

Solid-state Transformation of SAPO-37 Molecular Sieve above 1100 K

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The changes occurring in SAPO-37 upon heating it to 1273 K are studied using ^{29}Si , ^{27}Al and ^{31}P magic-angle-spinning nuclear magnetic resonance (MAS NMR), X-ray diffraction (XRD) and infrared spectroscopy. The removal of the template at 873 K leads to a shift of both ^{29}Si and ^{27}Al MAS NMR peaks, suggesting an interaction of the template with some SiO_4 and AlO_4 tetrahedra. A further solid-state transformation is shown to occur between 1073 and 1173 K. This involves the formation of siliceous islands, generating silicoaluminate domains. The faujasite crystal structure is maintained. At 1273 K the material is fully transformed to a mixture of tridymite and cristobalite structures. A model is proposed for the migration of atoms in the framework.

The formation of siliceous islands in SAPOs was first reported by Martens *et al.*^{1,2} in as-synthesized materials as opposed to 'isolated' Si atoms, *i.e.* with only AlO_4 tetrahedra as neighbours. In the case of SAPO-37, the isotope of faujasite, NMR results suggested the presence of an Si–Al faujasite phase in those islands.^{3,4} The sites active in catalysis were related to protons involved in Si–OH–Al species inside or at the border of the siliceous patches.^{3,4} Similar synthesis conditions gave rise, however, to different samples where the islands consist of only SiO_4 species with no AlO_4 included, as shown from NMR spectra.^{5,6} The acid sites were related to Si–OH–Al bridging OH created at the border of those pure SiO_4 islands. It has recently been shown that the proportion of Si atoms in SAPO-37 involved in the pure SiO_4 islands increases as the pretreatment temperature goes above 1075 K.⁷ Such an effect could be related to the simultaneous increase of the catalytic activity in the cracking of *n*-octane.^{8,9} The aim of the present paper is to determine the modifications in the hydroxy group infrared spectra, XRD diffractograms or unit cell parameters which accompany the change in location of atoms during this solid-state transformation.

Experimental

Material

A SAPO-37 material has been synthesized according to the procedures in ref. 10 and 11, using as a template a mixture of tetramethyl- and tetrapropyl-ammonium hydroxides (TMAOH and TPAOH, respectively). The as-synthesized sample is shown to be highly crystalline. Its chemical composition is $(\text{Si}_{0.14}\text{Al}_{0.48}\text{P}_{0.38})\text{O}_2$. Owing to the very high sensitivity of SAPO-37 free of template to water vapour below *ca.* 350 K,¹² special care was taken when handling these materials. Samples for NMR and XRD experiments were heated in a flow of dry air at a rate of 50°C h^{-1} to the desired temperature, *i.e.* between 873 and 1173 K. The temperature was maintained for 9 h in the dry air flow, then 20 h under vacuum unless otherwise specified. The samples were transferred into sealed tubes after cooling to room temperature (RT) under vacuum.

Infrared Spectroscopy

Self-supporting wafers (*ca.* 20 mg, 18 mm diameter) were heat-treated in flowing dry air up to temperatures in the range 873–1173 K. The desired temperature was kept constant for 6 h under the air flow and for 2 h under vacuum. The same wafer was used for the entire study. The hydroxy group spectra were recorded at RT using a Perkin-Elmer 1750 infrared Fourier-transform spectrometer equipped with a Data Station 3600.

X-Ray Diffraction

The samples pretreated as described above were transferred to a waterproof cell (see ref. 13) and studied with a Siemens D500 diffractometer. In some cases the crystallinity of the samples was checked after NMR studies. The solid was transferred from the rotor to the waterproof cell in a dry atmosphere. The high crystallinity of the samples was maintained.

