SMALL PORE $AlPO_4$/SAPO STRUCTURES FORMED IN DEPENDENCE ON THE SILICON CONTENT OF THE SYNTHESIS GEL*

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The synthesis of small pore $AlPO_4$/SAPO molecular sieves (structures 14, 17, 18, 34) has been investigated at varying silicon content in the gel and with different kinds of templating agents. The samples were characterized by X-ray diffraction, adsorption, thermoanalysis and infrared spectroscopy. Independently of the kind of template at high silicon offer in the gel the crystallization of SAPO-34 is favoured whereas e.g. the formation of SAPO-17 is suppressed. Without silicon, $AlPO_4$-18 is formed instead of $AlPO_4$-34. The nature of template-framework interaction is discussed as a structure-directing factor.

The isomorphous substitution of heteroatoms is an important reaction in the preparation of aluminophosphate-based molecular sieves. In $AlPO_4$ sieves isomorphic substitution of phosphorus and/or aluminium has been claimed for a large number of elements, including elements which do not fulfill Pauling's radii criterion for the tetrahedral coordination.

Concerning the experimental data it is often difficult to determine the manner and extent of heteroatom incorporation into the framework of $AlPO_4$ structures. Furthermore, literature data demonstrate difficulties in the isomorphous substitution for certain structures, and it seems that inherent limitations exist for the exchange of the tetrahedrally coordinated framework atoms. In this paper the isomorphous substitution of silicon in small pore $AlPO_4$ structures is studied.

EXPERIMENTAL

Sample Preparation

$AlPO_4$-18 and SAPO-34 were obtained with tetraethylammonium hydroxide and morpholine as templating agents on the basis of procedures derived from those given in the U.S. patents[1,2]. $AlPO_4$/SAPO-17 were prepared with cyclohexylamine[1]. The procedure for the synthesis of $AlPO_4$-14 with piperidine as template was published elsewhere. The typical crystal morphologies

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of the four structures are as follows: 17 — needles (30 μm (ref.[4])); 14 — tabular habits (10 μm (ref.[3])); 34 — cubes (1 μm); 18 — sheets (1 μm).

Measurements

The order structure of the synthesized samples was investigated by an X-ray powder diffraction method. These measurements were performed in the X-ray scattering range of 3·0 – 20·0° (scattering angel θ; monochromatic Cu-K_α-radiation) with a proportional counter diffractometer HZG 3 (Freiberger Präzisionsmechanik GmbH).

Adsorption isotherms were measured gravimetrically using a McBain balance fitted with a quartz spring. Equilibrium pressures were determined by means of a capacitance pressure meter (MKS Baratron) calibrated from 0·1 to 10^5 Pa.

The thermal analyses (DTA and TG) were carried out using a Derivatograph instrument (MOM, Budapest). Samples (200 mg) saturated with water at room temperature were heated from 293 to 1 073 K at a rate of 5 K min^{-1} in an air stream. For DTA measurements α-Al_2O_3 powder was used as the reference material.

The in-situ DRIFT (Diffuse Reflectance Infrared Fourier Transform) studies of the template decomposition were carried out with samples mixed with KBr (1 : 100) in a nitrogen stream up to a temperature of 700 K. All DRIFT measurements were performed with a Fourier spectrometer IRF 180 (resolution: 4 cm^{-1}) using a heated sample cup. DRIFT spectra are shown in Kubelka–Munk units[5] $f(R'_\infty)$ that are related to the absorbance coefficient k of the sample and its scattering coefficient s:

$$f(R'_\infty) = (1 - R'_\infty)^2/2R'_\infty = k/s\,,$$

where

$$R'_\infty = R'_\infty(\text{sample})/R'_\infty(\text{standard})\,.$$

R'_∞(sample) stands for the single-beam spectrum of the diluted sample and R'_∞(standard) represents the single-beam spectrum of the pure KBr. It was shown that DRIFT spectra of diluted samples are in good agreement with commonly used absorbance spectra[6,7].

