Novel Aluminophosphate-Based Compounds with a Layered Structure and Intercalation Behavior

Bettina Kraushaar-Czarnetzki,[*] Wim H. J. Stork, and Ronald J. Dogterom

Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research B. V.), P.O. Box 3003,
1003 AA Amsterdam, The Netherlands

Received April 27, 1993[⊗]

A novel group of aluminophosphates with the formula $R_{3/2}[Al_3H_3(PO_4)_4]$ where R represents a long-chain diamine $H_2N(CH_2)_nNH_2$ with $n \geq 8$ is described. In these aluminophosphates, referred to as SCS-22, aluminium and phosphorus are tetrahedrally coordinated. Isomorphous substitution, e.g. of Co for Al and Si for P, is possible as in the case of three-dimensional aluminophosphate molecular sieves. However, SCS-22 compounds exhibit a layered structure. It appears that the P–OH groups at the sheet surfaces interact with the amine groups of a monolayer of intercalating diamines. A linear relationship has been established between the chain length of the diamine and the interlayer distance, indicating that the diamine molecules are inclined at an angle of ca. 60° with respect to the aluminophosphate sheets.

Introduction

The application of the principles of templated zeolite synthesis to aluminophosphate chemistry has resulted in the generation of the so-called AlPO-based molecular sieves.[1–3] During the last 10 years this family of molecular sieves has been greatly extended by both the synthesis of novel structure types and the exploration of variations in the framework composition by isomorphous substitution. The incorporation of suitable elements to replace part of the aluminium and/or phosphorus can yield catalytically very interesting materials exhibiting cation exchange capacity, Brönsted and Lewis acidity, and/or redox properties.[4–6]

Typically, the structure of these AlPO-based molecular sieves can be related to three-dimensional (3D) networks in which alternating $AlO_{4/2}$ and $PO_{4/2}$ tetrahedra are interconnected via four shared oxygen atoms. Additional bondings of, e.g., the Al atoms to nonframework species like H_2O can be observed, but these species are normally released upon heating. The frameworks of AlPO-based molecular sieves are generally electroneutral or negatively charged, i.e., compounds with anion exchange capacity have never been observed. Hence, bonding rules for AlPO's have been postulated which imply that the sum of positively charged and electroneutral tetrahedral building units, e.g., $[PO_{4/2}]^+$ and $[SiO_{4/2}]^0$, cannot be higher than the sum of negatively charged tetrahedra like $[AlO_{4/2}]^-$ or $[CoO_{4/2}]^{2-}$.[3]

Besides the AlPO-based molecular sieves with 3D structure, the zirconium phosphates represent another class of phosphates with ion exchange capacity, acid properties and, to some extent, adsorption capacity. Zirconium phosphates and the group IV phosphate analogues exhibit layered (2D) structures, which may be intercalated by alkanols or alkyl(di)amines. The layers consist of a plane of octahedrally coordinated Zr(IV) or group IV metal sandwiched between tedrahedral (HPO_4) groups and exhibit an atomic P:M(IV) ratio of 2. The P-OH groups have acidic character and are accessible to cation exchange or interaction with organic compounds. Excellent reviews on the layered phosphates have been given by Clearfield[7] and Costantino.[8]

The present paper is concerned with SCS-22, the first member of a novel family of crystalline phosphates. SCS-22 is an aluminophosphate in which both aluminium and phosphorus are tetrahedrally coordinated and can be isomorphously substituted as in AlPO-based molecular sieves. However, SCS-22 exhibits a layered (2D) structure intercalated by straight-chain alkylenediamines which are added to the synthesis gel like "templates". In many respects, i.e. in terms of composition, structural features, and properties, SCS-22 takes an intermediate position between the 3D aluminophosphates and the 2D zirconium phosphates.