NMR Experiments

^{29}Si , ^{27}Al and ^{31}P solid-state NMR experiments were performed using a Bruker MSL-400 spectrometer at 79.5, 104.2 and 162.0 MHz, respectively. Chemical shifts are reported in ppm from external tetramethylsilane (TMS) for ^{29}Si , $\text{Al}(\text{H}_2\text{O})_6^{3+}$ in a nitric acid solution of $\text{Al}(\text{NO}_3)_3$ for ^{27}Al , and H_3PO_4 (85%) for ^{31}P . The sign convention of high-frequency (low-field, paramagnetic, deshielded) shifts being positive is used. MAS NMR spectra were recorded at RT. The samples were transferred under a dry atmosphere from the sealed tubes to the rotor.

For ^{29}Si spectra the standard Bruker double bearing probe and a 7 mm o.d. ZrO_2 rotor were used. The acquisition parameters are as follows: a $\pi/4$ pulse length of 2.5 μs is applied with a 5 s recycle delay and a rotor spinning rate of 4 kHz, 20 000–30 000 scans were acquired to obtain an adequate signal-to-noise ratio. The spectra were deconvoluted with the program GLINFIT 3004 using Gaussian lineshapes.

^{27}Al and ^{31}P MAS spectra were performed with a probe from DOTY Scientific and a 5 mm o.d. silicon nitride rotor spinning at 8 kHz. For ^{27}Al , a single $\pi/20$ radiofrequency pulse was used with a repetition time of 2 s. For ^{31}P we applied a pulse length of $\pi/2$ and a recycle delay of 5 s.

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Results and Discussion

^{29}Si , ^{27}Al and ^{31}P MAS NMR

An 'ideal' SAPO-37, as described in ref. 11 where there is only one type of environment for each of the atoms Si, Al and P, has the theoretical formula $\text{Si}_{0.125}\text{Al}_{0.50}\text{P}_{0.375}$. Each SiO_4 species is surrounded by four AlO_4 tetrahedra as first neighbours and nine PO_4 tetrahedra in the second layer. This is denoted as Si(4Al)(9P). In this nomenclature, the description for the AlO_4 and PO_4 tetrahedra environments gives Al(3P, 1Si)(9Al) and P(4Al)(3Si,6P). In this case no Si islands are present. At higher Si contents, some SiO_4 tetrahedra are not 'isolated' and begin to form islands.^{5,6} The NMR spectra reflect this formation and show in the ^{29}Si NMR spectra peaks corresponding to Si(*n*Al)(*x*Si,*y*P) with $n < 4$ and $x + y = 9$.^{5,6}

The as-synthesized present sample gives the ^{29}Si MAS NMR spectrum of Fig. 1(a). Small peaks in the range -92 and -106 ppm may be assigned to a small number of Si islands. This is in agreement with the atomic fraction of Si equal to 0.14.⁵ Fig. 1(b)–(e) are the spectra after heating from 873 to 1173 K, Fig. 1(d) and (e) correspond to the same heat-treatment temperature, 1173 K, with two different times (20 and 50 h). Fig. 2 reports deconvolution spectra for the as-synthesized sample (a) and after heating at 873 (b), 1073 (c) and 1173 K for 20 h (d) or 50 h (e) under vacuum. The observed ppm values on Fig. 1 are reported in Table 1. In this table the range of chemical shifts obtained for the as-synthesized materials is taken from ref. 5 for a series of SAPO-37 with various Si contents. At first, it appears that

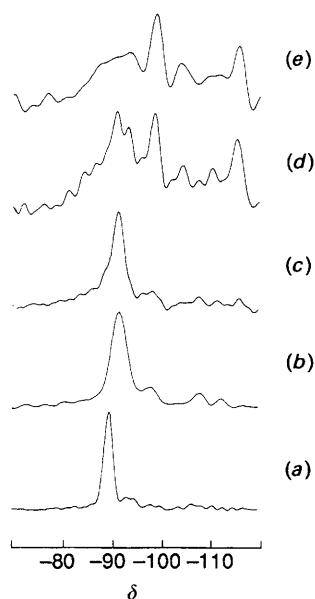


Fig. 1 ^{29}Si MAS NMR spectra of as-synthesized SAPO-37 (a) and after treatment at various temperatures (K); (b) 873, (c) 1073, (d) 1173 (20 h), (e) 1173 (50 h)

