Dependence of the Acidic Properties of SAPO-37 Molecular Sieve on Si Content and Heat Treatment

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A series of SAPO-37 samples with Si atomic fractions from 0.12 to 0.22 has been synthesized. The study of their properties is carried out by means of infrared spectroscopy, TPD of ammonia and MAS NMR of $^{27}$Al, $^{31}$P, and $^{29}$Si. The high thermal stability of protonic sites and the formation of Lewis acidity are not related to the presence of extra-framework species, as deduced from NMR and IR results. The absence of such species is confirmed firstly by the constancy upon thermal dehydroxylation of the mean acid strength evaluated from NH$_3$ TPD and secondly by there being no specific effect upon rehydration at 575 K of samples pretreated at 1175 K. The amount of hydroxyls and of acid centers is the highest for a silicon atomic fraction close to 0.12–0.13 which corresponds to a maximum of isolated Si atoms not involved in Si islands. The acid strength distribution is narrow, corresponding for its major part to Si–OH–Al species in Si(4 Al)(9 P) sites.


INTRODUCTION

SAPO-37 is the isotype of faujasite. The presence of P in the framework changes the chemical properties of the Si–OH–Al species particularly with regards to acidity and catalysis (1, 2). A main parameter which affects the protonic character is the environment of Si and Al atoms. It was shown early on by Martens et al. that Si may form siliceous crystal domains in SAPO's (3, 4). In the particular case of SAPO-37 the same authors propose that these silicon-rich patches contain Al and constitute an aluminosilicate phase as seen by $^{29}$Si MAS NMR (1, 5, 6). Three types of atom arrangements may then exist (1, 5, 6); these are the SAPO-37 phase where Si atoms have four Al atoms in the first shell of tetrahedra and nine P in the second layer (so-called isolated Si atoms: Si(4 Al)(9 P)); the aluminosilicate islands rich in silica with the faujasite structure where NMR detects a Si(4 Al) line at -84.7 ppm typical of Si–Al faujasite and the presence of Si(0 Al) and different from the aluminosilicate region may also be mentioned (6). More recently (7) the $^{29}$Si MAS NMR study of a series of as-synthesized SAPO-37 samples with increasing Si contents showed the absence of Si(4 Al) NMR lines at -84.7 ppm typical of Si–Al faujasite and the presence of Si(n Al) lines with n ≤ 3 whose chemical shifts do not fall in the range observed (8) for aluminosilicate faujasites. These results are explained by a model where only SiO$_4$ tetrahedra (no AlO$_4$) are connected in so-called “Si islands” (7). Hence, no aluminosilicate region is observed per se, in contrast with the findings for the SAPO-37 materials described above (1, 5, 6). In the samples described in Ref. (7) and in the present paper, the Si–OH–Al species exist only at the border of these pure silica domains with the SAPO-37 phase. The chance for a Si atom to be the neighbour of an Al atom decreases as the size of the Si islands increases. It follows that an average number of protons...
per Si atom in the Si–OH–Al species is calculated to decrease from 1 to 0.44 as the number of Si atoms in islands increases from 1 to 14. This is in line with the decrease in the number of template ions stabilized in the structure (7). In view of these results on the Si location in the framework, the aim of the present work is to consider the effect of the Si content, of the pretreatment temperature and of rehydration of the materials on the Al and P environments and on experimental acidity.

EXPERIMENTAL

Materials

A series of SAPO-37 materials has been synthesized using tetramethylammonium (TMAOH) and tetrapropylammonium (TPAOH) hydroxides as templates as in Refs. (9–11). Samples are referred to by their silicon atomic fraction. Materials Si-0.12 and Si-0.13 (Table 1) are obtained following very precisely the procedure described in Ref. (10) with regards particularly to the amounts of reactants, their mixing and the origin of the chemicals, which are also available in Europe. For Si richer samples only the amount of Si in the synthesis mixture is increased as in Ref. (11). Analysis by atomic absorption spectroscopy gives the contents in Si, Al, P reported in Table 1 within 1% accuracy. All the samples show XRD patterns similar to those of Y zeolites with regards to the position and intensities of lines. They are used in conditions which avoid any loss of crystallinity (12). Three faujasite type zeolites have also been used. These are an HY which contains 10 Na+/u.c., a Union Carbide LZY-82 which has a framework Si/Al ratio of 4.5 determined by NMR and a Y dealuminated with (NH₄)₄SiF₆, (HYD) (13), which is highly crystalline and which is a very good catalyst (14) with a Si/Al ratio of 7 (framework and total).

