

The Role of the Template in Directing the Si Distribution in SAPO Zeolites

R. Vomscheld, M. Briend, M. J. Peltre, P. P. Man,[†] and D. Barthomeuf*

Laboratoire de Réactivité de Surface, URA 1106 CNRS, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 PARIS CEDEX 05 – FRANCE

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X-ray diffraction and ²⁷Al and ²⁹Si MAS NMR are used to study the interaction of the templates (morpholine or TEOH) with the SAPO-34 framework (chabasite structure) and to characterize the distribution of Si in the lattice. The interaction of the template with Si–O–Al bonds suggests the formation of penta- and hexacoordinated Al. Specific limits of Si contents (x_{Si}) determine areas where Si(4Al) species are isolated (Si(4Al,9P)) or nonisolated (Si(4Al, n P, m Si)) or where Si forms islands. The two main parameters involved are the upper charge introduced by the template (b) and the upper x_{Si} values (d) derived from topology, to have isolated Si. Two main cases of the distribution of Si are whether $b < d$ or $b > d$. The results obtained for SAPO-34 are extended to any other SAPO.

Introduction

The use of organic templates in the synthesis of Si–Al zeolites gives rise to highly siliceous materials. It is well accepted that this arises from the large size of these molecules, which limits their number in the zeolite cages. Since they compensate the framework charge, this also restricts the number of negative charges (i.e., AlO₄ tetrahedra) which can be introduced in the framework. Such an effect should also occur in crystallized silicoaluminophosphates (SAPOs), in addition to any structure-directing and space-filling roles, the template being essential for the compensation of framework charge associated with SiO₄ tetrahedras.¹ It was proposed that when the charge, calculated from the Al content, exceeds the maximum number of template cations, other extraframework cations (H⁺ or inorganic ions) can supplement the available template.¹ In SAPO-34 (CHA) the size and morphology of the template should then govern the number of molecules in cages, i.e., the number of available positive charges and consequently the limit negative charge of the framework.¹ The aim of this paper is to show that in fact the template also orientates the distribution of Si in the lattice. In addition it was shown that isolated Si (i.e., Si with 4Al as first neighbors and 9P as second ones, Si(4Al,9P) which implies no Si closer than the fourth shell of tetrahedra) cannot exist in SAPO-34 above an atomic fraction of around 0.11.² This study will show that depending on the template, at high Si contents, Si may be incorporated either as an isolated species with only P as second neighbor (Si(4Al,9P)), as a nonisolated Si(4Al) species, Si having one or two Si as second neighbors (i.e., Si–Al–Si pairs or Si–Al–Si–Al–Si species), or as Si islands. The Si–Al–Si way of writing is used to represent Si–O–Al–O–Si species in the framework.

Experimental Section

Two series of materials were synthesized using either tetraethylammonium hydroxide (TEOH)^{3–5} or morpholine (C₄H₉NO)^{3,5,6} as templates. All the samples are highly crystalline. They are referred to as series T (TEOH) and M (morpholine), respectively. Their general formula is Si_xAl_yP_zO₂.

Table 1 gives the chemical composition of the materials as determined by energy dispersive X-ray spectrometry (EDX)

TABLE 1: EDX Analysis of Samples Synthesized with Morpholine (M) or TEOH (T)

sample	x_{Si}	y_{Al}	z_{P}	$y - z$
M-0.10	0.10	0.50	0.40	0.10
M-0.14	0.14	0.49	0.37	0.12
M-0.16	0.16	0.49	0.35	0.14
M-0.18	0.18	0.49	0.33	0.16
M-0.24	0.24	0.44	0.32	0.12
M-0.33	0.33	0.40	0.27	0.13
T-0.10a	0.10	0.49	0.41	0.08
T-0.10b	0.10	0.47	0.43	0.04
T-0.11	0.11	0.49	0.40	0.09

analysis. The samples are referred to by their total Si atomic fraction. The numbers in the last column correspond to the amount of Si incorporated through mechanism 2 in which Si replaces P in a theoretical AlPO₄ framework.⁷ They are obtained from $y - z$.¹ For the series T the chemical analysis, which gives access to $y - z$ is not accurate due to the deposition, on the external surface of grains, of very small particles of Al-rich components. The content in the template is determined from C and N by chemical analysis. The water content in the as synthesized materials estimated from TGA experiments is about 2.6 and 2 mol/cage for the series M and T, respectively.

