Multinuclear *MAS* n.m.r. and i.r. spectroscopic study of silicon incorporation into SAPO-5, SAPO-31, and SAPO-34 molecular sieves

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^{27}Al, ^{31}P, ^{29}Si, and ^{1}H *MAS* n.m.r. as well as diffuse reflectance i.r. spectroscopy were used to investigate the isomorphous substitution of silicon into the framework of aluminophosphate molecular sieves with different pore sizes. ^{29}Si *MAS* n.m.r. was found to be the only direct method to study this type of silicon incorporation. In all SAPOs investigated, the incorporation of silicon generates two different kinds of Brönsted acidic sites irrespective of the number of nonequivalent T sites in the framework. The results of both the i.r. spectroscopy and the ^{1}H *MAS* n.m.r. spectroscopy in the presence of sorbed molecules corroborate the commonly accepted assignment of these two different species to undisturbed hydroxyls and hydroxyls interacting with further framework oxygen, respectively.

Keywords: SAPO-5; SAPO-31; SAPO-34; silicon incorporation into aluminophosphates; *MAS* n.m.r. spectroscopy; diffuse reflectance *FT*i.r. spectroscopy; Brönsted acidic sites; interaction with sorbed molecules

INTRODUCTION

Crystalline silicoaluminophosphates (SAPO-*n*)[1] are a new family of microporous solids with a considerable potential as molecular sieves, ion exchangers, and catalysts. The catalytic properties are strongly related to the nature and amount of acidic sites in the framework. The Brönsted acidity of silicoaluminophosphates is attributed to a silicon incorporation into a hypothetical phosphorus T site of the aluminophosphate framework. A second possible mechanism involves the pairwise substitution of two Si atoms for one Al and one P, but also in this case, a certain amount of Si incorporation according to the first mechanism is necessary to avoid Si–O–P bonds.[2] The type of substitution as well as the nature of the generated acidic sites can be studied by different spectroscopic methods.[3–6]

MAS n.m.r. as well as i.r. spectroscopy yield valuable information on the structural environment of these acidic sites. The chemical shift of about −92 ppm obtained for the dominant line in the ^{29}Si n.m.r. spectra of most of the silicoaluminophosphates indicates that the silicon atoms are bonded via oxygen to four aluminum atoms.[7,8] A sometimes observed second line with maximum at about −110 ppm is attributed to silicon bonded via oxygen to four silicon atoms, i.e., pure silica building units located inside or outside the aluminophosphate framework.[9,10]

The nature and quantity of hydroxyls generated by the silicon incorporation can be studied by i.r. and ^{1}H *MAS* n.m.r. spectroscopy. Most of the i.r. studies investigating the hydroxyls in aluminophosphate-based molecular sieves were carried out on SAPO-5. Two bands at 3625 and 3520 cm^{-1}, [3,4,6,9,11] and sometimes an additional band at 3618 cm^{-1}, [3] were observed due to SiOHAl groups produced by substitution of silicon for phosphorus in the $AlPO_4$-5 framework. Bands at 3680 and 3800 cm^{-1} were assigned to POH and AlOH groups on the external surface.[4] In the case of SAPO-34, Flanigen et al.[2] attributed bands at 3626 and 3605 cm^{-1} to the silicon incorporation.

Since the extinction coefficient of the hydroxyl groups in the SAPO-type molecular sieves is unknown, i.r. spectroscopy suffers from the problem of obtaining reliable quantitative data on the number of different hydroxyls. This problem can be solved by the application of magic angle spinning proton n.m.r. (^{1}H *MAS* n.m.r.). Like the wavenumber in i.r. spectroscopy, the chemical shift of the hydroxyl protons

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Received 14 January 1991; accepted 24 June 1991

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Table 1 Synthesis procedures and chemical composition of the samples

Sample	Structure type[a]	Template	Reference	Pore size[b] (nm)	Chemical composition after calcination Si : Al : P
SAPO-5	AFI	Triethylamine	14	0.8	0.036 : 0.506 : 0.458
SAPO-31	–	di-*n*-Propylamine	15	0.65	0.081 : 0.518 : 0.401
SAPO-34	CHA	Tetraethylammonium-hydroxid/di-*n*-propylamine	16	0.43	0.114 : 0.500 : 0.386

[a] See Ref. 17
[b] Taken from Ref. 18

can also be used to distinguish between hydroxyls of different strength of acidity.[12] As shown for zeolites, both methods complement one another.[13]

The goal of the present paper is to show the advantages and disadvantages of three spectroscopic methods, ^{29}Si *MAS* n.m.r., ^{1}H *MAS* n.m.r. and i.r. spectroscopy, concerning the investigation of isomorphous substitution of silicon into an aluminophosphate framework and the Brönsted acidic sites generated by this substitution. For this purpose, three different silicoaluminophosphate molecular sieves with quite different framework structures and pore sizes were chosen. It is an advantage of our paper that the different spectroscopic methods were applied to identical silicoaluminophosphate samples.

EXPERIMENTAL

Samples

The molecular sieves investigated were synthesized according to the procedures cited in *Table 1*. The different structure types were checked by XRD. No crystalline byproducts were detected. The adsorption properties were tested by sorption of *n*-hexane (SAPO-5 and SAPO-31) and of methanol (SAPO-34).