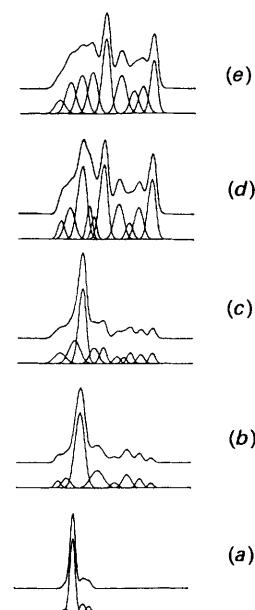


Fig. 2 Deconvolution of the spectra in Fig. 1 of SAPO-37, (a)–(e) as for Fig. 1

the removal of the template at 873 K moves the Si(4Al)(9P) chemical shift from -89.1 to -91.5 ppm and for the Si(3Al) environments from *ca.* -93 to around -98 ppm. On Fig. 1(b), the Si(4Al) peak at -91.5 ppm is broadened, indicating a less homogeneous environment. After heating the sample at 1073 K [Fig. 1(c)] there is no further shift of this peak, but new bands appear in the range -85 to -90 ppm. Deconvolution of spectra (a)–(c) [Fig. 2(a)–(c)] shows peaks of increasing intensity from (a) to (c), which are assigned (Table 2) to Si(4Al) and Si(3Al) species in an Si–Al faujasite phase, *i.e.* with no PO_4 as second nearest neighbours. The other peaks correspond to the chemical shifts observed in a SAPO-37 phase,⁵ and are reported in Table 1.

A drastic change is seen after the treatment at 1173 K. Fig. 1(d) (evacuation for 20 h) shows the decrease of the peak at -91.5 ppm and a large increase in the peaks at around -98.6 , -104 and -115 ppm. The deconvolution [Fig. 2(d)], difficult to perform exactly because of the large overlapping of peaks, gives the proposed peaks reported in Tables 1 and 2, depending on the chemical shifts specific of SAPO-37 or of Si–Al faujasite phases. A longer evacuation at 1173 K [50 h for Fig. 1(e)] leads to an increase of the trends seen in spectrum (d). The higher peaks are the ones at around -98.6 and -115 ppm. The Si(4Al)(9P) peak at -91.5 ppm is now small and embedded in a very broad peak. Table 3 shows the decrease in the percentage of isolated Si atoms Si(4Al)(9P) species as the treatment temperature increases. Only *ca.* 12% is left after the 50 h evacuation at 1173 K. The peak at around -115.6 ppm may be assigned¹⁴ to a silica polymorph structure like for instance tridymite.⁷ Fig. 1 shows that its

Table 1 Chemical shifts (ppm) for SAPO-37 as-synthesized and after heating at various temperatures

SAPO-37 sample	Si(4Al)	Si(3Al)	Si(2Al)	Si(1Al)	Si(0Al)
as-synthesized	-89.1	-92.1 – -94.4	-98.0 – -98.4	-101.8 – -103.0	-106.2 – -106.7
873 ^a	-91.5	-97.8 – -98	nd	nd	-107.6 – -108
1073 ^a	-91.2 – -91.7	-95.8 ; -98.9	-102.7 – -103.6	-106.0	-107.0 – -108.2
1173 ^{a,b}	-91.3	-95.5 ; ^c -98.6 ^c	-104.1 ^c	nd	-107.7
1173 ^{a,d}	-90.7	-94.5 ; ^c -99.0 ^c	-104.4 ^c	nd	-108.8

nd, not detected. ^a Pretreatment temperature (in K). ^b After evacuation for 20 h. ^c Alternatively partly assigned to the Si–Al faujasite phase in Table 2. ^d After evacuation for 50 h.