²⁹Si and ²⁷Al MAS NMR spectra were obtained as previously described on as synthesized materials.^{8–10} A Bruker MSL-400 multinuclear spectrometer was used for ²⁹Si (79.5 MHz) and ²⁷Al (104.2 MHz) spectra. Chemical shifts are reported in ppm from external tetramethylsilane (TMS) for ²⁹Si and Al(H₂O)₆³⁺ in a nitric acid solution of Al(NO₃)₃ for ²⁷Al. The sign convention of high-frequency (low-field, paramagnetic, deshielded) shifts being positive is used. For ²⁹Si spectra the standard Bruker double bearing probe and a 7 mm o.d. ZrO₂ rotor were used. The acquisition parameters are as follows: a $\pi/4$ pulse length of 2.5 μ s is applied with a 5 s recycle delay and a rotor spinning rate of 4 kHz and 30 000–35 000 scans were acquired to obtain an adequate signal to noise ratio. The spectra were deconvoluted with the program GLINFIT 3004 using Gaussian line shapes. Spin-locked cross-polarization (CP/MAS) spectra were obtained with proton high-power decoupling. The setting of the Hartmann–Hahn condition was performed with a polydimethylsiloxane (PDMS) sample. The proton $\pi/2$ pulse length, the contact time, and the recycle delay for our samples were 6.5 μ s, 5 ms, and 5 s, respectively; 10 000 scans were acquired. ²⁷Al MAS spectra were acquired with a probe from DOTY Scientific and a 5 mm o.d. silicone nitride rotor spinning

[†] Laboratoire de Chimie des Surfaces, URA 1428 CNRS, Université Pierre et Marie Curie, same address.

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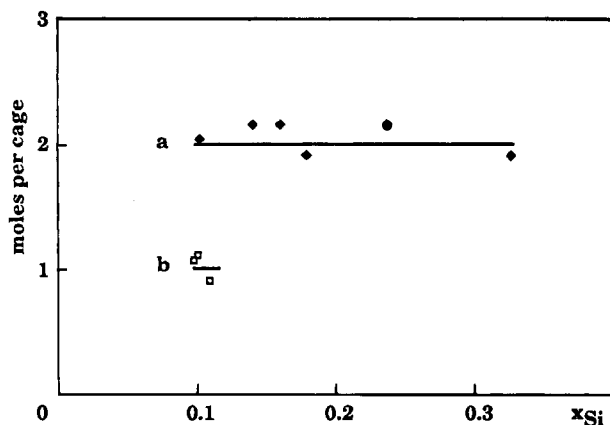


Figure 1. Content in template per cage of SAPO-34 as a function of Si level. (a) Morpholine and (b) TEOAH.

TABLE 2: Unit Cell Parameters and Volume of Samples Synthesized with Morpholine (M) or TEOAH (T)

sample	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)
M-0.10	13.76 ± 0.01	14.83 ± 0.01	2432 ± 5
M-0.14	13.80 ± 0.01	14.86 ± 0.01	2451 ± 5
M-0.16	13.82 ± 0.01	14.87 ± 0.01	2458 ± 5
M-0.18	13.83 ± 0.01	14.89 ± 0.02	2468 ± 7
M-0.24	13.82 ± 0.01	14.86 ± 0.01	2458 ± 5
M-0.33	13.83 ± 0.01	14.87 ± 0.01	2465 ± 5
T-0.10a	13.80 ± 0.01	14.80 ± 0.02	2440 ± 7
T-0.11	13.79 ± 0.01	14.83 ± 0.01	2444 ± 5

at 8 kHz. A single $\pi/20$ radio frequency pulse was used with a repetition time of 2 s.

Results and Discussion

SAPO-34 Template Interaction. Figure 1 reports the changes in the content of morpholine (moles per cage) as a function of Si content. The constancy of the value indicates that the cages are saturated with the template already at the lowest Si content (M-0.10 sample). Lower template contents are obtained for TEOAH. It was already observed that less TEOAH per average TO₂ was introduced in SAPO-34 compared to morpholine.^{1,5} In order to have a better understanding of this result the two series of materials are studied since both morpholine and TEOAH can neutralize one negative charge.