RESULTS AND DISCUSSION

In Figures 1 – 3 the X-ray line diagrams are given. They are related to the variation of silicon content in the synthesis gel and different kinds of templates whereas the other gel composition and the conditions of crystallization remained constant. As shown in Fig. 1 the pure erionite-like structure 17 (ref.[8]) crystallizes only in a narrow range of the SiO_2/Al_2O_3 molar ratio. From the calorimetric measurements of the heat of NH_3 chemisorption[4] and from the ^{29}Si MAS NMR spectra[9] it follows that up to 1 silicon atom per unit cell the silicon offered in the gel is a monomer and completely incorporated in the structure. At $SiO_2/Al_2O_3 \geqq 0{\cdot}1$ chabazite-like phases 35 and 34 (ref.[10]) start to crystallize. The X-ray lines of sample B in Fig. 1 are in full agreement with those given in the patent[1]. At higher silicon content the structure 17 is suppressed, and a pure SAPO-34 may be obtained.

Figure 2 demonstrates the results of the SAPO-34 synthesis with tetraethylammonium hydroxide (TEAOH) as the templating agent. In the range of SiO_2/Al_2O_3 =

= 0·3 – 0·6 a good crystallization of SAPO-34 is observed. The monomeric silicon incorporation in the structure (substitution of phosphorus by silicon corresponding to 1 silicon atom per unit cell) is revealed by the ^{29}Si MAS NMR spectra[11]. Nevertheless, patches of silicon within the crystals are detectable when the SiO_2/Al_2O_3 ratio in the gel exceeds 0·6. The gel preparation without silicon leads to the crystallization of pure $AlPO_4$-18, but $AlPO_4$-34 seems not to be present. Mixtures of $AlPO_4$-18 and SAPO-34 were obtained in the intermediate range of 0 – 0·3 SiO_2/Al_2O_3.

The X-ray powder diffraction patterns of $AlPO_4$-14 are given in Fig. 3. This structure is related closely to that of $GaPO_4$-14 (refs[4,12].) $AlPO_4$-14 crystallizes as a pure phase. However, the addition of only one drop of SiO_2 sol (<0·1 ml) to the synthesis gel ($SiO_2/Al_2O_3 \approx 0{\cdot}02$) suppresses the crystallization of the structure 14. Instead of structure 14, layer structures are formed now. At higher silicon content in the gel

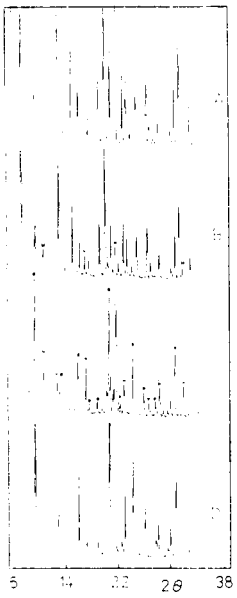

FIG. 1

X-Ray diffraction diagrams of structures obtained with cyclohexylamine as templating agent. Gel composition 1 Al_2O_3 . 1 P_2O_5 . . x SiO_2 . 1 cyclohexylamine. 50 H_2O. A 0·1 ≧ SiO_2, structure 17; B 0·1 SiO_2, structure 17 and 35*; C 0·3 SiO_2, structure 17, 34' and 35*; D 0·4 SiO_2, structure 34

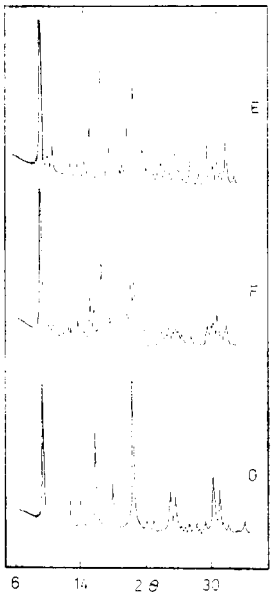

FIG. 2

X-Ray diffraction diagrams of structures obtained with tetraethylammonium hydroxide as templating agent. Gel composition 1 Al_2O_3 . 1 P_2O_5 . x SiO_2 . 0·7 $(TEA)_2O$ . . 55 H_2O. E 0 SiO_2, structure 18; F 0·1 SiO_2, structure 18 and 34; G ≧ 0·3 SiO_2, structure 34

(SiO_2/Al_2O_3 = 0·25) the structure 34 is formed also with piperidine as the template (Fig. 3).