Table 2 Chemical shifts (ppm) of Si–Al faujasite from ref. 20 and after heating SAPO-37 at various temperatures

Si–Al faujasite	Si(4Al)	Si(3Al)	Si(2Al)	Si(1Al)	Si(0Al)
ref. 20	–84.7	–89.1	–94.0–95.7	–98.8–101.6	–103.0–107.8
873 ^a	nd	nd	nd	nd	nd
1073 ^a	–84.7	–89.2	nd	nd	nd
1173 ^{a,b}	–84.3	–87.2	–93.9, –95.5 ^c	–98.6 ^c	–104.1 ^c
1173 ^{a,d}	–83.5	–87.0	–94.5 ^c	–99.0 ^c	–104.4 ^c

nd, not detected. ^a Pretreatment temperature (in K). ^b After evacuation for 20 h. ^c Alternatively partly assigned to the SAPO-37 phase (Si islands) in Table 1. ^d After evacuation for 50 h.

Table 3 Change in the percentage of Si(4Al)(9P) species in the SAPO-37 phase after pretreatment at increasing temperatures

pretreatment temperature/K	Si(4Al)(9P) (%)
as-synthesized	77
873	55
1073	40
1173 ^a	21
1173 ^b	12

^a Evacuation for 20 h. ^b Evacuation for 50 h.

percentage increases as the treatment becomes more severe. The results suggest a large modification of Si environments due to a solid-state transformation starting at around 1073 K and being favoured by heating at 1173 K for a long time. This may be explained by a diffusion at high temperatures of Si atoms of SiO₄ tetrahedra from one location, step by step, to another one. It is, therefore, necessary to check for any changes in the Al or P environments.

²⁷Al MAS NMR spectra are reported in Fig. 3 after pretreatments up to 1173 K. The as-synthesized sample gives two peaks [Fig. 3(a)]. The one at 36 ppm is assigned to tetra-coordinated Al (Al^{IV}). The 7 ppm peak already discussed¹³ and which disappears after the template removal at 873 K may be assigned to AlO₄ tetrahedra interacting with the template^{11,15} and giving Al^V species. Increasing the treatment temperature up to 1173 K does not modify significantly the shape of the ²⁷Al peak.

It has already been reported that the decomposition of the template at 873 K in other SAPO-37 materials induces a 3–4

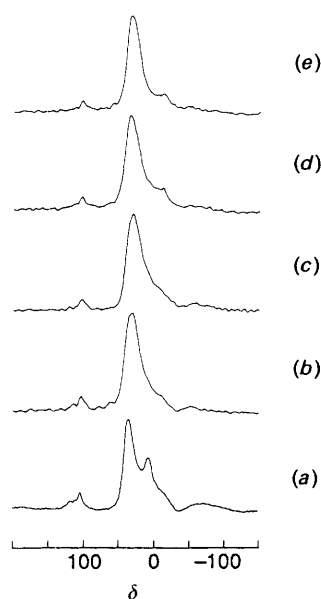


Fig. 3 ²⁷Al MAS NMR spectra of SAPO-37 as-synthesized (a) and after treatment at various temperatures (K): (b) 873, (c) 973, (d) 1073, (e) 1173 (20 h)

ppm decrease in the chemical shift (δ_{Al}) of ²⁷Al.¹³ The adsorption of compounds like H₂O, NH₃, pyridine or piperidine moves the chemical shift to higher values.¹³ A similar decrease, upon template decomposition, is obtained with the present sample (Fig. 4). Despite the inaccuracy of the chemical shifts, a similar trend observed in ref. 13 and here suggests that the decrease is meaningful. Since a simultaneous shift is observed in the ²⁹Si spectra (Fig. 1, Table 1), this suggests that a strong interaction with the template involves SiO₄ and AlO₄ tetrahedra. This may result from an interaction with the oxygen shared by the two tetrahedra. The changes in δ_{Al} as a function of the pretreatment temperature show an increase for the heat treatments at 1073 and 1173 K. The comparable increase seen in the presence of adsorbates¹³ was explained by the modification of the environment of some AlO₄ tetrahedra upon their interaction with these compounds. In the present case, the increase in δ_{Al} , also connected with a modification of the AlO₄ tetrahedra environment, results very likely from the new distribution of atoms in the framework. The increase in the number of Si(*n*Al) (*n* < 4) environments seen in Fig. 1 implies the appearance of AlO₄ tetrahedra surrounded by more than one SiO₄.