The crystal has a rhombohedral symmetry with parameters of the hexagonal unit cell close to those of chabasite.^{6,7} Each unit cell contains 3 cages and 36 T sites. The multiplicity of T sites is one. The values of *a* and *c* and those of the unit cell volume are given in Table 2 for the various samples. For a comparable Si content the two series M and T have similar values of *V* the unit cell volume and the parameter *c* and a slightly lower *a* value for M-0.10. In the M series, increasing the Si content tends to give higher *a*, *c*, and *V* values.

The results do not seem to be dependent on the size of the two template molecules which is not very different. It is close to 6.5–7.5 Å for TEOAH¹¹ and is estimated for morpholine to be similar (6.7 Å) to that of cyclohexane, which has also a chair conformation. Nevertheless TEOAH is more bulky with the four ethyl groups.

An interaction between the template and the framework of SAPOs is well documented.^{8,10,12–14} The negatively charged framework oxygens of Si–O–Al bonds are neutralized by the positive ions issued from the template. This may perturb the corresponding AlO₄ and SiO₄ tetrahedra.

The interaction between the template and the AlO₄ tetrahedra was studied using ²⁷Al MAS NMR.¹³ Figure 2 reports the spectra of samples of the two series M and T. All spectra show

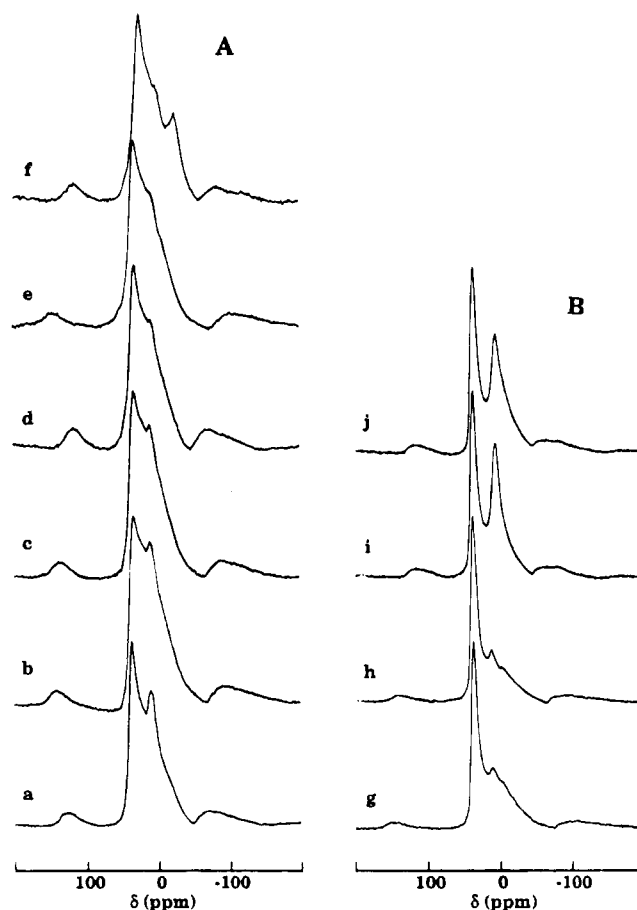


Figure 2. ²⁷Al MAS NMR spectra of as synthesized SAPO-34 prepared with (A) morpholine or (B) TEOAH as templates. (a) M-0.10, (b) M-0.14, (c) M-0.16, (d) M-0.18, (e) M-0.24, (f) M-0.33, (g) T-0.10a, (h) T-0.10b, (i) T-0.11, and (j) ultrasonicated T-0.11.

a peak at 37–39 ppm assigned to tetrahedral Al (Al^{IV}). A difference is observed between the two series for the other peaks. TEOAH gives (Figure 2B) two types of peaks depending on the batch, at 7 and 12 ppm.