Measurements

The ^{27}Al, ^{29}Si, and ^{31}P *MAS* n.m.r. spectra were recorded on a Bruker MSL 400 spectrometer. The experimental conditions for the measurements are summarized in *Table 2*. All spectra shown in this paper were obtained by single-pulse excitation for the calcined and dehydrated samples. In the case of ^{29}Si and ^{31}P *MAS* n.m.r., high-power proton decoupling was applied. The chemical shifts reported for ^{27}Al are not corrected for second-order quadrupole effects.

^{1}H *MAS* n.m.r. spectra were measured at room temperature using a Bruker MSL 300 spectrometer and homemade magic-angle-spinning equipment that allows for spin sealed glass ampules.[19] The total concentration of OH groups in the activated samples was determined by comparing the line intensity with that of a standard. The samples were pretreated in a glass tube of 5.5 mm inner diameter and with 10 mm bed-depth. Starting at room temperature, the samples were heated under vacuum with a rate of 10 K/h. After keeping them for 2 h at 670 K, the molecular sieves were evacuated up to a pressure below 0.01 Pa for 20 h and sealed off. Before sealing, a part of the samples was loaded at room temperature with pyridine, ammonia, and cyclohexane. The molecular sieves were exposed to defined amounts of sorbate corresponding to about 0.8 molecules per bridging hydroxyl in the case of pyridine and cyclohexane and to about 0.8 and 3.0 molecules per bridging hydroxyl in the case of ammonia. With cyclohexane, the samples were tempered for 1 h at 320 K and subsequently evacuated a second time for 2 h at the same temperature.

For the DRIFT (diffuse reflectance infrared fourier transform) spectroscopic investigations of OH groups, the samples were activated under vacuum in a special cell with a heating rate of about 2–5 K/min. After maintaining the samples for 4 h at 720 K under a pressure of less than 0.1 Pa, they were cooled to room temperature. The DRIFT measurements were performed with a Fourier spectrometer IRF 180 (Zentrum für wissenschaftlichen Gerätebau, Berlin) with a resolution of 4 cm^{-1}. A rough copper surface was employed as the standard.

RESULTS AND DISCUSSION

^{27}Al and ^{31}P *MAS* n.m.r.

The ^{27}Al and ^{31}P *MAS* n.m.r. spectra of the three silicoaluminophosphates studied in this paper are given in *Figure 1*. Except for small differences in the exact line position (cf. *Table 3*), the spectra are quite similar. In all cases we observe only one line, confirming the strict alternative of P and Al at T positions of

Table 2 Experimental conditions for *MAS* n.m.r. measurements

Nucleus	Resonance frequency (MHz)	Pulse duration (μs)	Flip angle	Repetition time (s)	*MAS* frequency (kHz)	No. scans	Reference (external)
^{29}Si	79.5	2.5	π/4	5.0	4.2	> 2000	TMS
^{27}Al	104.2	0.6	π/12	0.5	5.1	800	$Al(H_2O)_6^{3+}$
^{31}P	161.9	3.0	π/2	15.0	4.8	64	H_3PO_4, 85 wt%
^{1}H	300.0	4.0	π/2	10.0	2.5	400	TMS