The ³¹P spectra of SAPO-37 pretreated up to 1095 K have already been published.⁶ The present sample gives similar spectra. No change is seen after further heating at 1173 K. The main characteristics of the spectra are, after heat treatment, a small broadening of the ³¹P peak, no significant change in the chemical shift and the non-systematic presence of a small peak around –30 ppm. These results suggest that no important modification in the second-nearest neighbours of the PO₄ species is taking place. The first neighbours have to be AlO₄ since no Si–O–P has been shown to exist in SAPO-37.¹¹

X-Ray Diffraction

The crystallinity was checked after each pretreatment temperature. Fig. 5 reports the XRD patterns obtained for some samples. It gives the diffractogram of the as-synthesized

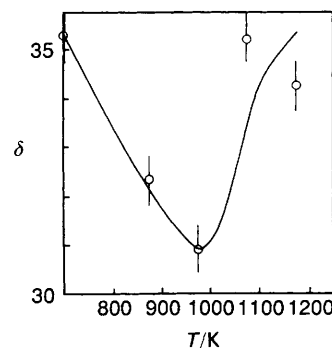


Fig. 4 Chemical shift of the ²⁷Al MAS NMR peak of SAPO-37 as a function of the pretreatment temperature (K)

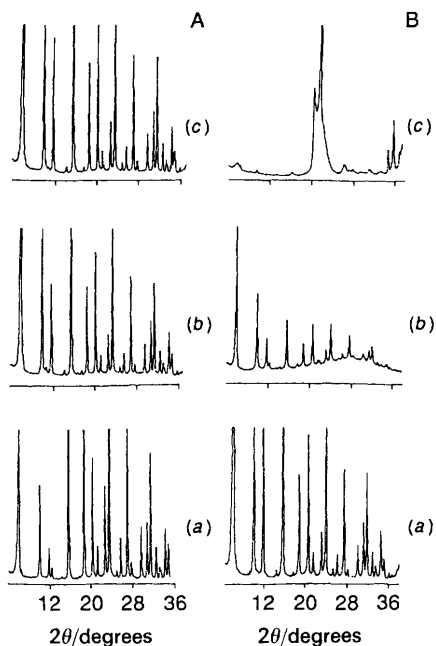


Fig. 5 XRD patterns of SAPO-37: A, (a) as synthesized, (b) evacuated at 873 K, (c) evacuated at 1173 K (20 h). B, (a) evacuated at 1173 K (50 h), (b) sample (a) kept for four months in a confined atmosphere, (c) as-synthesized, treated at 1273 K in an oven.

materials together with those recorded for the heated samples and after the ^{29}Si MAS NMR experiments. Such a check was performed in order to be sure that no crystallinity was lost, due to possible rehydration, during the long time needed to record the ^{29}Si MAS NMR spectra. Heating at 873 K, which removes the template, changes slightly the relative intensities of some bands [Fig. 5A(b)] and the unit cell parameter (a_0), as seen in Fig. 6. Further heat treatments at 973, 1073 or 1173 K (for 20 h) do not modify the general feature of the XRD pattern [Fig. 5A(c)], but change a_0 . Evacuation at 1173 K for 50 h does not give a different result [Fig. 5B(a)]. Keeping this sample in a confined atmosphere for four months at RT involves a rehydration since the XRD pattern [Fig. 5B(b)] shows a considerable loss of crystallinity comparable to that observed after heat treatments from 873 to 1073 K and rehydration at RT. The possible formation of a phase with a tridymite structure was suggested from NMR results of Fig. 1 and 2. This new phase does not give any characteristic peak in the XRD diffractograms. In order to favour this solid-state transformation, a sample was heated in the open air in an oven at 1273 K for 8 h. The diffractogram obtained

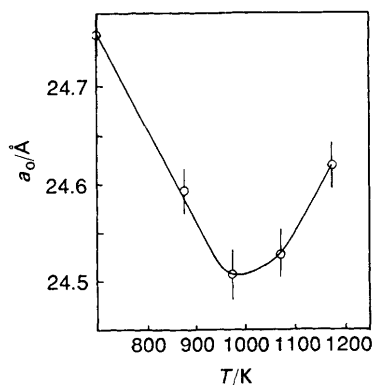


Fig. 6 Unit cell parameter, a_0 , of SAPO-37 as a function of the pretreatment temperature (K)

[Fig. 5B(c)] shows a drastic change. A mixture of tridymite and crystalalite structures is formed. This confirms the assignment of the -115.6 ppm ^{29}Si NMR peak in Fig. 1 and 2 to silica polymorphs.