In the M series, a regular change is seen as the Si level rises. Starting from the M-0.10 sample, a peak near 12 ppm becomes progressively less defined while the Al^{IV} peak broadens and a new peak is growing at around –11 ppm. It is rather well resolved in sample M-0.33. For both series M and T the peaks at 7, 12, or –11 ppm cannot be removed by ultrasonication but disappear after the template decomposition at 873 K. Peaks different from the Al^{IV} were already observed for other SAPOs¹³ at chemical shifts (ppm) for SAPO-34 at 3.4¹³ and for SAPO-37 at 2.4,¹³ 15.8,¹² 9,¹⁵ 4.3,¹⁶ or 7.8.¹⁰ When quadrupolar^{12,13} or impurities effects¹⁵ are considered, the peaks were assigned to an interaction of the template with some AlO₄ tetrahedra.^{8,10,12,13} With these ideas in mind, the peaks at 7 or 12 ppm could be assigned to the pentacoordination Al^V of some AlO₄ close to SiO₄ tetrahedra. It might not be surprising to find different values, either 7 or 12 ppm depending on the template and the sample. The distortion of the tetrahedra may be very different due to the shape and chemical reactivity of TEOAH or morpholine and to the synthesis conditions. This would be in line with the various chemical shifts cited above in SAPO-37 for different preparation modes.

The peak at –11 ppm in the M samples is in a range already observed upon water adsorption in template-free SAPO-34¹³ or SAPO-37.^{8,16} It may be related to hexacoordinated Al (Al^{VI}), but no specific connection with adsorbed water was found in the present case.

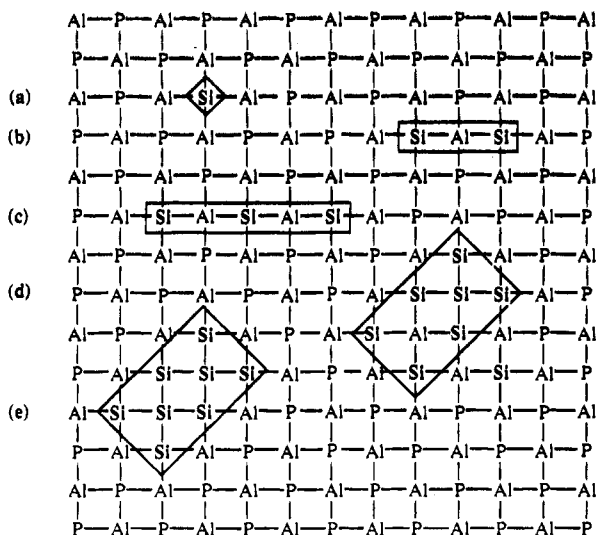


Figure 3. Scheme showing various possible ways of introducing Si in a planar, nonzeolitic, AIPO network. (a) isolated Si, (b) independent Si-Al-Si pair, (c) nonisolated Si(4Al) species, (d) Si-Al phase, and (e) Si island (oxygen atoms are not represented for clarity).

At low Si levels the peak at -11 ppm is very likely present in the broad basis of the spectra in Figure 2 parts A and B. It becomes more distinct in Figure 2A as the Si content rises, simultaneously with the observation by electron microscopy of some amorphous silica. Nevertheless it appears not clear how this amorphous phase would change the ^{27}Al MAS NMR spectra. It could be proposed that the increased formation of this peak assigned to Al^{VI} , as the Si content rises, may be related to more AlO_4 tetrahedra in a configuration favoring the interaction template/ TO_4 . No extraframework Al is detected. As concerns framework Al, as will be seen further, at high Si levels, the environment of some AlO_4 tetrahedra is changed. Starting from four PO_4 neighbors in AIPOs, this number may reach up to four SiO_4 (Figure 3d). The interaction of the template with the framework could depend on this parameter.

The influence of the template on SiO_4 tetrahedra is seen from the shift, detailed elsewhere,¹⁷ of the Si(4Al) MAS NMR peak from -91.6 to -94.2 ppm upon removal of TEAOH.