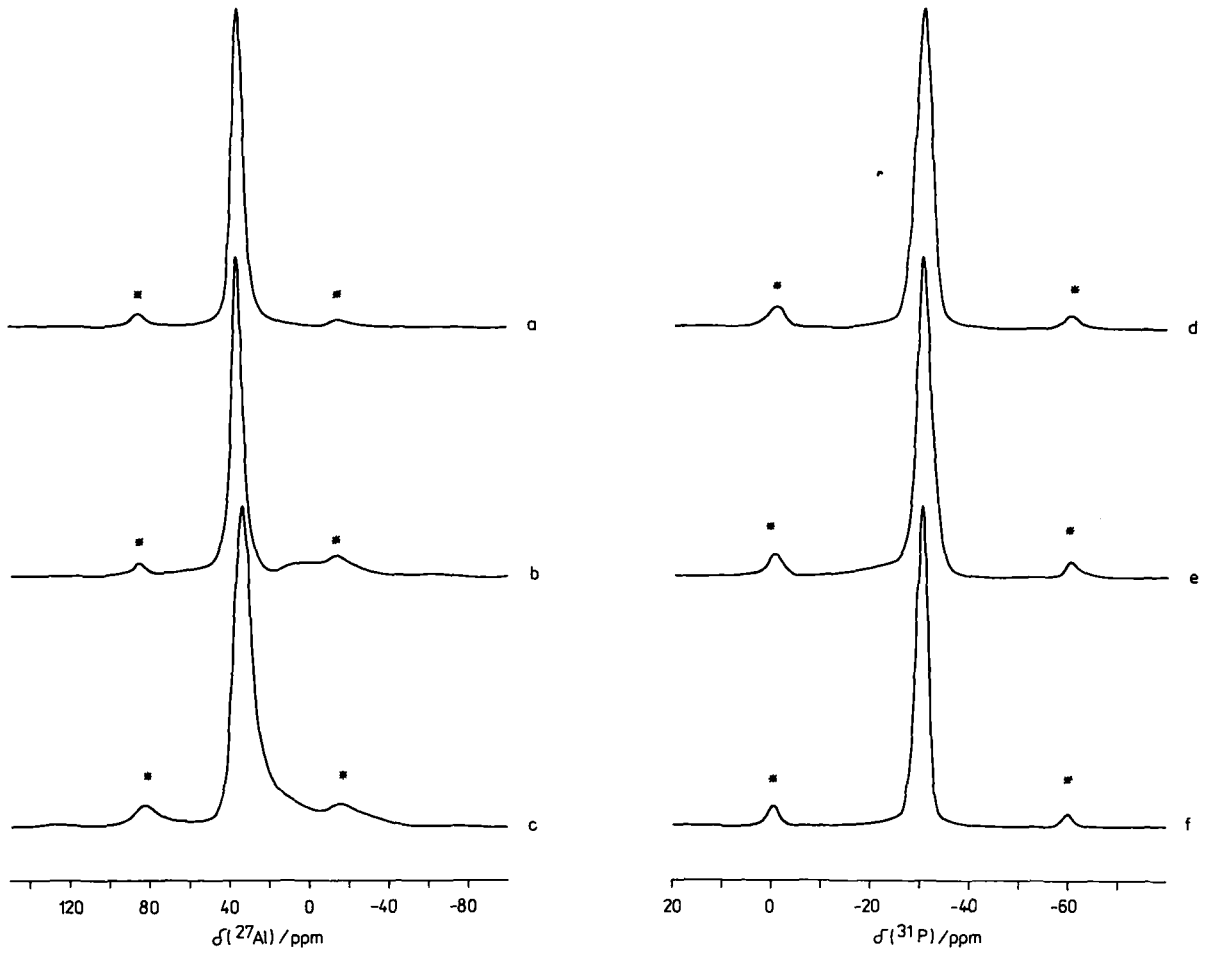

Figure 1 ^{27}Al (left) and ^{31}P *MAS* n.m.r. spectra (right) of calcined and dehydrated SAPO-5 (a,d), SAPO-31 (b,e), and SAPO-34 (c,f). Spinning sidebands are denoted by asterisks

the aluminophosphate framework.[20] Furthermore, for SAPO-5 and SAPO-34, this finding corresponds to the XRD results, indicating that only one crystallographic type of T position is present in the framework.[17] It was shown both for hydrated (SAPO-35,[8] $AlPO_4$-21,[8] VPI-5[21]) and for dehydrated samples ($AlPO_4$-14[22]) that lines caused by nonequivalent T atoms can be resolved. In contrast to these findings, the lines of the two nonequivalent T atoms that should be present in SAPO-31[23] are obviously not resolved in the ^{27}Al and ^{31}P *MAS* n.m.r. spectra.

The chemical shifts obtained for phosphorus and aluminum are typical of aluminophosphates irrespective of their framework structure.[20,24] Neither in the ^{27}Al nor in the ^{31}P *MAS* n.m.r. spectra shown in *Figure 1* are there any hints of silicon incorporation. The single resonance line obtained for phosphorus corroborates that P–O–Si bonds are unlikely to occur.[2] The different environments of the phosphorus nuclei in the case of a silicon incorporation on aluminum T sites should be detectable in ^{31}P *MAS* n.m.r. spectra.

^{29}Si *MAS* n.m.r.

Among the methods applied in this study, ^{29}Si *MAS* n.m.r. is the only direct method to investigate this type of silicon incorporation. The ^{29}Si n.m.r. spectra of the SAPOs under study are shown in *Figure 2*. Signals with maxima between −91 ppm and −96 ppm are ascribed to silicon atoms bonded via oxygen to four aluminum atoms.[7–10,26] Consequently, the silicon present in the SAPO-5 and SAPO-34 samples is almost exclusively incorporated on phosphorus T sites of the aluminophosphate framework. Each silicon atom incorporated in this way should cause a Brönsted acidic site in the calcined sample. A second line in the ^{29}Si n.m.r. spectra at about −110 ppm stems from silicon atoms bonded via oxygen to four silicon. This signal is clearly present in the SAPO-31

Table 3 Line positions observed in *MAS* n.m.r.

Sample	δ (^{27}Al)[a]/ppm	δ (^{31}P)/ppm	δ (^{29}Si)/ppm
SAPO-5	35.3	−30.7	−95.5 (−111)
SAPO-31	36.0	−30.5	−91 −110
SAPO-34	33.0	−30.3	−95.3