The changes in the unit cell parameter are presented in Fig. 6. The a_0 values decrease until a pretreatment at around 973 K. Heating at higher temperatures then increases the a_0 parameter. These changes, which are somewhat higher than the range of accuracy (± 0.01 Å), reflect modifications in the bond angles and bond distances as the pretreatment temperature rises. The decrease related to the removal of the template at 873 K has already been observed in other SAPO-37 materials.^{12,13} The further decrease of a_0 down to a temperature of 973 K might be related to dehydroxylation. Above this temperature, the rise in a_0 is very likely related to the changes in the location of atoms, as seen from ^{29}Si and ^{27}Al MAS NMR spectra (Fig. 1–3). The new environment of the SiO_4 tetrahedra was shown to involve the formation of an Si–Al faujasite phase (Fig. 1 and 2, Tables 1 and 2). The unit cell parameter of this type of zeolite at low silicon content is higher than the values obtained for SAPO-37.⁵ This arises from the absence of phosphorus, which involves changes in bond angles and bond lengths since the P–O bond (0.152 nm)⁴ is shorter than the Si–O and Al–O bonds (0.160 and 0.174 nm, respectively). This might explain the rise in a_0 in Fig. 6 as the formation of the Si–Al faujasite phase is favoured.

Hydroxy Groups

A previous study¹⁶ using infrared absorption spectroscopy showed that a temperature of at least 823 K is necessary to decompose the template and to generate a maximum number of hydroxy groups. Fig. 7 reports the changes in the hydroxy group absorption range as a function of the pretreatment temperature from 873 to 1173 K. In addition to the usual pair of bands,^{8,16–19} Fig. 7 shows that the high-frequency (HF) band contains at least three bands at wavenumbers

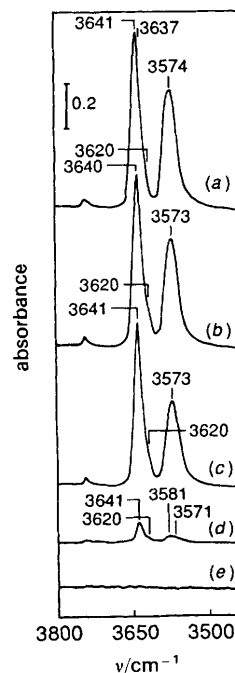


Fig. 7 Hydroxy group bands of SAPO-37 as a function of the pretreatment temperature (K) (6 h in dry air, 2 h vacuum). (a) 873, (b) 973, (c) 1073, (d) 1173 (8 h in air, vacuum), (e) 1173 (70 h in air, vacuum).

3641, 3637 and 3620 cm^{-1} . The broader, low-frequency (LF) band seems to include bands at around 3581 and 3571 cm^{-1} . The small band near 3745 cm^{-1} contains bands at 3740 and 3747 cm^{-1} . The very large overlapping of the components of bands precludes any detailed study. Nevertheless, Fig. 7 shows no significant sign of a specific decrease or increase of one of the components as the treatment temperature increases and as the environment of bridging hydroxy groups is changed. The main feature is that hydroxy groups are still present after heating at 1173 K for 10 h. A longer treatment time removes all the hydroxy groups [Fig. 7(e)]. The results show that between 1073 and 1173 K, where the framework atoms are moving, there are still some hydroxy groups which might facilitate this solid-state transformation.