With morpholine as the templating agent SAPO-34 is formed in the range of gel composition of SiO_2/Al_2O_3 = 0·3–0·4, but only dense phases were obtained when the gel was prepared without silicon.

The determination of the pore volume by measurement of the adsorption isotherms is useful for the evaluation of the samples. Small amounts of amorphous material or dense $AlPO_4$ phases can be determined exactly from the reduction of the adsorption capacity. Adsorption isotherms for n-hexane, methanol and water are plotted in Figs 4–6 for $AlPO_4$-18, SAPO-34, $AlPO_4$/SAPO-17 and the aluminosilicate erionite. In Table I the saturation capacities are summarized. The observed sequence of the pore volume $AlPO_4$-18 > SAPO-34 > $AlPO_4$/SAPO-17 is in accordance with the larger free volume of the chabazite structure (0·32 $cm^3\ g^{-1}$) in comparison with erionite (0·23 $cm^3\ g^{-1}$) (ref.[13]). Unfortunately, the available erionite sample exhibited a diminished crystallinity. The experimental values in Table I are slightly higher than those given in the patent literature and agree with the data for $AlPO_4$-18 published by Zhdanov et al.[14]. The small uptake of n-hexane in the SAPO-34 sample J synthesized with morpholine confirms the results in ref.[2] but cannot be explained up to now.

As shown in Fig. 5, the adsorption of methanol at lower adsorption pressure ($< 10^2$ Pa) is higher for the SAPO than for the $AlPO_4$ samples. This should be due

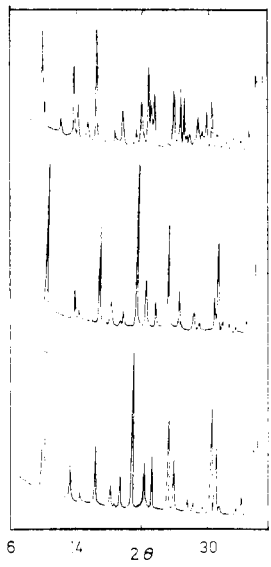

FIG. 3

X-Ray diffractions diagrams of structures obtained with piperidine and morpholine as templating agent. Gel composition 1 Al_2O_3 . . 1 P_2O_5 . x SiO_2 . y R . 50 H_2O. H 0 SiO_2, 2 piperidine, structure 14; I 0·25 SiO_2, 2 piperidine, structure 34; J 0·45 SiO_2, 2 morpholine, structure 34

to the specific interaction of the methanol molecules with the acidic bridging hydroxyls (Si···O(H)···Al) of the SAPO samples.

An unusual shape of the water isotherms (strong increase in the adsorbed amount at nearly constant pressure) (Fig. 6) was reported[15,16] already earlier for $AlPO_4$-5. The isotherms for the $AlPO_4$/SAPO-17 samples confirm these results. It is interesting to note that such a "condensation" characteristics is found also for the adsorption of methanol on $AlPO_4$-18.

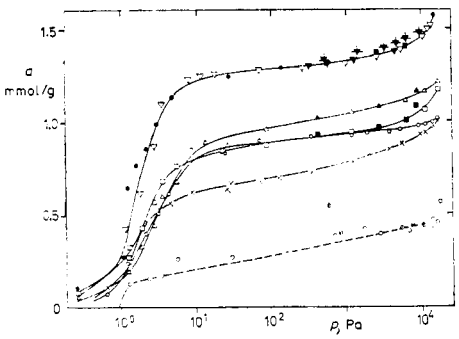

FIG. 4

Adsorption isotherms of n-hexane at 298 K ▽ ▼ SAPO-34 (G), ● ▲ (covered with +) $AlPO_4$-18 (E), □ ■ $AlPO_4$-17 (A), △ ▲ SAPO-17/1 (A), ○ SAPO-17/2 (A), × Erionite, ○ ⊙ SAPO-34 (J). Full symbols: desorption