Distribution of Si Atoms. SAPO-34 Case. Figures 4 and 5 give the ^{29}Si MAS NMR spectra of the samples with that of their Si-Al counterpart chabasite. In the M series only the peak at -90.3 ppm is observed in M-0.10. It is assigned to Si(4Al) species.^{13,14,18} It may be described as isolated Si (Si-(4Al,9P)). When the Si content in the same M series is increased, the progressive appearance of peaks in the range -93 to -115 ppm is evident. These peaks were ascribed in other SAPOs to Si(n Al) species in siliceous domains (pure Si islands or Si-Al phase).^{9,15,19,20} These peaks start to be seen for the samples with $x = 0.14$ – 0.16 . No well-defined peak is seen in all the M materials in the Si-Al chabasite range, i.e., at around -84.8 , -88.5 , -93.5 , -98.8 , and -104.5 ppm (Figure 5d). This suggests the absence of a Si-Al chabasite phase except perhaps to a minute extent for the M-0.33 sample. The CP MAS results confirm the shifts of the peaks found in MAS experiments. Not significant enhancement of any specific peaks is detected (Figure 4B). The SAPOs synthesized with TEAOH and which have a low Si level (Figure 5 parts Aa–Ac and Bc) show peaks in the range -93 to -110 ppm in addition to the -90.3 ppm peak. This is in contrast with the case of the morpholine series for the same Si content. It indicates the existence of siliceous domains even at low Si levels ($x_{\text{Si}} = 0.09$ – 0.11). Some of the chabasite phase may not have been excluded in sample T-0.11 giving the shoulders around -85 to -88 ppm.

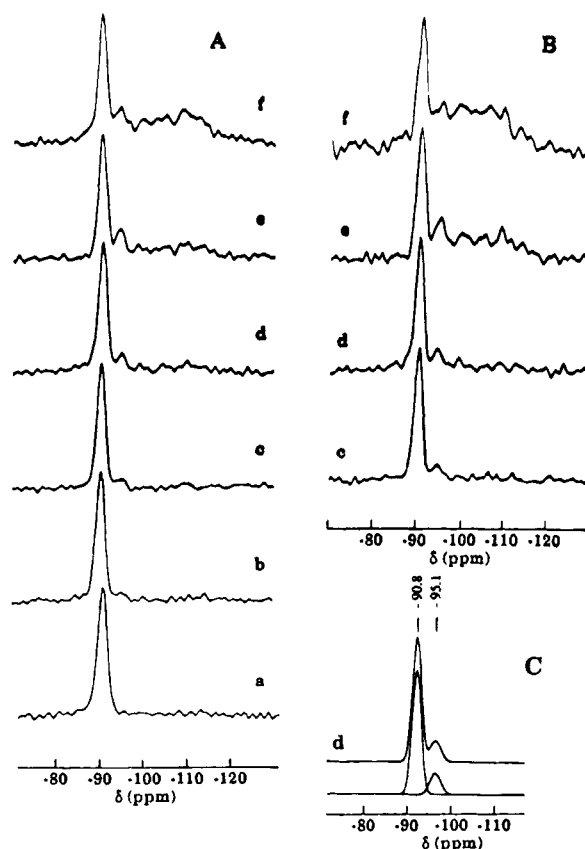


Figure 4. ^{29}Si MAS (A), CP MAS (B), and simulated (C) NMR spectra of SAPO-34: (a) M-0.10, (b) M-0.14, (c) M-0.16, (d) M-0.18, (e) M-0.23, and (f) M-0.33.

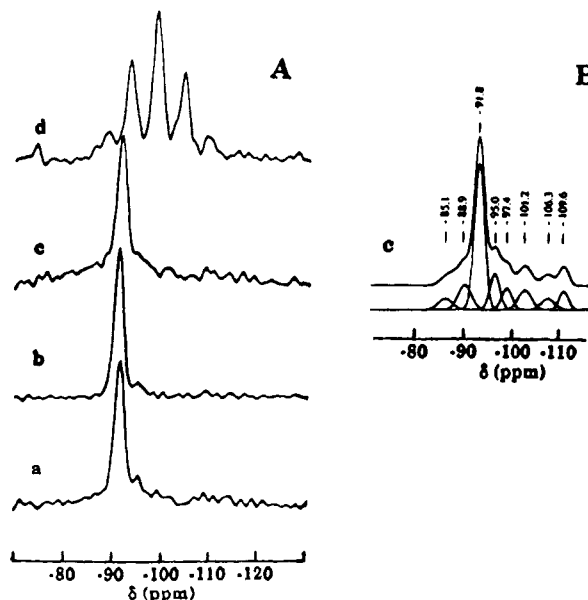


Figure 5. ^{29}Si MAS (A) and simulated (B) NMR spectra of SAPO-34: (a) T-0.10a, (b) T-0.10b, (c) T-0.11, and (d) chabasite with Si/Al = 2.34.