Experimental Section

SCS-22 can be synthesized using 1,8-octylenediamine ($R = C_8DN$) or related templates with longer chains (e.g., $R = C_{10}DN$, $C_{12}DN$). A CoAPSO form of SCS-22, for instance, can be prepared as follows: aluminium triisopropylate, water, orthophosphoric acid, and 1,8-octylenediamine are combined under vigorous stirring. Subsequently, an aqueous solution of cobalt acetatetetrahydrate, silicasol, and water are added to this mixture. After homogenization, the resulting gel of the composition $0.5Al_2O_3{\cdot}1P_2O_5{\cdot}0.3CoO{\cdot}0.3SiO_2{\cdot}1R{\cdot}80H_2O$ is transferred to an autoclave where crystallization takes place at 393 K during 24 h. Synthesis procedures for other chemical compositions of SCS-22 are described elsewhere.[9]

Elemental analyses of Al, P, Si, and Co were performed by means of X-ray fluorescence on a Philips PW 1480 spectrometer. C, H, and N were determined by means of combustion mass spectrometric element analysis. Compositional homogeneity was monitored performing electron microprobe analyses on a Jeol EM840 microscope equipped with a Tracor TN 5400 instrument. X-ray diffraction patterns were recorded on a Philips PW 7200 spectrometer using Cu Kα radiation. For variable-temperature measurements, an Anton Paar HTK instrument was used. Samples were ground and roughened at the probe surface in order to prevent preferential orientation of the crystals.

Thermoanalysis was performed on a Mettler Thermoanalyzer TA-1. The samples were heated at a rate of 4 K/min in an 8 L/h gas flow of 7.5% oxygen in nitrogen, and the outgassed products were analyzed by means of an on-line Balzers quadrupole mass spectrometer.

^{13}C and ^{31}P NMR spectra were acquired on a Bruker MSL-300 spectrometer at 75.4 and 121.4 MHz, respectively, under magic-angle

---

[*] To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1993.

(1) Wilson, S. T.; Lok, B. M.; Messina, C. A.; Cannan, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1982**, *104*, 1146–1147.

(2) Lok, B. M.; Messina, C. A.; Patton, R. L.; Gajek, R. T.; Cannan, T. R.; Flanigen, E. M. *J. Am. Chem. Soc.* **1984**, *106*, 6092–6093.

(3) Flanigen, E. M.; Patton, R. L.; Wilson, S. T. In "*Innovation in Zeolite Materials Science*"; Grobet, P. J., et al., Eds.; Studies in Surface Science and Catalysis, 37, Elsevier: Amsterdam, 1988, pp 13–27.

(4) Flanigen, E. M.; Lok, B. M.; Patton, R. L.; Wilson, S. T. In *New Developments in Zeolite Science Technology*; Murakami, Y., et al., Eds.; Kodansha: Tokyo, 1986; pp 103–112.

(5) Pellet, R. J.; Coughlin, P. K.; Shamshoum, E. S.; Rabo, J. A. In *Perspectives in Molecular Sieve Science*; ACS Symposium Series 368; American Chemical Society: Washington, DC, 1988; pp 512–531.

(6) Kraushaar-Czarnetzki, B.; Hoogervorst, W. G. M.; Andrea, R. R.; Emeis, C. A.; Stork, W. H. J. *J. Chem. Soc. Faraday Trans.* **1991**, *87*, 891–895.

(7) Clearfield, A. In *Inorganic Ion Exchange Materials*; Clearfield, A., Ed.; CRC Press: Boca Raton, FL, 1982; pp 1–74.

(8) Costantino, U. In *Inorganic Ion Exchange Materials*; Clearfield, A., Ed., CRC Press: Boca Raton, FL, 1982; pp 111–132.

(9) Clark, D. M.; Kraushaar-Czarnetzki, B.; Dogterom, R. J. EP-A-483927, 1992.

0020-1669/93/1332-5029$04.00/0

Table I. Chemical Composition of Samples of SCS-22

sample	R^a	element ratio (relative to P = 1)				
		P	Al	Si	Co	R^a
SAPO-1	C_8DN	1	0.87	0.06		0.39
SAPO-2	C_8DN	1	0.90	0.04		0.38
CoAPSO-1	C_8DN	1	0.84	0.09	0.05	0.40
CoAPSO-2	$C_{10}DN$	1	0.83	0.08	0.05	0.39
CoAPSO-3	$D_{12}DN$	1	0.88	0.09	0.06	0.39

[a] C_nDN is a straight-chain $H_2N(CH_2)_nNH_2$ alkylenediamine.

spinning conditions. The single-pulse ^{27}Al NMR spectra were recorded on a Bruker AM-500 spectrometer applying a high magnetic field (11.7 T; 130.3 MHz) and high-speed magic-angle spinning conditions using a Doty probe.