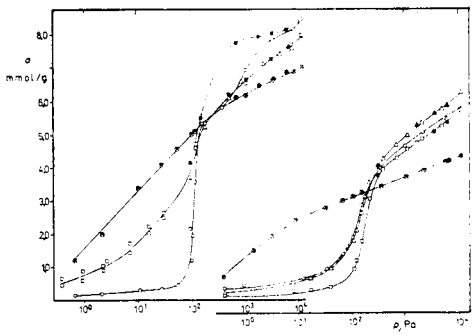

FIG. 5

Adsorption isotherms of methanol at 298 K. Left side: ○ ● $AlPO_4$-18 (E), □ △ ■ SAPO-34 (G), ⊗ ● SAPO-34 (J); right side: □ ■ $AlPO_4$-17 (A), △ ▲ SAPO-17/1 (A), ○ SAPO-17/2 (A), ⊗ ● erionite. Full symbols: desorption

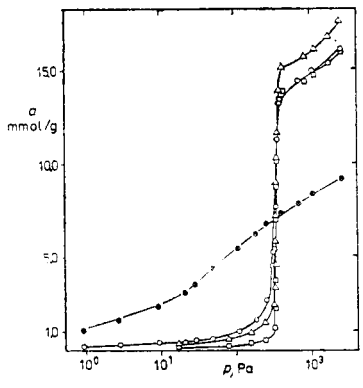

FIG. 6

Adsorption isotherms of water at 298 K. □ $AlPO_4$-17 (A), △ SAPO-17/1 (A), ○ SAPO-17 (2 (A), ⊗ erionite

Information about the state of the templating agents and their interaction with the framework is gained from elementary analysis (C, H, N), thermoanalysis and infrared spectra of the as-synthesized samples. The numbers of template and water molecules located in the chabazite/erionite cage (36 TO_2 units) are summarized in Table II. From the elementary analysis it follows that in the studied systems the templating agents are not decomposed during the crystallization process. Furthermore, it was found that for a given structure the ratio of template to water molecules in the cages is nearly constant.

As shown from thermoanalysis for $AlPO_4$/SAPO-17 in Fig. 7, the main part of the water molecules is enclosed in the cages till it is desorbed at the relatively high temperature of 553 K (endothermic peak in the DTA curve, step in the TG curve). Only a low amount of water (about 1 molecule per unit cell) is desorbed in the range from the room temperature up to 553 K. Immediately after water desorption (at 553 K) the oxidation of cyclohexylamine starts. The coupling of water and amine degradation supports the idea that the amine forms ions by reaction with water:

$$(CHA) + H_2O \underset{573K}{\rightleftharpoons} CHAH^+ + OH^- . \qquad (1)$$

As published in ref.[4], the ^{13}C MAS NMR spectra give evidence for $CHAH^+$ ions. Obviously, the creation of OH^- and its reception in the framework is the reason for

TABLE I

Adsorption capacities of $AlPO_4$/SAPO samples for n-hexane, methanol and water (*a*, mmol/g; *b*, cm^3/g; *c*, number of molecules per chabazite/erionite cage)

Sample	X-Ray diffraction diagram	n-Hexane			Methanol			Water		
		a	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*
$AlPO_4$-18	E	1·5	0·20	3·3	8·4	0·34	18·4	20·0	0·36	43·9
SAPO-34 (TEAOH)[a]	G	1·5	0·20	3·3	8·0	0·32	17·5	18·8	0·34	41·1
SAPO-34 (morpholine)	J	0·5[b]	0·07[b]	1·1[b]	7·0	0·28	15·3	15·2	0·27	33·2
$AlPO_4$-17	A	1·1	0·14	2·4	5·8	0·23	12·7	16·0	0·29	35·0
SAPO-17/1	A	1·15	0·15	2·5	6·2	0·25	13·6	17·5	0·32	38·3
SAPO-17/2	A	1·0	0·13	2·2	5·8	0·23	12·7	16·0	0·29	35·0
Erionite	—	0·95	0·12	2·1	4·4	0·18	9·6	9·0	0·16	19·7

[a] Tetraethylammonium hydroxide; [b] non-equilibrium.

TABLE II

Composition of the as-synthesized samples

Sample	X-Ray diffraction diagram	Number of template and water molecules per chabazite/ /erionite cage[a]	Number of monomerically incorporated silicon atoms per chabazite/ /erionite cage[b]
$AlPO_4$/SAPO-17	A	4 cyclohexylamine (CHA) + 5 H_2O	0—1
$AlPO_4$-18	E	3 tetraethylammoniumhydroxide (TEAOH) + 3 H_2O	0
SAPO-34	G	3 tetraethylammonium ions (TEA^+) + 6 H_2O	~3
SAPO-34	J	5 morpholine + 9 H_2O	—[c]

[a] Estimated from elementary analysis (C, H, N) and thermal analysis; [b] estimated from the calorimetric measurement of the NH_3 chemisorption (number of acidic centres) (refs[4,13]); [c] not determined.