Ammonia and Pyridine TPD

The samples (10 mg for pyridine and 20 mg for ammonia) were pretreated at 875 K in a U-tube for 6 h under an air flow and then 6 h under vacuum in order to decompose the templates. The bases were adsorbed for 1 h at room temperature and the excess was evacuated for 6 h at 385 K for NH₃ and 425 K for pyridine. A rate of 5 K per minute was used for the thermodesorption. A quadrupole mass spectrometer Quadruvac PGA 100 Leybold-Heraeus was used for the online analysis of the gas evolved.

Infrared Spectroscopy

Self-supported wafers (15 mg, 18 mm diameter) were evacuated at 875 K for the decomposition of the templates. After a 2-h treatment under O₂ followed by a 6-h evacuation at 875 K or higher, the OH spectra were recorded at room temperature with a Perkin-Elmer 580 B spectrophotometer equipped with a Data Station. The adsorption of pyridine was performed as already described (15). After evacuation at 425 K for 6 h the spectra were recorded. The Brønsted/Lewis ratio acidities (B/L) were determined from the ratio of the peak areas.

NMR

²⁷Al, ²⁹Si, and ³¹P solid-state MAS NMR were performed on a Bruker MSL-400 multinuclear spectrometer at 104.2, 79.5, and 161.9 MHz, respectively. Their chemical shifts were reported in ppm from external Al(H₂O)₃⁺ in Al(NO₃)₃ aqueous solution, tetramethylsilane and 85% H₃PO₄, respectively. The sign convention of high-frequency (low-field, paramagnetic, deshielded) shifts being positive is used. For

### Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>Si_i</th>
<th>Al_i</th>
<th>P_i</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.12</td>
<td>0.50</td>
<td>0.38</td>
</tr>
<tr>
<td>Si-0.13</td>
<td>0.13</td>
<td>0.49</td>
<td>0.38</td>
</tr>
<tr>
<td>Si-0.16</td>
<td>0.16</td>
<td>0.48</td>
<td>0.36</td>
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<td>Si-0.20</td>
<td>0.20</td>
<td>0.50</td>
<td>0.30</td>
</tr>
<tr>
<td>Si-0.22</td>
<td>0.22</td>
<td>0.46</td>
<td>0.32</td>
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</table>
\(^{27}\text{Al}\) MAS spectra, radiofrequency (RF) pulses of 2 \(\mu s\) duration \((\pi/12\text{ pulse length})\) were applied with a 2 s recycle delay and a rotor spinning rate of 5 kHz. For \(^{29}\text{Si}\) MAS spectra, RF pulses of 2.5 \(\mu s\) duration \((\pi/4\text{ pulse length})\) were applied with a 10-s recycle delay and a rotor spinning rate of 4 kHz. For \(^{31}\text{P}\) MAS spectra, RF pulses of 6.2 \(\mu s\) duration \((\pi/2\text{ pulse length})\) were applied with a 20-s recycle delay and a rotor spinning rate of 5 kHz. The setting of the \(^{31}\text{P}\) Hartmann–Hahn condition was performed with \(\text{NH}_4\text{H}_2\text{PO}_4\). Spin-locked cross-polarization spectra were obtained with proton high-power decoupling. The proton \(\pi/2\) pulse length, the contact time and the recycle delay for our samples were 6.2 \(\mu s\), 1 ms, and 5 s, respectively. The number of scans is given in each figure. The samples pretreated under vacuum at the desired temperature were kept in sealed tubes. Just before the NMR experiments the powders were transferred into the rotors in a dry nitrogen atmosphere and studied in these dry conditions. Each pretreatment was conducted on an as-synthesized sample.