[a] Not corrected for second-order quadrupole effects

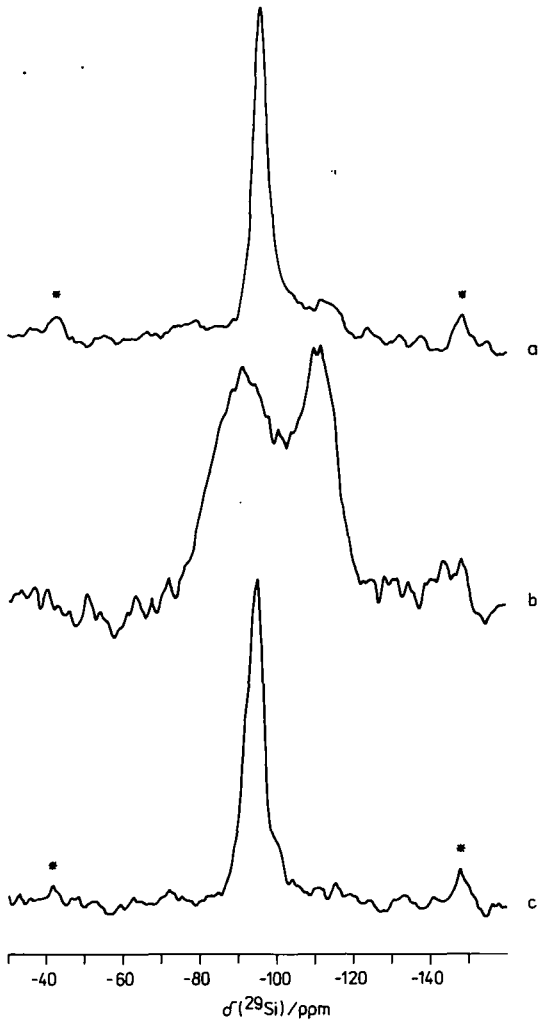

Figure 2 ^{29}Si *MAS* n.m.r. spectra of calcined and dehydrated samples of the investigated silicoaluminophosphates: (a) SAPO-5, 9000 scans; (b)SAPO-31, 13,000 scans; (c) SAPO-34, 2000 scans

sample under study, but there is also a small indication of it in the case of SAPO-5. Two different explanations for this signal are possible: silicon in silica-rich islands in the silicoaluminophosphate framework and silicon in silica byproducts.[5,9,10,24]

Nevertheless, the presence of both forms of silica would lead to a number of Brönsted acidic sites lower than the total number of silicon atoms present in the sample as found by chemical analysis. It means that the knowledge of the overall chemical composition of the synthesis product is far from enough to predict the acidic properties of SAPO materials.

From the intensities of the lines in between −91 ppm and −95 ppm in the ^{29}Si n.m.r. spectra (*Figure 2*), we can derive that the number of Brönsted acidic sites should decrease in the order SAPO-34, -5, and -31. This estimation agrees well with the results of proton n.m.r. (*vide infra*). The advantage of the ^{1}H *MAS* n.m.r. is its ability to quantify the number of acidic sites. The low natural abundance of the ^{29}Si isotope together with the low sensitivity render a reliable quantitative determination by ^{29}Si *MAS* n.m.r. impossible in the case of SAPO-type materials.

^{1}H *MAS* n.m.r.

Figure 3 shows the ^{1}H *MAS* n.m.r. spectra of SAPO-5, SAPO-31, and SAPO-34. The spectra consist of a maximum of three lines: a line at (1.5 ± 0.3) ppm, which was ascribed to SiOH an POH groups,[5,12]; a line of bridging hydroxyls in SiOHAl groups at (3.8 ± 0.1) ppm; and, in the case of SAPO-5 and SAPO-31, a second one due to another kind of bridging hydroxyls at (4.8 ± 0.2) ppm. In an accompanying study,[27] concentrations of bridging hydroxyls between 1.5×10^{20} and 4.5×10^{20} OH/g were determined by ^{1}H *MAS* n.m.r. for SAPO-5 samples with concentrations of silicon atoms in the range of $1.0–5.0 \times 10^{20}$ Si/g. The intensity ratio of the lines at about 3.8 and 4.8 ppm amounts to 1: (0.85 + 0.05), independent of the total concentration of bridging OH groups and silicon atoms. The concentration of hydroxyl groups with the line at about 1.5 ppm was observed as constant to $(0.5 \pm 0.1) \times 10^{20}$ OH/g. From the well-resolved ^{1}H n.m.r. lines of bridging hydroxyls at about 3.8 and 4.8 ppm, it can be concluded that the jump frequency υ_j of hydroxyl protons between the different oxygens must fulfil the condition $\upsilon_j \ll 300$ Hz.

The overall concentrations of bridging OH groups together with the silicon contents of the samples under study are summarized in *Table 4*. Except for SAPO-31 where a higher amount of nonacidic hydroxyls was found, the concentration of bridging hydroxyls corresponds to the silicon content of the sample as determined by chemical analysis.

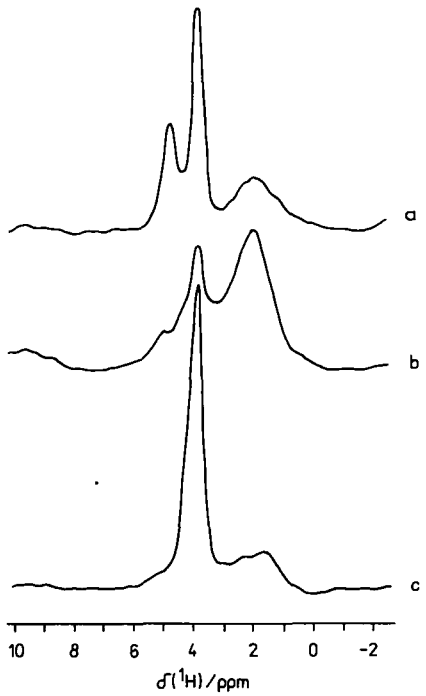

Figure 3 ^{1}H *MAS* n.m.r. spectra of the calcined and dehydrated silicoaluminophosphates: (a) SAPO-5; (b) SAPO-31; (c) SAPO-34

Table 4 Silicon content obtained by chemical analysis and number of hydroxyl groups determined by ^{1}H *MAS* n.m.r.