In order to explain the different behavior of the two series M and T at low Si contents and that of the M samples at increasing Si levels, attention should be paid to the distribution of Si in the framework. It results from the balance between the number of framework charges made possible by the number of template molecules encaged in the structure and that introduced by the Si atoms. A constraint is that the second number cannot be higher than the first one. This implies that

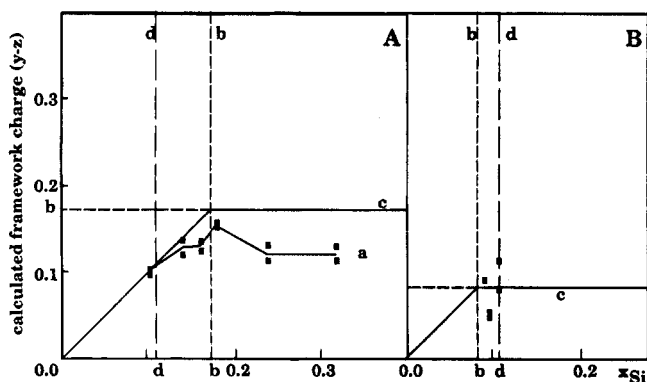


Figure 6. Charge ($y - z$) as a function of Si content x_{Si} in SAPO-34 framework. Experimental charge (n) for the (A) M and (B) T series. Experimental points: (a) maximum possible charge introduced by the template and Si, (b) theoretical upper ordinate of experimental results, (c) maximum Si content to have isolated Si species and (d) data from ref 2.

SiO_4 tetrahedra will reach a configuration which adjusts the overall charge to the upper limit determined by the amount of template.

A second known constraint as to the distribution of Si atoms is that above $x_{\text{Si}} \approx 0.11$ in SAPO-34 the SiO_4 tetrahedra cannot be isolated.² This value results from the topology of the structure. It means that a SiO_4 tetrahedron may have, as neighbor in the second shell, another SiO_4 if $x_{\text{Si}} > 0.11$. In order to better understand the consequence of these two constraints on the arrangement of Si in the framework, one may recall that Si may, in a hypothetical AlPO framework, replace only P (substitution mechanism 2 SM2) or both P and Al (SM3).⁷ Since this last mode would involve Si—O—P bonds, which are unlikely,^{1,13,21} SM3 must be accompanied by SM2. This is schematically illustrated in Figure 3 for a planar, i.e., nonzeolitic framework. Figure 3a represents an isolated Si where the second shell of SiO_4 tetrahedra consists of only PO_4 tetrahedra. Figure 3b shows the possibility of formation of Si—Al—Si pairs not yet described per se as existing in a SAPO phase. Species Si(4Al) involving more than two Si can also be envisioned (Figure 3c). Such species give Si(4Al) peaks in ^{29}Si MAS NMR identical to those of isolated Si. Mechanism SM3 + SM2 gives rise to siliceous islands as in Figure 3d and e. A Si—Al phase is seen in Figure 3d while a pure Si island is represented in Figure 3e. In SAPO-5 or SAPO-37 the existence of a Si—Al phase was shown to exist in some cases from ^{29}Si NMR experiments.^{19,22,23} It has not been observed in SAPO-34 (no significant peaks in Figures 4 and 5 in the chabasite ppm range at -84.8 to -104.5 ppm). The negative charge introduced in the framework with Si is one for Figure 3a—c, i.e., for the SM2 case and less than one in Figure 3d and e (SM2 + SM3).^{9,20,24}

The above results and the information schematically illustrated in Figure 3 lead to Figure 6. It gives on the ordinate the charge of the framework calculated from the chemical composition (Table 1). It is equal to $y - z$ and also to the amount of Si incorporated through mechanism 2 since in SM3 the replacement of Al + P generates no charge. The value is expressed in Figure 6 for the formula $\text{TO}_2\text{:Si}_x\text{Al}_y\text{P}_z\text{O}_2$, i.e., per average theoretical TO_2 , T consisting in this case of the hypothetical $\text{Si}_x\text{Al}_y\text{P}_z$ species ($x + y + z = 1$). The abscissa is the atomic fraction of Si from Table 1. The experimental results give the curve a for the M series. The horizontal line b represents the charge brought by the template. This is from Figure 1, around two charges per cage for morpholine and one for TEOH. This gives for the formula TO_2 experimental values of 0.170 and 0.083 for the M and T series, respectively. The values referred to as b