Results and Discussion

The preparation of SCS-22 is in many respects similar to that of AlPO-based molecular sieves. A hydrogel containing an organic additive and reactive sources of phosphorus and aluminium is autoclaved under autogenous pressure until crystallization is complete. As in the case of AlPO-based molecular sieves, isostructural analogues of diverging composition can be synthesized. The addition of appropriate cobalt and silicon compounds to the hydrogel, for instance, results in the formation of isomorphously substituted SCS-22 which will be denoted as the "CoAPSO" form by analogy with the classification of AlPO-based molecular sieves.[3,4]

However, elemental analyses of SCS-22 samples (Table I) reveal an important difference from those of the "classical" molecular sieves. In SCS-22 compounds the ratios (P + Si):(Al + Co) are generally larger than unity, whereas in molecular sieves they are equal to or smaller than unity. In the latter case, interconnected tetrahedra $[AlO_{4/2}]^-$, $[PO_{4/2}]^+$, $[CoO_{4/2}]^{2-}$, and $[SiO_{4/2}]^0$ build a three-dimensional framework, which is electroneutral (no Co and Si present) or negatively charged.[3] If SCS-22 would exhibit such a three-dimensional structure, the charge of the framework would be positive, clearly conflicting with the widely accepted bonding rules.[2,3]

The major part (87–100%) of the cobalt atoms in our samples of CoAPSO-SCS-22 are, indeed, tetrahedrally coordinated. The deep-blue crystals investigated by means of diffuse-reflectance UV–vis spectroscopy give a strong electron absorption band at 500–650 nm, which is characteristic of tetrahedral cobalt in d^7 configuration (not shown). The integrated intensities of these absorption bands can be related to the amount of tetrahedral cobalt (in the framework). The application of electron absorption spectroscopy for the quantitative determination of tetrahedral cobalt in Co-substituted molecular sieves has been reported elsewhere.[6,10]

As to aluminium atoms, we used ^{27}Al MAS NMR to identify their coordination. A typical spectrum as shown in Figure 1 exhibits a strong signal at 44.8 ppm stemming from tetrahedral Al and a weak signal at −16.8 ppm stemming from octahedral Al, while the humps at 135 ppm and −45 ppm are spinning sidebands. In all samples the intensity ratio of tetrahedral and octahedral Al is approximately 9:1. Since electron microprobe analyses indicated the presence of small, Al-rich particles, it can be assumed that the octahedrally coordinated aluminium belongs to an alumina impurity.

The ^{31}P MAS NMR spectra of SCS-22 (Figure 2A) generally exhibit two strong signals at −8.4 and −16.2 ppm in an intensity ratio varying between 1:2.5 and 1:3.5. In most cases an additional weak signal around −3.8 ppm can be observed, which we ascribe to impurities. All signals also appear in a ^1H–^{31}P cross-polarization spectrum (Figure 2B). We can conclude that (at least) two types of phosphorus sites are present in SCS-22, which interact with hydrogen or hydrogen-containing species.

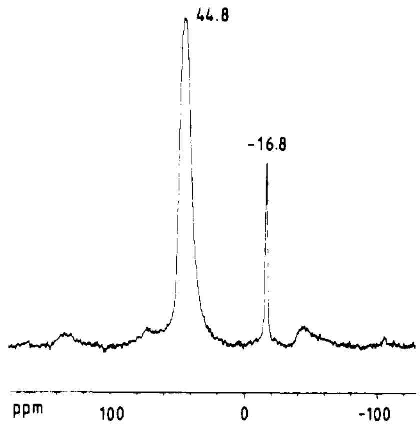

Figure 1. ^{27}Al MAS NMR spectrum of SCS-22 (CoAPSO-1).