RESULTS AND DISCUSSION

A. Acid Sites after the Template Decomposition at 875 K

A.1. Hydroxyls. After treatment at 875 K two main hydroxyl bands are obtained at 3640 and 3575 cm\(^{-1}\) \((15, 16)\) as in Si–Al faujasites. Figure 1 compares the spectra for samples Si-0.16 and Si-0.22. A weak band is seen near 3680 cm\(^{-1}\). It may be assigned to POH hydroxyls \((17, 18)\). Figure 1 shows a lowest absorbance of the hydroxyls of silicon richer material. This was already observed for materials Si-0.12 and Si-0.20 \((15)\) and related to the formation of Si islands at high silicon contents \((7)\). No aluminosilicate faujasite domains, as seen in Refs. \((1, 5, 6)\), were observed here from \(^{29}\text{Si}\) MAS NMR spectra after the 875-K treatment. The hydroxyls should then arise from isolated Si(4 Al)\((9\text{ P})\) species and from Si at the border of the Si islands. The proposal of such domains relies on \(^{29}\text{Si}\) NMR results and on the topology of SAPO-37 \((7)\). Figure 2 gives as an example the \(^{29}\text{Si}\) NMR spectrum of sample Si-0.22. A detailed study on the influence of first and second neighbours of Si atoms on the chemical shifts suggested to assign the various peaks in Figure 2 to Si atoms of the

![Fig. 1. Infrared spectra of samples Si-0.16(a) and Si-0.22 (b) after heat treatment for 6 h at 875 K in O\(_2\) and evacuation for 6 h at 875 K.](image)

![Fig. 2. \(^{29}\text{Si}\) MAS NMR spectrum of sample Si-0.22 as synthesized (number of scans NS = 30,000).](image)
SAPO-37 structure surrounded by 4 to 0 Al. The formation of Si islands may be visualized in Fig. 3, which gives as an example a scheme for the incorporation of Si atoms in a hypothetical bidimensional AlPO network. It is not, of course, the tridimensional framework of SAPO-37, particularly for second neighbours of any given atom. Nevertheless it shows that besides isolated Si surrounded by 4 Al as first neighbours and 8 P as second neighbours - Si(4 Al)-(zone 1) there are domains (zone 2) where the environment of Si atoms varies as to the first and second neighbours. For instance, in zone 2 out of the 11 silicons, five are surrounded by 3 Al, three by 0 Al, two by 2 Al and one by 1 Al, the number of Al may be written as Si(nAl). The very detailed study of the topology of the faujasite structure shows that the order of occurrence in SAPO-37 is Si(4 Al) > Si(3 Al) > Si(2 Al) > Si(1 Al) (7). This is in agreement with the $^{29}$Si NMR results of Fig. 2.

The acidic hydroxyls are bridging OH in Si–OH–Al species. The number of protons will then depend for each island on the number of Si–OH–Al, i.e., on the environment of Si atoms in the framework. A Si(nAl) will generate n/4 proton, i.e., from a value of one for Si(4 Al) down to zero for Si(0 Al). A detailed calculation of the number of protons formed shows that one may expect a decrease in the number of acidic hydroxyls as the Si content in the SAPO-37 increases, i.e., as there are more Si islands and/or as islands are larger (7). The maximum number of acidic hydroxyls is obtained for isolated Si in Si(4 Al) species.

In the SAPO-37 structure, isolated Si atoms were well described by Sierra de Saldariagga et al. (10). They consist of Si replacing P atoms in the hypothetical AIPO-37 structure according to mechanism 2. They are surrounded by 4 Al as first neighbours and 9 P as second neighbours. In this ideal SAPO-37 where all Si are isolated, the first neighbours of Al atoms are 1 Si and 3 P and those of P are 4 Al. No Si–O–P bonds exist (10). This model corresponds to 96 Al, 72 P and 24 Si per unit cell, i.e., to $x = 0.125$. This happens for samples Si-0.12 and Si-0.13. Attempts were made to introduce less Si in the SAPO-37 structure in order to have, besides isolated Si atoms, some AlPO domains with no Si. This failed up to now. At Si contents higher than $x = 0.125$ one may expect a progressive increase in the number of Si involved in islands and consequently a decrease in the number of Si–OH–Al species as shown in Fig. 1. This is confirmed by the simultaneous decrease in the number of template molecules necessary to compensate the framework charge in the as-synthesized materials (7).

A.2. Al and P environments. The $^{27}$Al MAS NMR spectrum of sample Si-0.12 after removal of the template at 875 K shows mainly the tetrahedral Al (Al$^{IV}$) peak (Fig. 4). The other samples behave similarly. Upon rehydration at room temperature by exposure to ambient atmosphere an intense octahedral (Al$^{VI}$) peak is formed. Simultaneously the structure collapses. Such a loss of crystallinity was observed when SAPO-37 is contacted with water (liquid or vapour) below 350 K (12). The Al$^{VI}$ species are related to the splitting of TO bonds leading very probably to extraframework Al as in Si–Al faujasites. No reversibility of the process was observed.