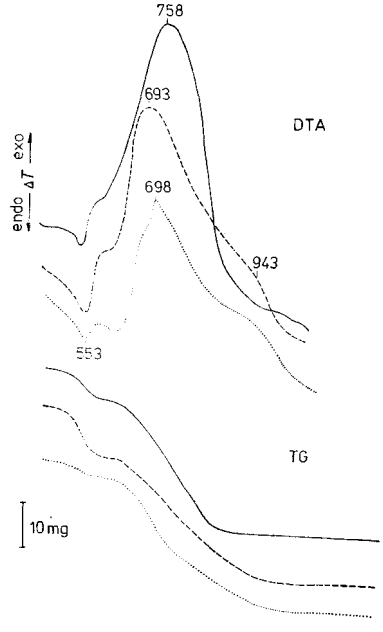

FIG. 7

DTA and TG curves ——— $AlPO_4$-17 (A), – – – – – SAPO-17/1 (A), ····· SAPO-17/2 (A)

the observed trigonal-bipyramidal coordination of aluminium in the as-synthesized $AlPO_4$/SAPO-17 samples[4].

Furthermore, we succeeded in obtaining the direct proof of the existence of hydroxyl groups in the as-synthesized samples from the infrared spectra. The template decomposition was studied by recording in-situ DRIFT spectra at increasing temperatures in a nitrogen stream. Figure 8 shows the spectra of the template decomposition in $AlPO_4$-17. The assignment of the bands is given in Table III. In the

TABLE III

Assignment of the bands observed in the as-synthesized $AlPO_4$/SAPO-17 samples

$\tilde{\nu}$, cm^{-1}	Assignment
3 650	$\nu(OH^-)$
3 325[a]	$\nu_{as}(NH_2)$
3 250—3 000	$\nu_{as}(NH_3^+)$; $\nu_s(NH_3^+)$
2 945	$\nu_{as}(CH_2)$
2 863	$\nu_s(CH_2)$
1 600	$\delta_{as}(NH_3^+)$
1 580[a]	$\delta(NH_2)$
1 502	$\delta_s(NH_3^+)$
1 450	$\delta(CH_2)$
1 385	—

[a] Observed after the decomposition of $CHAH^+$.

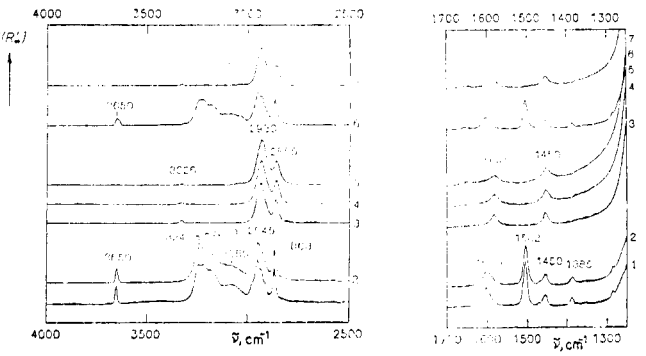

FIG. 8

DRIFT spectra of the as-synthesized sample $AlPO_4$-17 (A) at various temperatures, K: 1 293, 2 420, 3 570, 4 670, 5 720, 6 293 after 5 with water addition, 7 570 after heating of 6

as-synthesized $AlPO_4$-17 broad bands of the NH_3^+ stretching vibrations (3 250 to 3 000 cm^{-1}) are observed. The NH_3^+ deformation vibrations appear at 1 600 and 1 502 cm^{-1}. In addition to these bands of the $CHAH^+$ ions, the OH^- vibration is observed at 3 650 cm^{-1}. The parallel degradation of the bands of OH^- and $CHAH^+$ species can be seen in Fig. 8. At 573 K (spectrum *3*) only the bands of CHA are observed. The disappearance of the bands of $CHAH^+$ and OH^- at 573 K correlates with the water desorption in the DTA/TG curves (Fig. 7) and shows that the reaction in Eq. (*1*) is reversed completely at this temperature. The readsorption of a small amount of water (Fig. 8, spectrum *6*) leads to the reappearance of the OH^- and $CHAH^+$ bands, they vanish again with repeated heating up to 573 K (spectrum *7*). These results demonstrate that the Eq. (*1*) describes a reversible process.

