on ^{27}Al channel of 10 kHz, (c) 15 kHz, (d) 20 kHz, (e) 30 kHz, and (f) 40 kHz.

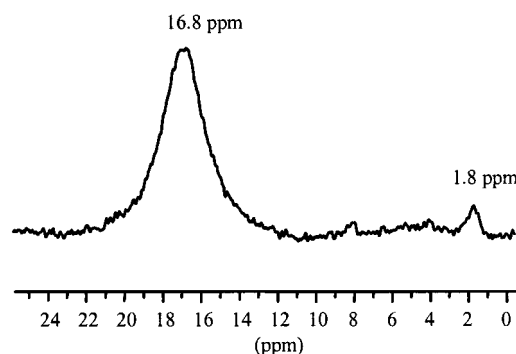


Figure 5. ^1H MAS NMR spectrum of H-SAPO-37 adsorbed with perdeuterated pyridine.

(Figure 4f) all signals except that of the silanol band disappear, indicating that the protons of the 3.4 ppm signal act similarly with the Brönsted acid hydroxyls and thus are linked to Al atoms.

Perdeuterated pyridine is often used as probe molecules to characterize the acid strength of OH groups in molecular sieves. The acidic protons will transfer to the probe molecules, forming the pyridinium ions, which gives lines at chemical shifts in the range 15.5–19.5 ppm; at the same time, the signals of the acidic hydroxyls involved in the proton-transfer disappear.¹⁹ To test whether the 3.4 ppm signal protons act like the acidic hydroxyls of the SAPO-37, perdeuterated pyridine was adsorbed on the calcined SAPO-37 sample. The ^1H spectrum of this sample is shown in Figure 5. A peak at 16.8 ppm emerges and is assigned to the proton signal of pyridinium ions; the 1.8 ppm protons correspond to the silanol groups that survived after the pyridine adsorption because of their weak acidity. All the other signals disappear, giving evidence that the 3.4 ppm protons act like the Brönsted acidic sites.

From a neutron diffraction study of SAPO-37,²⁰ three Brönsted hydroxyls sites were identified, i.e., H-1 in the plane of the 12-ring window, H-2 in the six-ring window and slightly protruding into the supercage, and H-3 in the plane of the six-ring window between the β -cage and the double-six-ring. In our ^1H NMR spectrum (Figure 3), H-1 may correspond to the

3.7 ppm signal of the protons in the supercages while H-3 corresponds to the 4.2 ppm signal of the protons in the sodalite cages. If this newly found 3.4 ppm proton signal were due to H-2, by its possible hydrogen bond with the framework oxygen, its chemical shift should have appeared at a position between H-1 and H-3, i.e., between 3.7 and 4.2 ppm; but this is not the case here. So the possibility that the 3.4 ppm signal is due to the H-2 Brönsted acidic protons can be excluded.

Extraframework Al—OH at around 2.7 ppm can be observed in a 1173 K calcined SAPO-37 sample (data not shown here). For the SAPO-37 calcined at only 873 K, no dealumination occurs, so the 3.4 ppm ^1H signal cannot be assigned to extraframework Al—OH groups.

It should also be noted that, in Figure 4, the radio frequency strength of ^{27}Al irradiation was used as the editing parameter, as an alternative of the spin echo editing method. High resolution is also obtained here because of the difference in the Al—proton dipolar interaction of the different sites. In Figure 4a, without double resonance, the 3.4 ppm signal is only an unobvious shoulder, while in Figure 4b–d, this shoulder becomes more and more pronounced. In the double-resonance experiments, the greater the dipolar coupling between the spins, the greater the dephasing effect.²¹ When the double-resonance spectra subjected to different strengths of ^{27}Al irradiation are compared, it could be concluded that though the 3.4 ppm hydroxyls act like the Brönsted acidic protons at 4.2 and 3.7 ppm (a perdeuterated pyridine adsorption experiment supports this behavior), they possess weaker dipolar interaction with Al than the 3.7 ppm Brönsted acidic protons; i.e., they are less related to aluminum than the Brönsted acidic hydroxyls are.