The $^{31}$P MAS NMR spectra of the initial
Si-0.12 sample is given in Fig. 5 with those after various treatments. For the material containing the templates (curve a) the spectrum is similar to the ones reported by others with the peak representing P(4 Al) (5, 6, 10, 19, 20). The other SAPO-37 samples studied here have the same sharp peak at \(-26.4\) ppm. The Si-0.12 sample shows in addition (curve a, Fig. 5) two weak peaks at \(-16.3\) and \(-19.9\) ppm which are considerably less intense or even do not exist for the other samples. After treatments at 875 K or 1095 (curves b, c) only the \(-26.4\) ppm peak is left with no change in chemical shift. The \(^{31}\text{P}\) cross polarization MAS NMR experiments reported in Fig. 6 show for the starting solid (curve a) two enhanced peaks at the same \(\delta\) as in the MAS NMR spectrum (Fig. 5, curve a). This suggests that a small number of atoms in this specific SAPO-37 material might exist as defects in the structure. A transfer of polarization occurs between these P atoms and protons very probably belonging to the templates. The heat treatment at 875 or 1095 K would reorganize the neighbours of these P atoms. The rehydration at room temperature of these heated materials does not give a large change in the MAS NMR spectrum (curve b and d, Fig. 5).
ACIDIC PROPERTIES OF SAPO-37

5) despite the loss of crystallinity. A weak and broad peak is detected near -30 ppm.

A.3. Brønsted and Lewis acidity. The two usual types of acid centers (Brønsted and Lewis) are present in all the samples as seen by pyridine adsorption. A major difference with Si-Al faujasites is the very small number of Lewis acid sites (15) after pretreatment at 875 K. This gives a high Brønsted/Lewis ratio (B/L) for all the SAPO-37 materials (Table 2). It is even higher than for HYD which has a theoretical proton content close to those of Si-0.12 and Si-0.13 samples and which does not contain much Lewis acidity (13, 21). Another point in Table 2 is the high B/L ratio for the two SAPO-37 samples with the lowest Si atomic fraction (x = 0.12 and 0.13). As stated above, this corresponds to the theoretical maximum of acidic hydroxyls. It is also observed that these samples have the largest absorbance of the pyridinium ion band (1540 cm$^{-1}$ band). Since all the materials have a low and comparable intensity of the 1456-cm$^{-1}$ band (Lewis acidity), the formation of Si islands explains the lower B/L ratios for the SAPO-37 with atomic fraction x higher than 0.12-0.13.

A.4. Total acidity. The thermoprogrammed desorption of ammonia and pyridine gives the curves shown in Fig. 7. For both bases, SAPO-37 materials show only one peak near 500 K (NH$_3$) or 665 K (pyri-

![Fig. 6. $^{31}$P CP MAS NMR of sample Si-0.12: (a) as-synthesized; (b) after heating at 1095 K and rehydrated for 1.5 months at room temperature (NS = 300).](image)

![Fig. 7. TPD (heating rate 5 K/min) of ammonia (A) and pyridine (B) for samples: (a) HY, (b) HYD, (c) Si-0.12, (d) Si-0.13, (e) Si-0.16, and (f) Si-0.22.](image)

TABLE 2

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<th>S$^b$</th>
<th>B/L$^c$</th>
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<td>145</td>
<td>0.2$^{ce}$</td>
</tr>
<tr>
<td>Si-0.16</td>
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<td>104</td>
<td>0.4$^d$</td>
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<td>Si-0.20</td>
<td>7$^e$</td>
<td></td>
<td>0.1$^{ce}$</td>
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<tr>
<td>Si-0.22</td>
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<td></td>
</tr>
<tr>
<td>HY</td>
<td>1.8$^e$</td>
<td>215</td>
<td></td>
</tr>
<tr>
<td>HYD</td>
<td>4$^d$</td>
<td></td>
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</tr>
<tr>
<td>LZY-82</td>
<td>0.4$^e$</td>
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$^a$ Ratio of Brønsted to Lewis acidity after pretreatment at 875 K and desorption of pyridine at 425 K.

$^b$ Peak area (arbitrary units) for NH$_3$ desorption.

$^c$ From Ref. (15).

$^d$ From Ref. (13).