Model for the Solid-state Transformation

The changes observed in the location of framework atoms are illustrated in Fig. 8. Note that this does not represent a zeolite material since the scheme is planar. The number of second-nearest-neighbours (eight here) is also different from that of SAPO-37 (*i.e.* nine). Nevertheless, it shows the principle of the generation of Si, Al and P atoms with various environments for a constant number of Si, Al and P. The study implies that Al—O—Al or Si—O—P bonds cannot exist.¹¹ In Fig. 8I, all Si atoms are surrounded by four Al as first neighbours and eight P as second [*i.e.* Si(4Al)(8P)], which represents the isolated Si atoms. An increase in temperature increases the vibration of the atoms from their equilibrium positions. This may favour the exchange of Si in SiO₄ with a next-nearest neighbour. For instance, atom C7 in Fig. 8I may exchange with C6 (Fig. 8II). Since Si—O—P bonds would be formed, the Si atom has to move to another place, for instance D6. At this point one may consider two possibilities. In Fig. 8III, all the Si atoms of Fig. 8I come closer to the central E5 Si atom using paths similar to that seen in Fig. 8II. This gives rise to an Si—Al faujasite phase, as seen in the ²⁹Si MAS NMR spectra. In Fig. 8IV, the D6 Si atom of Scheme 8II moves to D5, as is suggested in the hypothetical mechanism of replacement of an Al—P pair by two Si atoms in a theoretical AlPO₄ framework.¹⁷ The situation depicted in Fig. 8IV is highly unstable, since forbidden bonds are formed (two Si—O—P and three Al—O—Al). The system has to be modified so that the P atoms at D4 and C5 have to be exchanged with Si atoms, for instance those previously located at C3 and A5. The Al atom in D6 (Fig. 8IV) has to be either removed from the framework or replaced by an Si atom, coming, for example, from E9. The formation of Si islands like the one exemplified in Fig. 8V giving rise to Si(0Al) species is seen from ²⁹Si NMR experiments (Fig. 1 and 2, Tables 1 and 2). Since the numbers of each of the atoms Al, Si, P have to be constant in a crystal, this involves the possible formation of some defects, with few Al atoms being expelled (from E9 for instance) at the places where Al—O—Al bonds have to be avoided. The exchange of SiO₄ with PO₄ or AlO₄ tetrahedra could maintain the regular

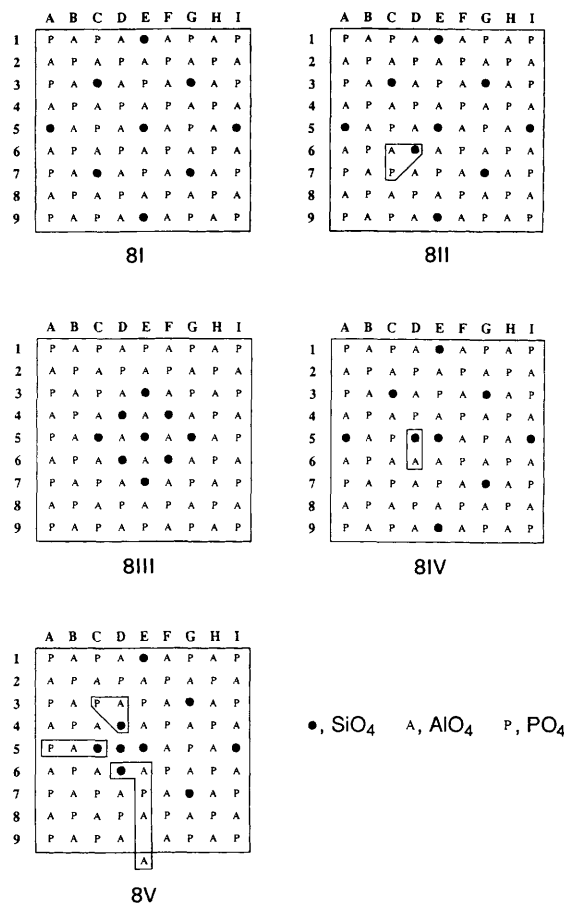


Fig. 8 Atom migration model in a planar system. I, Ideal homogeneous distribution of atoms; II, migration of one Si atom; III, formation of an Si—Al phase; IV, migration of one Si atom giving an unstable system; V, formation of Si islands.