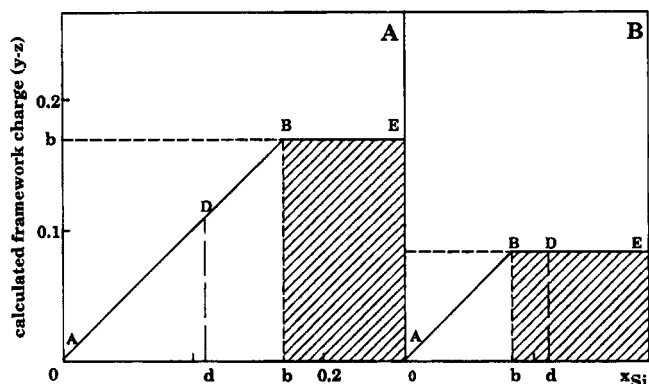


Figure 7. General representation for SAPOs of the framework charge ($y - z$) as a function of x_{Si} . See the legend to Figure 6 for b and d. Line ABDE: upper charge possible. See text for meaning of points B, D, and E. Portion with grids: areas where Si islands cannot be avoided.

also represent the upper charge which can be introduced by Si in the framework. So it gives (vertical line b) the upper amount of Si which can enter the framework through SM2 since, as said above, the charges created by Si cannot exceed those linked to the template. The full line c is the envelope which should limit all the experimental points. The charge of the framework is at the most equal to x_{Si} for $x_{\text{Si}} < b$, or constant and equal to b for $x_{\text{Si}} > b$.

The x_{Si} limit value² above which the Si content is too high to have incorporation of additional Si as isolated species, as in Figure 3a, is referred to as the abscissa d. At higher Si levels other Si sites must be formed at the expense of isolated Si. They may be of the Si(4Al) type (Figures 3b and c) and/or consist with siliceous islands (Figure 3e, eventually 3d). This x_{Si} limit is represented in Figure 6 by the vertical straight line d. It must be noted that at a Si content lower than the abscissa d, nonisolated Si(4Al) entities (Figure 3b and c) or Si islands might already be formed depending on synthesis conditions, together with the isolated ones.

Considering first the M series (Figure 6A), only one sample (M-0.10) is in a range where the Si atoms can be isolated. It gives in Figure 4a only the Si(4Al) peak. For the SAPOs M-0.14 and M-0.16, the Si content is still lower than the upper authorized charge but too high for isolated species ($x_{\text{Si}} > d$). The Si must come closer forming various types of nonisolated Si(4Al) species (Figure 3b and c) and eventually some Si islands (Figure 3d and e). This is reflected in curves b and c in Figure 4A by the intense Si(4Al) peak which represents both isolated and nonisolated species and by small peaks at Si(n Al) with $n < 4$ characteristic of few Si in islands. The sample M-0.18 reaches the range where in addition to the previous case the charge generated has to be at the most 0.170. Some Si must agglomerate in islands to fulfill the charge requirement by reducing the average charge per Si.⁹ The decomposition (Figure 4Cd) of the corresponding spectrum (d in Figure 4A) indicates that approximately 0.14 Si contributes to the -90.8 ppm peak of Si(4Al). This is more than the x_{Si} limit value of 0.11 for isolated Si. This confirms that in addition to Si islands, some Si are present as nonisolated Si(4Al) species in this sample. At higher Si levels the formation of islands is important, greatly decreasing the framework charge. This is corroborated by the ^{29}Si MAS NMR spectra, Figure 4A curves e and f, where peaks of Si(n Al), with $0 < n < 4$, are growing.