$^{ce}$ Ratio of Brønsted to Lewis acidity after pretreatment at 1095 K (e) or 1125 K (f) and after desorption of pyridine at 425 K.
For HY or HYD two peaks are obtained as was already observed for faujasites (21, 22). The results suggest that the acid strength distribution is narrower in SAPO-37, the mean strength being lower than that of the strong sites in HY or HYD. The sites responsible for this medium acid strength in SAPO-37 are very likely the isolated \( \text{Si}(4\text{Al})(9\text{P}) \) atoms.

The approximate amount of acidity is given in Table 2 by the area of the TPD peak of \( \text{NH}_3 \). No quantitative measurement is possible for the pyridine because of the saturation of the cathode. The \( \text{NH}_3 \) peak area is higher for HY indicating a larger number of acid sites. In the SAPO-37 series the Si-0.12 and Si-0.13 samples tend to give the most important peak which is in line with the largest number of acid sites for these samples.

**B. Change in Acidity as a Function of the Pretreatment Temperature**

**B.1. Hydroxyls.** A preliminary study showed that the loss of crystallinity of SAPO-37 occurs at temperatures around 1300 K (12). This material is much more stable than solids of the Si-Al faujasite family which become amorphous at temperatures 300–400°C lower in the same experimental conditions (HY: 750, HYD: 950, and LZY-82: 850 K).

Upon evacuation at increasing temperatures above 875 K the absorbance of the two acidic hydroxyls at 3640 and 3575 cm\(^{-1}\) decreases progressively. For none of the present SAPO-37 samples new bands are formed as is usual for Si-Al faujasites, where these bands are characteristic of extraframework Al (23). As an example, Fig. 8 gives the changes in the hydroxyl region for Si-0.22 pretreated for 6 h up to 1075 K. Only the two initial hydroxyl bands are observed. This suggests that no hydroxylated extraframework species are formed upon evacuation. The changes in the absorbance of the hydroxyls are reported in Fig. 9 for this sample and for Si-0.12. Not only for these two materials but for all the SAPO-37 materials studied the hydroxyls fully disappear at temperatures higher than around 1175 K. Up to 975 K, a significant amount of OH is still present. This is quite different from the OH stability in HY where the major part of the hydroxyls are lost at this temperature. The hydroxyls of SAPO-37 are slightly more stable than those of LZY-82, which in the same experimental conditions disappear at 1125 K.

**B.2. Al and P environments.** Figure 4 gives the \(^{27}\text{Al}\) MAS NMR spectrum of the as-synthesized sample Si-0.12 after heating at 1095 K (curve c). No major difference is observed with the spectrum after heating at 875 K (curve a). No \( \text{Al}^{VI} \) line is seen. The \(^{31}\text{P}\) MAS NMR and CP MAS NMR spectra...
after heat treatment of the as-synthesized Si-0.12 sample at 1095 K are given in Figs. 5 and 6. The MAS spectrum shows the weak broad peak near -30 ppm already mentioned whether the sample is rehydrated or not. Since the crystallinity is good before the rehydration at room temperature, the peak cannot be related to the structure collapse. The cross polarization experiments on the rehydrated material show the presence of some ill-defined peaks which could arise from some hydroxyls transferring polarization to a small number of P atoms different from P (4 Al) in SAPO 37.

Neither $^{27}$Al nor $^{31}$P MAS NMR experiments detect significant differences for pre-treatments at 875 or 1095 K. If Al$^{VI}$ is formed in large amount but, invisible in our $^{27}$Al NMR experimental conditions, this should modify the P (4 Al) sites as this happens for the Si (n Al) environment in Si-Al faujasites. The minor changes in the $^{31}$P spectrum (Fig. 5) such as the small - 30 ppm peak can not reflect a significant modification in the surrounding of a large number of P atoms.

This study shows that the heat treatment at 1095 K does not modify significantly the environment of the major part of Al and P atoms.