Al—O—P—O—Al net in domains of the crystal not containing Si. The schemes presented in Fig. 8 are only some hypotheses among many others. They show the limiting cases. Table 4 gives the various types of environment created for SiO₄ and AlO₄ tetrahedra in these specific cases. For Si, there may be some Si in the first shell with possible Si, Al or P atoms in the second layer, depending on the first-nearest neighbours. For Al, the first shell may contain various amounts of Si and some Si as second-nearest neighbours. Note that the species Al(4Si)(8Al) generated in Fig. 8III is similar to the one which exists in X faujasite (with, of course, in the true faujasite structure, nine Al instead of eight in the second layer). The P environments always contain four Al in the first sphere of coordination (no Si—O—P bonds). They may have two or more Si in the second sphere. One may imagine that in the true SAPO-37 structure such species exist after heating at 1173 K, with even more complex situations, if

Table 4 Si and Al environments from model in Fig. 8

scheme	Si environment	atom	Al environment	atom
8III	Si(4Al)(8Si)	E5	Al(4Si)(8Al)	D5, E4, F5, E6
	Si(4Al)(3Si,5P)	C5, E3, G5, E7	Al(1Si,3P)(8Al)	B5, E2, H5, E8
	Si(4Al)(5Si,3P)	D4, F4, F6, D6	Al(2Si,2P)(8Al)	C4, D3, F3, G4, G6, F7, D7, C6
8V	Si(4Si)(8Al)	D5	Al(2Si,2P)(1Si,7Al)	C4, E4, E6, C6
	Si(1Si,3Al)(3Si,5P)	C5, D4, E5, D6	Al(1Si,3P)(1Si,7Al)	B5, D3, F5, D7
initial	Si(4Al)(8P)	E5	Al(1Si,3P)(8Al)	

one considers all the possible transformations. Islands may be larger than that considered here and they may include a variable number of Al atoms. This approach explains the results obtained after the 1173 K pretreatment, *i.e.* the formation of complex ^{29}Si NMR spectra with the generation of Si–Al faujasite peaks, the shifts of δ_{Al} , the slight broadening of the ^{31}P NMR peak and the changes in the unit cell parameters. The present model starts from the case where all the Si atoms are 'isolated' (Fig. 8I). This is close to the present experimental situation [Fig. 1(a)]. For materials in the as-synthesized form already having siliceous islands with Si–Al faujasite phases and AlPO_4 zones,^{3,4} Fig. 8I–8V would apply to the parts of the framework where the Si atoms are initially isolated (AlPO_4 zones). This would generate new silicon-rich and Si–Al domains and/or increase the size of the as-synthesized ones.

Conclusion

The crystal structure of SAPO-37 has been shown to be stable up to around 1200 K.¹² Since XRD does not distinguish between the location of Si, Al and P atoms, the result masks a large change occurring in the material above around 1100 K. In this range of temperature, the atoms may start to diffuse in the solid in order to reach a better thermodynamic equilibrium. SiO_4 tetrahedra tend to form clusters probably leaving small AlPO_4 domains free of silicon atoms. The faujasite structure is maintained up to the point (above around 1200 K) where it is transformed to a mixture of tridymite and cristobalite structures. The kinetics of all these modifications are slow, as seen from the progressive increase with time of the -115.6 ppm peak of ^{29}Si in MAS NMR after heating at 1173 K.

These transformations are particularly important in catalysis where the acidity of the material depends on the phases present. The increase in *n*-octane cracking up to 1173 K can be explained⁹ by the formation of new Si–O–Al bonds where the environments for Si (richer in Si) are more favourable to strong acidity.¹⁹

Materials showing after synthesis Si atoms either 'isolated' or non-uniformly distributed, could also be modified upon heating by the migration of atoms. This would reduce the amount of 'isolated' Si atoms and increase the size and/or the number of siliceous patches in AlPO_4 domains.

This study shows that the chemistry of molecular sieves of the SAPO type is very different from that of silicoaluminate type zeolites. New properties are likely to be discovered.

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