Sample	Silicon content (10^{20} g^{-1})	Nonacidic hydroxyls (10^{20} g^{-1})	Bridging hydroxyls (10^{20} g^{-1})
SAPO-5	3.6 ± 1.0	0.7 ± 0.2	4.5 ± 0.5
SAPO-31	8.0 ± 1.0	2.5 ± 0.3	1.5 ± 0.3
SAPO-34	11.2 ± 1.0	0.9 ± 0.2	12.0 ± 1.0

As stated above, the deficit of SiOHAl groups relative to the total amount of silicon in the SAPO-31 sample under study has to be explained by silicon atoms in silica islands of framework and/or as silicon in an amorphous byproduct. Assuming that the two ^{29}Si n.m.r. lines observed for SAPO-31 are symmetric, it follows that only 60% of the total silicon is incorporated as silicon on phosphorus T sites. This would partially explain the discrepancy between the silicon content determined by chemical analysis and the number of bridging hydroxyls determined by ^{1}H *MAS* n.m.r. (cf. *Table 4*). The percentage of isolated silicon derived from ^{29}Si n.m.r. should be taken as an upper limit, since the ^{29}Si n.m.r. line shape of amorphous silica is often far away from being symmetric.[28] The enlarged intensity of the ^{1}H n.m.r. line at about 1.5 ppm, in comparison to that of SAPO-5 and SAPO-34, is a hint at a contribution of silanol groups to this line, but corresponds only to about 30% of the observed deficit of hydroxyl groups.

Diffuse reflectance i.r.

In *Figure 4* the diffusive reflectance i.r. spectra of SAPO-5, SAPO-31, and SAPO-34 are presented in the region of fundamental OH stretching vibrations υ_{0-1}. Independent of the structure of the molecular sieve, a hydroxyl band at about 3625 cm^{-1} is observed in all spectra. For both the large and the intermediate pore type, SAPO-5 and SAPO-31, a second band due to the incorporation of silicon appears at 3520 cm^{-1}, whereas for the small-pore SAPO-34, the second band is found at 3600 cm^{-1}. In accordance with the literature,[3,4,6] we propose that these two different bands are characteristic of undisturbed SiOHAl groups (3625 cm^{-1}) and SiOHAl groups interacting with oxygen atoms of the framework (3520 and 3600 cm^{-1}). Recently, Zubkov et al.[29] suggested that the disturbed OH groups in SAPO-34 are located inside the hexagonal prisms.

Further evidence for the existence of different kinds of bridging hydroxyls in SAPOs under study is obtained by the appearance of the bands at 3973 and 3941 cm^{-1} in the case of SAPO-5 and SAPO-34, respectively (*Figure 4*). In a previous paper,[30] we proposed the assignment of bands in the range of 3900–4000 cm^{-1} to combination modes of stretching and out-of-plane bending vibrations (υ_{0-1} + γ) of bridging OH groups forming hydrogen bonds with framework oxygen atoms or adsorbed molecules. Hence, in the case of SAPO-5, the out-of-plane vibration frequency of disturbed SiOHAl groups with the stretching vibration at 3520 cm^{-1} can be calculated to γ = 453 cm^{-1}, whereas for SAPO-34, the corresponding out-of-plane vibration frequency of the same type of hydroxyls (3600 cm^{-1}) amounts to γ = 341 cm^{-1}.

It is interesting to note that while in the ^{1}H *MAS* n.m.r. spectrum of SAPO-34 only one line at 3.8 ppm due to bridging hydroxyls is observed the corresponding DRIFT spectrum exhibits two well-resolved bands. This cannot be an artifact of the i.r. spectroscopy, since the existence of the band at 3941 cm^{-1} reveals that there are bridging hydroxyls interacting with framework oxygen in addition to the undisturbed ones.

In accordance with the results of ^{29}Si and ^{1}H *MAS* n.m.r., the intensities of the bridging hydroxyl bands are quite different for the samples under study. Especially for SAPO-31, the intensity of the bands assigned to bridging hydroxyls is low and three additional bands at 3675, 3745, and 3790 cm^{-1} can be clearly realized.[15] The bands at 3675 and 3790 cm^{-1} are very close to those observed by Peri[31] in an amorphous aluminophosphate. They were ascribed to the fundamental stretching vibrations of surface POH and AlOH groups, respectively.