In our recent work on zeolite HY,²² a similar 3.1 ppm ^1H signal was also identified by the spin echo editing NMR and was assigned to a kind of framework Al—OH. These framework Al—OH species are formed as a result of the partial hydrolysis of framework Al—O bonds during the hydration process of the calcined zeolite HY at low temperature (400 °C). Here, the treatment of the SAPO-37 is somewhat different. To get rid of the templates, a calcination at 873 K is needed. During the process of the calcination, two factors should be taken into account on the modification of the SAPO-37 framework. One is the effect of water produced by burning the templates, and the second is the effect of dehydroxylation. As it has been reported in zeolite ZSM-5,²³ the small amount of water, generated during the burning of the template deposits in oxygen, may cause partial hydrolysis of the Al—O bonds. Similarly, although no extra hydration took place during our sample treatment, some residual water is generated during the calcination of the templates of SAPO-37 in oxygen. Because the H—SAPO-37 framework is very sensitive to water, this residue water may cause some partial hydrolysis of the Al—O bonds at high temperature (873 K) and thus be responsible for the formation of 3.4 ppm proton species. On the other hand, dehydroxylation may take place when the sample is calcined at 873 K, although aluminum was considered thermally stable at this temperature. During the process of the dehydroxylation, some bridging hydroxyls may stay at an initial stage, i.e., the hydroxyls are not totally detached from the framework, while at the same time, the Al—O bond may become partially broken.

Here, by our experiments on SAPO-37, the newly found 3.4 ppm proton line may give evidence of the existence of the Al—OH species, caused by partially broken Al—O bonds, acting still as the Brönsted acid sites but with different spin—spin relaxation time $T_{2\text{H}}$, chemical shift, and lower ^{27}Al double-

resonance dephasing efficiency compared with those of the Brönsted acid protons.

It is also interesting to note that in zeolite HY, this kind of Al—OH is at 3.1 ppm, while in the isotype SAPO-37, its chemical shift is at 3.4 ppm. This means that the chemical shift of the species of protons is related to the chemical composition of the framework, implying that they reside in the framework. The newly found proton signal can be due to the formation of framework defects during the initial stage of dehydroxylation and/or dealumination.

Conclusion

The silicoaluminophosphate molecular sieve SAPO-37 exhibits a complex interaction and coordination with adsorbed water and occluded templates. The ^{27}Al 2D MQ MAS technique enhances the resolution of Al sites of the SAPO-37 and made it possible to study these complex host—guest interactions. Four different Al species in the as-synthesized sample were identified, i.e., tetrahedral Al sites with 4P, tetrahedral Al sites with one (or more) Si as nearest neighbors interacting with TPA, and framework Al coordinated with TMA or water. The Al with or without Si as neighbors in the template-free sample is distinguished for the first time by the MQ MAS method, providing another useful technique to detect framework changes in SAPO-37 after high-temperature calcination. By use of ^1H spin echo editing MAS NMR experiments, a new proton signal at 3.4 ppm is observed in the calcined H—SAPO-37. By $^1\text{H}\{^{27}\text{Al}\}$ and $^1\text{H}\{^{31}\text{P}\}$ spin echo double-resonance experiments, this new signal is assigned to a kind of framework Al related hydroxyls caused by Al—O bond rupture. These aluminum defect sites originate either from the attack by a residual small amount of water, generated during the burning out of templates at high temperature in SAPO-37, or from the initial stage of the dehydroxylation process during calcination. These combined ^1H NMR techniques are expected to give more information on different proton species in other molecular sieves.

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Supporting Information Available: One figure showing the XRD pattern of SAPO-37 and another figure showing the ^{29}Si MAS NMR spectrum of SAPO-37. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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