**B.3. Brønsted and Lewis acidity.** The well known increase in Lewis acidity in Si–Al zeolites as the dehydroxylation proceeds, with a decrease in Brønsted acidity, is usually related to the formation of Al$^{VI}$ extraframework species upon Al removal from the lattice (23). The NMR results do not detect changes in the Al and P spectra between 875 and 1095 K the Al being tetracoordinated (Figs. 4–6). As mentioned above, one might suspect that invisible Al$^{VI}$ could be formed but remain invisible in the experimental conditions. Nevertheless in addition to no change in the $^{31}$P NMR spectra, two other parameters which are known to be modified with the formation of Al$^{VI}$ in Si-Al faujasites are not changed. Figure 8 shows that no new OH bands are formed upon heating up to 1075 K and the $a_0$ parameter does not decrease between 973 and 1300 K (12). None of the changes associated with Al removed from Si-Al faujasites is observed in SAPO-37. This might be due to the fact that only a very small number of extraframework Al sites is formed and is not detected or to the fact that the Lewis acidity would not be, as in Si-Al zeolites, of the Al$^{VI}$ type. The rise in the 1456-cm$^{-1}$ band after treatment at high temperature does reflect a large number of Lewis sites. This increase may be due to an interaction of the adsorbed molecule with some distorted AlO$_4$ tetrahedra. This point is under study.

**B.4. Total acidity.** The total acidity,
which includes both Brønsted and Lewis sites, reflects the loss of acidic centers upon heating. The decrease in the amount of NH$_3$ desorbed in TPD experiments as the pretreatment temperature goes up is seen in Fig. 11 for sample Si-0.13 and in Fig. 12 for three materials. Figure 11 shows no significant shift in the maxima of the NH$_3$ desorption temperatures. This tends to indicate that the mean strength of the acid sites does not change significantly as their number decreases upon heating.

This is in agreement with a narrow and homogeneous distribution of acid strengths related to isolated Si(4 Al)(9 P) involved in Si–OH–Al species. Since these hydroxyls are apart from each other there is no interaction between them and their progressive removal upon heating does not modify the acid strength of the remaining ones. Figure 12 reports the changes in the areas of the peaks of NH$_3$ TPD as a function of the pretreatment temperature. It shows a similar behaviour for the three samples, all of them losing their acidic properties at 1225 K where the crystalline structure starts to be damaged.

**REHYDRATION**

In order to check the possible reversibility of the transformation of Lewis to Brønsted sites, the rehydration of the samples was conducted. As stated previously, the crystalline structure of SAPO-37 free of templates is not stable below 350 K in the presence of water (12). The rehydration was carried out at 575 K after a 6-h evacuation of the samples at 1125 K. Water vapour at the pressure of room temperature was used. Figure 13 gives the OH spectra of samples Si-0.16 and Si-0.22 before and after rehydration and further evacuation at 875 K for 6 h. Contacting the 1125 K evacuated samples with water vapour restores a part of the hydroxyls as compared to the OH spectra after a single 875 K pretreatment. Figure 14 shows for sample Si-0.16 that simultane-

![Graph](image1.png)

**Fig. 12.** Changes for samples Si-0.13 (a), Si-0.16 (b), and Si-0.22 (c) of the area of the peaks in TPD of ammonia as a function of pretreatment temperature. Samples rehydrated at 575 K after a first heating at 1125 K: (a') Si-0.13, (b') Si-0.16, and (c') Si-0.22.

![Graph](image2.png)

**Fig. 13.** Infrared spectra of samples Si-0.16 (A) and Si-0.22 (B) after heating at 875 K (a); after heating at 1125 K (b); rehydration of (b) at 575 K and evacuation at 875 K (c).

![Graph](image3.png)

**Fig. 11.** TPD of ammonia (heating rate 5 K/min) for sample Si-0.13 after pretreatment for 6 h at: (a) 875 K, (b) 975 K, (c) 1075 K, (d) 1175 K, and (e) 1225 K.
ACIDIC PROPERTIES OF SAPO-37

The present paper shows that the increase in the Si content does not modify the environment of Al or P atoms in a detectable manner. The acidity (protonic and total), associated with the presence of Si atoms is shown to be the highest for the materials which have a maximum of isolated Si(4 Al) (9 P) atoms. Upon heating on the one hand and after further rehydration on the other hand, the behaviour of SAPO-37 is different from that usually observed with Si–Al faujasites. No AlVI peak is seen in NMR, no hydroxyls due to an extraframework phase are observed even after a rehydration in conditions which avoid the loss of crystal structure and no decrease in the $a_0$ parameter occurs. Such differences with faujasites suggest that the increase in Lewis acidity upon heating cannot be related to AlVI species. All the results show that the presence of P stabilizes the SAPO-37 framework. Even though some points need further studies, it is clear that SAPO-37 and Si–Al faujasites are quite different materials with the same crystalline structure.

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REFERENCES