Until now, the assignment of the band at 3745

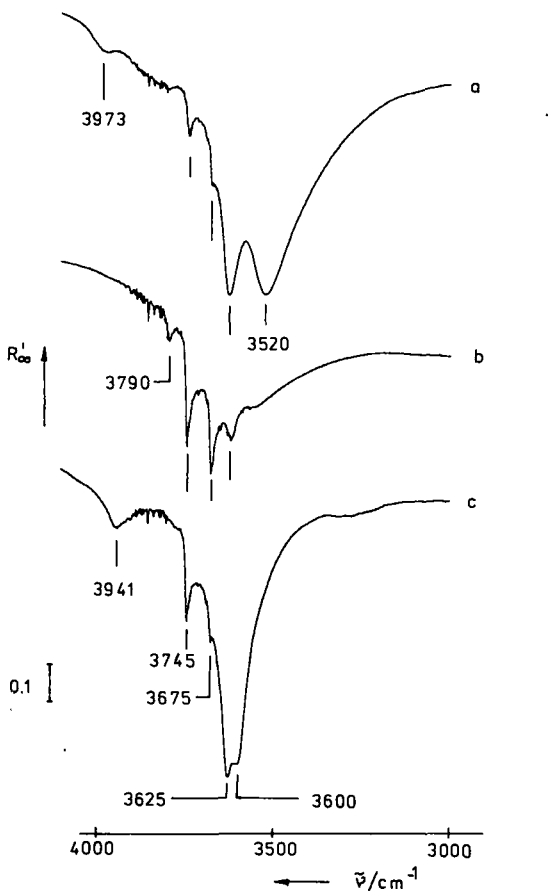

Figure 4 DRIFT spectra of the calcined and activated silicoaluminophosphates in the fundamental region: (a) SAPO-5; (b) SAPO-31; (c) SAPO-34

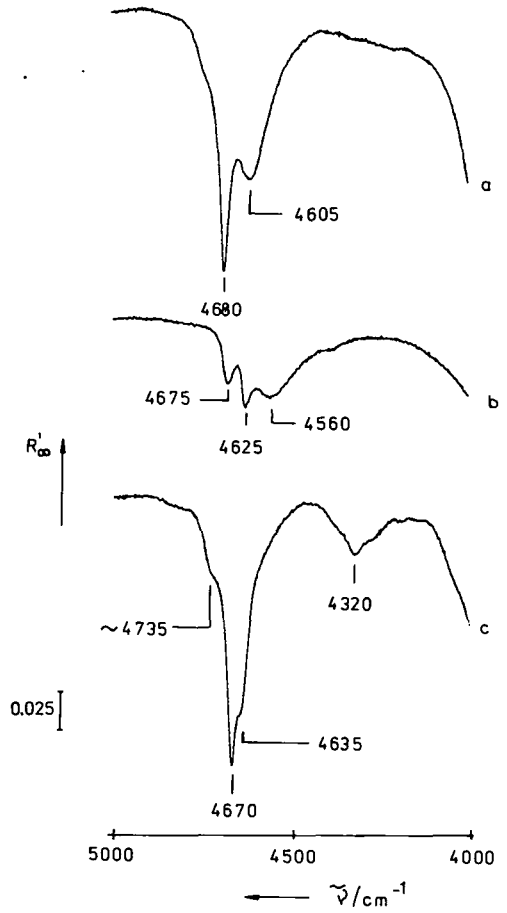

Figure 5 DRIFT spectra of the calcined and activated silicoaluminophosphates in the combination region: (a) SAPO-5; (b) SAPO-31; (c) SAPO-34

cm^{-1} was undetermined.[29] Hegde et al.[4] attributed a band at 3740 cm^{-1} to AlOH groups on the external surface. However, in zeolites[32] and other SAPO-type molecules sieves,[3,15] a band at this position was believed to be caused by terminal SiOH groups at the outer surface and/or amorphous impurities of the sample. To distinguish between these two possibilities, we investigated the region of combination tone bands $\nu_{O-1} + \delta$ (*Figure 5*). It is known that the combination tone band of SiOH and AlOH groups occur at about 4550 cm^{-1} (Ref. 33) and 4450 cm^{-1} (Ref. 34), respectively. In the case of SAPO-31, relatively intense bands at $\nu_{O-1} = 3745$ cm^{-1} (*Figure 4*) and at $\nu_{O-1} + \delta = 4560$ cm^{-1} (*Figure 5*) are observed. Furthermore, from the ^1H n.m.r. results, it follows that especially in the SAPO-31 sample investigated a considerable number of SiOH groups are present. Consequently, we assign the band at 3745 cm^{-1} to terminal silanol groups, but it cannot be excluded that also a small quantity of AlOH contributes to this line.

Sorbed molecules

Concerning the location and acidity of hydroxyl groups, the ^1H *MAS* n.m.r. spectroscopy offers the opportunity to study the interaction of Brösted centers with sorbed molecules. The obtained ^1H *MAS* n.m.r. spectra are given in *Figures 6* and 7.