Furthermore, it is possible to distinguish between the NH_2 deformation vibration of CHA at 1 580 cm^{-1} and the corresponding vibration of NH_3^+ of $CHAH^+$ at 1 600 cm^{-1}. So it follows that in the as-synthesized $AlPO_4$-17 sample the cyclohexylamine is almost exclusively incorporated in the ionic form. This conclusion is in good agreement with the ^{13}C NMR spectra[4].

In Fig. 9 the template decomposition in the case of SAPO-17 is shown. The spectra are quite similar to those discussed above. Also in this sample the templating agent forms $CHAH^+$ ions. From the intensity ratio of the ν_{OH} band at 3 600 cm^{-1} to the $\delta_{NH_3^+}$ band at 1 502 cm^{-1} it follows that about 30% of the $CHAH^+$ ions are not compensated by OH^-. As the sample in Fig. 9 contains 1 silicon atom per unit cell (Table II), the scheme of charge compensation

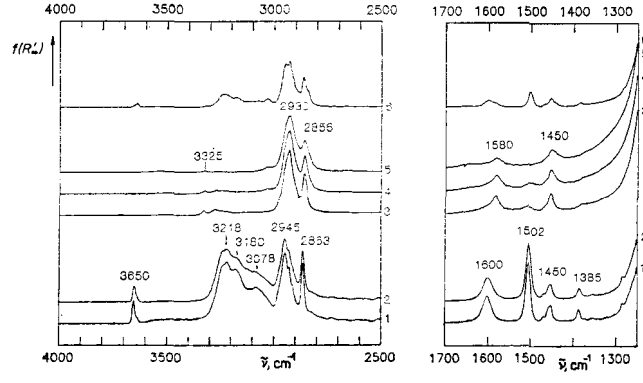

FIG. 9

DRIFT spectra of the as-synthesized sample SAPO-17/2 (A) at various temperatures, K: 1 293, 2 420, 3570, 4 670, 5 720, 6 293 after 5 with water addition

$$4\,CHAH^+ = 3\,OH^- + 1\ \begin{array}{c} | \quad (-) \quad | \\ -Al-O-Si- \\ | \qquad | \\ \text{(framework)} \end{array} \qquad (2)$$

is confirmed by the infrared spectra.

The arguments used in the discussion concerning the state of the template are valid also for $AlPO_4$-14. In the as-synthesized sample a OH stretching vibration is found at 3 605 cm^{-1} (Fig. 10). For a detailed interpretation of the template vibration further studies are necessary.

In the case of SAPO-34 the template ions (TEA^+) are compensated completely by the negative charge of the framework. In the infrared spectra (Fig. 11) the band at 3 640 cm^{-1} is due to physically adsorbed water. In accordance with the results of thermoanalysis (Fig. 12) this water is desorbed already at about 373 K. In contrast

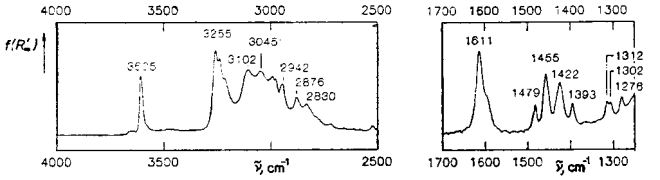

FIG. 10

DRIFT spectra of the as-synthesized sample $AlPO_4$-14 at 420 K

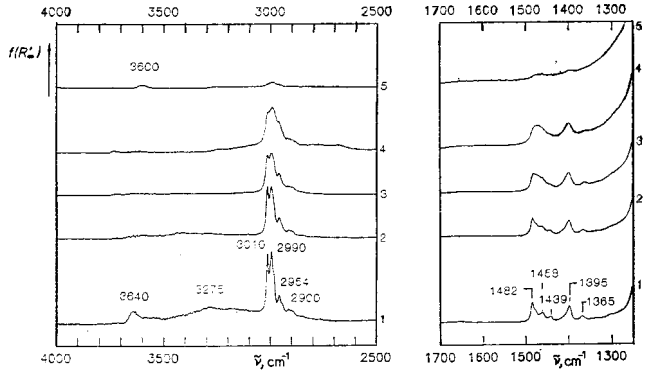

FIG. 11

DRIFT spectra of the as-synthesized sample SAPO-34 (G) at various temperatures, K: 1 293, 2 420, 3 570, 4 670, 5 720