For the materials series T (Figure 6B) the abscissas b and d are in reverse order compared to series M due to the low maximum charge permitted by the template content. Experimentally, no high Si content could be obtained. The low

accuracy on $y - z$ for this series mentioned in the Experimental Section leads to approximate coordinates of the experimental points in Figure 6B. Nevertheless they fall in the range where Si islands must be formed ($x_{\text{Si}} > b$). This is confirmed by the ^{29}Si MAS NMR results of Figure 5A, curves a–c, and Figure 5B which show a variety of Si(n Al) peaks.

General Case of SAPO's. The constraints imposed in SAPO-34 to draw Figure 6 exist in any SAPO. (i) The framework charges introduced by Si cannot exceed the charge b brought by templates. (ii) Above a given Si level (point d in Figure 6) the SiO_4 tetrahedra can no longer be isolated and should form nonisolated Si(4Al) entities or islands. The trends given in curve c of Figure 6 deduced from these grounds are then valid for other SAPOs. This is experimentally verified. The general shape of curves giving the acid site number as a function of x_{Si} is comparable to this curve c in Figure 6 for SAPO-5²⁴ and SAPO-37,²⁰ for example.

Figure 7 gives a more general representation, for any SAPO, showing the two cases $b > d$ (Figure 7A) or $b < d$ (Figure 7B). The shaded area represents the range where Si must form islands in order to reduce the average charge per Si and not introduce more charges than is acceptable to the template. The straight line AD Figure 7A or AB Figure 7B is the place where each Si creates one charge (isolated or nonisolated Si(4Al) species).

The straight line DB Figure 7A corresponds to Si forming nonisolated Si(4Al) species since Si still generates one charge per atom but can no longer be isolated ($x_{\text{Si}} > d$). This domain does not exist in Figure 7B since on the abscissa $b < d$. The horizontal BE line in both parts A and B Figure 7 belongs to the domain where Si islands must be formed in addition to the previous states. Knowing b and d for any SAPO will allow one to predict if one may expect nonisolated Si(4Al) species or at what Si content Si islands cannot be avoided. For instance in SAPO-37 it is well accepted that the number of template molecules is around 24 per unit cell.^{9,12} This corresponds to 0.11 charge per average TO_2 (b value). The abscissa of d is 0.125.^{2,12,15} This means that $b < d$, and then the SAPO-37 case is relevant to Figure 7B. This is comparable to the T series in SAPO-34. Experimental studies of ^{29}Si MAS NMR^{9,20} confirm this point. They show unambiguously that peaks in the range of Si(n Al) with $n < 4$ are observed at $x_{\text{Si}} \geq 0.12$ – 0.13 . There is no experimental case like that in SAPO-34, Series M, (Figures 4A and 6A) where nonisolated Si(4Al) entities can be suspected to exist, i.e., where for $x_{\text{Si}} > d$ the contribution of the Si (4Al) NMR peak is very large with small Si(n Al) peaks ($n < 4$). Below the AB line, Si islands might eventually be formed at any x_{Si} at the expense of isolated Si. This is not observed in SAPO-37.²⁰ For various SAPOs the value of d is estimated from the topology of the structures.² It varies from around 0.13 for AFY to 0.08 for AEL structures. Depending on the size or shape of the template different b values can be expected for the same structure. This determines not only the total possible charge as in the usual case of Si–Al zeolites but also the distribution of Si as isolated atoms or nonisolated Si(4Al) species or as Si islands. In addition, synthesis conditions may also affect the Si arrangement for similar Si contents as is seen when comparing for SAPO-37 for instance the very different ^{29}Si MAS NMR results published.^{9,19,23,25} The effect may be related to the interaction template framework discussed above. Nevertheless experimental points must lie on or below the ABE line in Figure 7.

In conclusion, at first, the interaction of the template with the SAPO-34 framework disturbs both the AlO_4 and SiO_4 tetrahedra as seen from MAS NMR. New ^{27}Al peaks suggest the formation of penta- and hexacoordinated Al depending on the synthesis conditions. Second, the importance of the template appears not only in its role of directing the structure but also of governing the distribution of Si in the framework. For a given structure topology which gives the limit number of Si present as isolated species,² the number of template molecules (or ions) determines the maximum charge possible. This controls in turn the way Si is distributed, as isolated or nonisolated Si(4Al) species or as Si islands. The hypothesis of the existence of such nonisolated Si(4Al) entities, for instance Si–Al–Si pairs, in an AIPO structure was not yet described per se.

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