Loading of activated SAPO-5 with pyridine (diameter of 0.59 nm[35]) quenches the lines of hydroxyl protons in SiOHAl groups at about 3.8 and 4.8 ppm (*Figure 6a*). The new line at (16 ± 1) ppm has to be attributed to pyridinium ions.[12] Therefore, the bridging hydroxyls giving rise to the line at about 3.8 ppm as well as those giving rise to the line at 4.8 ppm are involved in the protonation of pyridine-to-pyridinium ions. The signals at (8.2 ± 0.4) ppm and (7.2 ± 0.4) ppm are caused by ring protons of pyridine molecules. A similar behavior is observed for the adsorption of ammonia (*Figure 7a* and *b*). Adsorbed ammonia molecules are protonated in the same manner by both types of bridging hydroxyls, producing a line of ammonium ions at (7.0 ± 0.2) ppm.[12] In the ^1H *MAS* n.m.r. spectra of samples that were loaded with a number of ammonia molecules higher than the number of bridging hydroxyls in the sample, a line at 3.0–7.0 ppm can be observed (cf. *Figure 7b*) caused by a rapid exchange of ammonium ions and physisorbed ammonia molecules.[19]

As shown in *Figure 6c*, after adsorption of perdeuterated cyclohexane (diameter of 0.6 nm [Ref. 35]), only the ^1H *MAS* n.m.r. line at about 3.8 ppm disappears due to the deuteration of corresponding bridging hydroxyls. The line at 4.8 ppm due to the other type of bridging hydroxyls is unaffected.

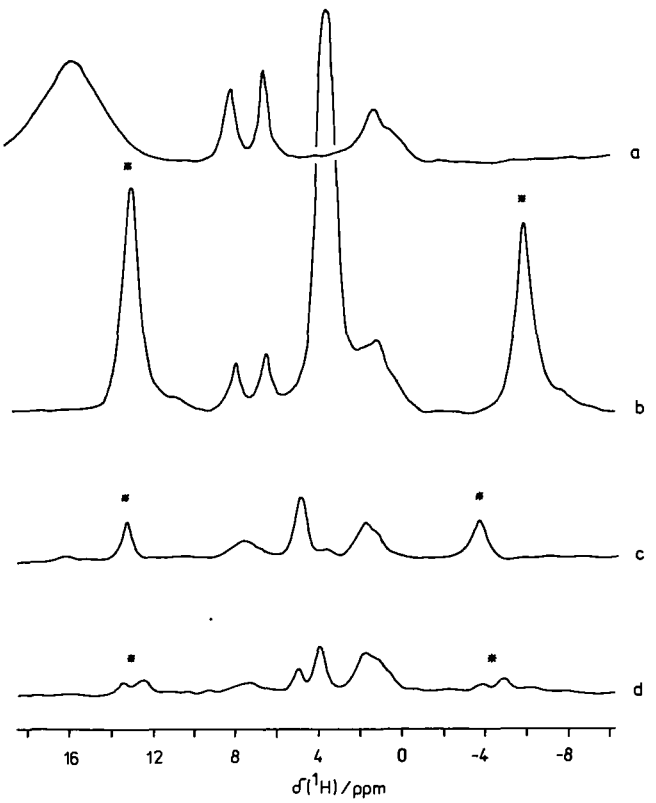

Figure 6 ^1H *MAS* n.m.r. spectra of SAPO-5 (a,c,d) and SAPO-34 (b), activated and subsequently loaded with perdeuterated pyridine (a,b) and cyclohexane (c,d). The spectrum given as (d) was recorded 10 d after preparation of the sample

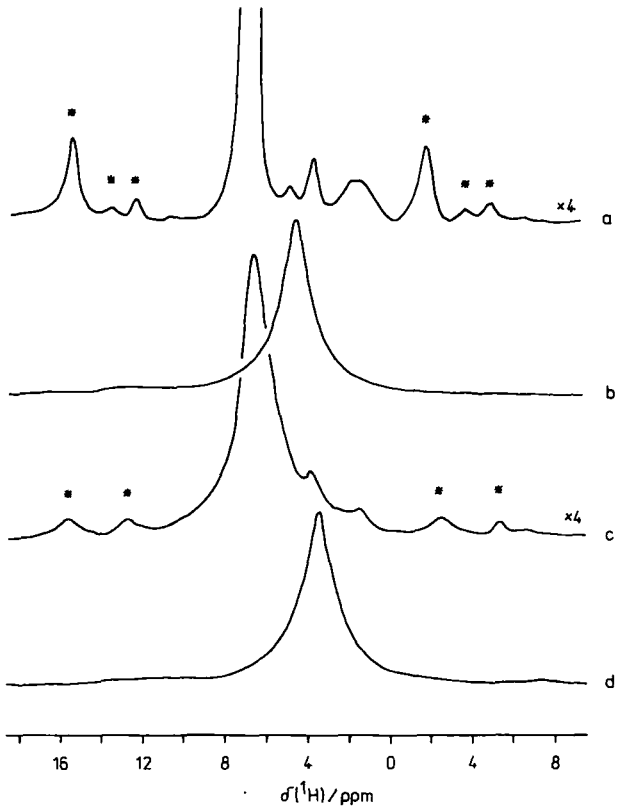

Figure 7 ^{1}H *MAS* n.m.r. spectra of SAPO-5 (a,b) and SAPO-34 (c,d) activated and subsequently loaded with 0.8 molecules (a,c) and 3.0 molecules (b,d) ammonia per bridging hydroxyl