to the findings for $AlPO_4$/SAPO-17 here no coupling of water and template degradation can be found. Simultaneously with the decomposition of the template the band of the acidic bridging hydroxyls (Si···O(H)···Al) at 3 600 cm^{-1} (Fig. 11, spectrum *5*) appears. It is interesting to note that for $AlPO_4$-18 the degradation of the template occurs at a distinctly lower temperature in comparison to SAPO-34 (Fig. 12). This illustrates the different state of the template in the both samples (Table II). The area of the high temperature peak of the template oxidation in the DTA curves (Figs 7, 12) correlates with the silicon content of the sample. It is possible that oxidation products are stabilized on the acidic centres.

CONCLUSIONS

The main problems resulting from the synthesis experiments with small pore $AlPO_4$/SAPO samples are the following ones:

- the preference of the crystallization of SAPO-34 at high silicon content in the gel,
- the suppression of SAPO-17 with increasing silicon offer and
- the impossibility of forming $AlPO_4$-34 and SAPO-14.

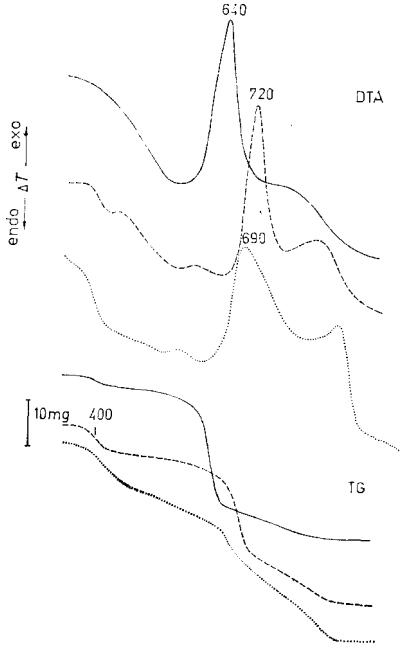

FIG. 12
DTA and TG curves ——— $AlPO_4$-18 (E), – – – – – SAPO-34 (G), ····· SAPO-34 (J)

In the electroneutral $AlPO_4$ framework the charge of the template ions is compensated by non-framework counterions which must be stabilized within the structure. For $AlPO_4$-17, from the X-ray diffraction results[8] a position within the cancrinite cage was suggested for OH^-. The arrangement of R^+, OH^- and water within the cavities of the structure is directed by strong electrostatic interactions. Consequently, it should be highly ordered, and as shown by the obtained results the package is very dense. Four molecules of cyclohexylamine are encapsulated in the erionite cage during the synthesis (Table II) whereas only 2·5 n-hexane molecules can be adsorbed (Table I). Evidently, the introduction of further charges in the system (substitution of phosphors by silicon) disturbs the subtle balance of electrostatic and other interaction. In this way the structure-directing effect for the structure 17 could be lost.

In this connection the theoretical work published recently by van Santen et al.[17] is interesting. From solid-state chemical lattice-calculations it follows:

- the flexibility of the $AlPO_4$ frameworks and
- the existence of only a narrow range of the formation energies of the $AlPO_4$ polymorphs.

In contrast to structure 17 the structure 34 is stabilized by the framework charges. Because of the delocalization of the framework charges the template ions should occupy positions which correspond to cation places in the analogous aluminosilicate structures. Indeed, this was found[18] for CoSAPO-34. Further investigations are necessary to clarify the suggestion that the structure 34 exists only with a definite number of framework charges.

From the results it has to be concluded that the possibility of varying the number of active sites is rather restricted in small pore $AlPO_4$ structures.

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