Owing to the second evacuation of this sample, a line of partially protonated cyclohexane molecules produced by this H/D exchange is absent. The ^{1}H *MAS* n.m.r. spectrum of the same sample recorded 10 d later shows two weak lines at about 3.8 and 4.8 ppm (*Figure 6d*) as a result of deuteron exchange among all bridging hydroxyls. The bridging OH groups of SAPO-5 that are not involved in a deuteration in the first step should be considered as not accessible for cyclohexane molecules. Consequently, the hydroxyls giving rise to the line at 4.8 ppm should be located outside the main channel, i.e., probably in the six-membered rings. In the absence of strong bases, the mean residence time of the hydroxyl protons at their lattice oxygen must be at room temperature in the order of several hours. In contrast to this finding, the interaction with the strong base pyridine can be explained by a migration of bridging hydroxyl protons to the main channel of SAPO-5 as a result of the higher proton affinity of this probe molecule.

The described behavior of the two kinds of bridging hydroxyls in SiOHAl groups in SAPO-5 as observed in ^{1}H *MAS* n.m.r. agrees with the conclusions of i.r. spectroscopic studies. It was found that OH groups causing the band at 3625 cm^{-1} interact with benzene,[3,4,9] ethylene,[4] ammonia, and pyridine.[3] On the basis of these results, the band at 3625 cm^{-1} was attributed to SiOHAl groups pointing into the 12-membered ring.[3] Since the band at 3518 cm^{-1} disappeared after adsorption of ammonia, but not after adsorption of benzene and ethylene, it was suggested that the corresponding hydroxyl groups are located in the six-membered ring. It is important to remember that there is only one crystallographic position of T atoms in SAPO-5,[36] which causes two kinds of bridging hydroxyls in result of charge compensation by protons. From the relative intensities observed, these protons should be located with nearly the same probability at oxygen atoms pointing toward the main channel and those in the six-membered rings, respectively.

As distinct from SAPO-5, after loading of activated SAPO-34 with pyridine, no interaction of the adsorbed molecules with the acidic bridging hydroxyls is observed (*Figure 6b*). Ring protons of the pyridine molecules cause small signals in the range of chemical shifts of 8.6 to 6.8 ppm. Since the line of POH and SiOH groups at about 1.5 ppm remains nearly unchanged, one has to conclude that these hydroxyls are not preferentially located on the outer surface of the crystallites. Like bridging hydroxyls that are situated in the main channels (diameter of ca. 0.4 nm), most of the POH and SiOH groups are unaccessible for pyridine molecules. On the other hand, adsorption of ammonia on SAPO-34 causes a protonation of the probe molecules by bridging hydroxyls producing a ^{1}H n.m.r. line at (6.5 ± 0.2) ppm (*Figure 7c*). The broadening of the ^{1}H n.m.r. line of ammonium protons in SAPO-34 in comparison to the signal of ammonium protons in SAPO-5 (*Figure 7a*) by a factor of three can be attributed to a decreased molecular mobility of this ionic species in the small channels of the SAPO-34 framework. In the ^{1}H *MAS* n.m.r. spectra of SAPO-34 samples that were loaded with a surplus of ammonia, the ^{1}H n.m.r. line at 3.8 ppm is completely vanished (*Figure 7d*).

CONCLUSIONS

In the silicoaluminophosphate under study, silicon was found to substitute to a considerable extent for phosphorus in the framework. Neither conventional ^{27}Al nor ^{31}P *MAS* n.m.r. are suitable to detect this isomorphous framework substitution. By means of ^{29}Si *MAS* n.m.r., not only the presence of silicon, but also the type of incorporation into the aluminophosphate framework, can be directly monitored.

The problem of quantifying the amount of the silicon incorporated on phosphorus T positions can be solved indirectly by applying ^{1}H *MAS* n.m.r., measuring the concentration of acidic hydroxyl groups. Only in the case of silicon incorporation on phosphorus T sites does the number of acidic hydroxyls agree with the number of silicon atoms found by chemical analysis. Furthermore, the ^{1}H *MAS* n.m.r. was again shown to be appropriate to distinguish between different acidic hydroxyls. Although all T atoms in SAPO-5 are crystallographically equivalent, the incorporation of silicon produces two different acidic hydroxyls. This result is in excellent agreement with findings of i.r. spectroscopy.

The commonly accepted assignment of two different i.r. bands of acidic hydroxyls to bridging hydroxyls interacting and noninteracting with further oxygen atoms of the framework is supported by the i.r. results in the combination tone region as well as by the ^1H *MAS* n.m.r. results for sorbed molecules. The hydroxyls pointing into six-membered rings of SAPO-5 do not interact with the relatively large cyclohexane molecule. Nevertheless, a protonation of the basic molecule pyridine that has nearly the same size takes place via migration of protons due to the higher affinity of the acceptor. Therefore, the term accessibility should be used with caution.

ACKNOWLEDGEMENTS

The authors want to thank Dr. G. Finger, Dr. H.-L. Zubowa, and Mrs. I. Girnus for the preparation of the SAPO-5, SAPO-31, and SAPO-34 samples, respectively. Furthermore, we are indebted to Dr. J. Caro for valuable comments on the manuscript.

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