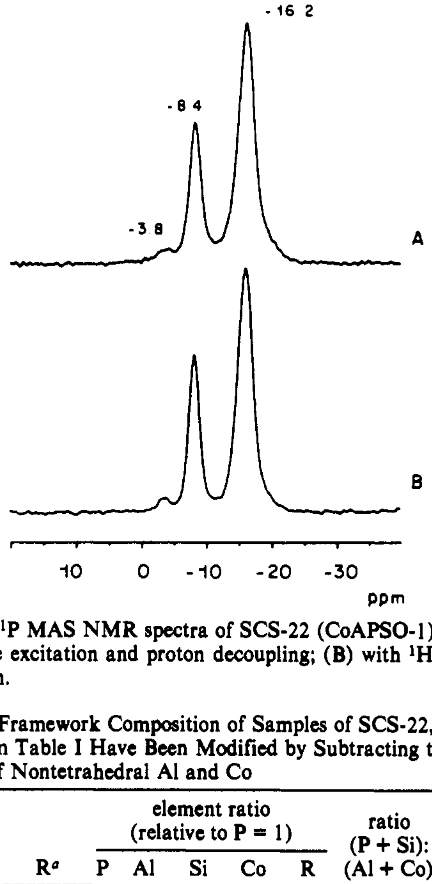

Figure 2. ^{31}P MAS NMR spectra of SCS-22 (CoAPSO-1): (A) with single pulse excitation and proton decoupling; (B) with ^1H–^{31}P cross-polarization.

Table II. Framework Composition of Samples of SCS-22, Where Values from Table I Have Been Modified by Subtracting the Amounts of Nontetrahedral Al and Co

sample	R^a	element ratio (relative to P = 1)					ratio (P + Si): (Al + Co)	ratio (P + Si): R
		P	Al	Si	Co	R		
SAPO-1	C_8DN	1	0.8	0.06		0.39	4:3.03	4:1.47
SAPO-2	C_8DN	1	0.81	0.04		0.38	4:3.1	4:1.46
CoAPSO-1	C_8DN	1	0.76	0.09	0.05	0.40	4:2.98	4:1.47
CoAPSO-2	$C_{10}DN$	1	0.76	0.08	0.05	0.39	4:3	4:1.44
CoAPSO-3	$C_{12}DN$	1	0.78	0.09	0.05	0.39	4:3.04	4:1.43

[a] C_nDN is a straight-chain $H_2N(CH_2)_nNH_2$ alkylenediamine.

If we combine our findings concerning the chemical composition of SCS-22 and account for the amount of impurities (six-coordinated Co and Al) as indicated by means of electron absorption and NMR measurements, we arrive at an (P + Si):(Al + Co) element ratio of about 4:3 (Table II), which indicates that tetrahedral Co^{2+} substitutes for tetrahedral Al^{3+} and silicon predominantly substitutes for phosphorus. Moreover, this element ratio suggests the P and Si tetrahedra to be three-connected, while Al and Co tetrahedra are four-connected. We can propose the following formula for SCS-22 where $x < 3$, $y < 4$, and R represents a diamine $H_2N(CH_2)_nNH_2$ with $n \geq 8$: $R_{3/2}$-

---

(10) Kraushaar-Czarnetzki, B.; Hoogervorst, W. G. M.; Andrea, R. R.; Emeis, C. A.; Stork, W. H. J. In *Zeolite Chemistry and Catalysis*; Jacobs, P. A., et al., Eds.; Studies in Surface Science Catalysis, 69, Elsevier: Amsterdam, 1991, pp 231–240.

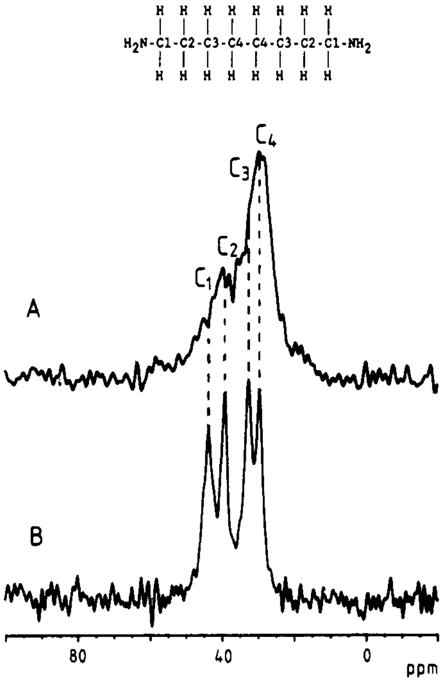

Figure 3. ^{13}C CP MAS NMR spectra of (A) 1,8-octylenediamine occluded in SCS-22 and (B) pure 1,8-octylenediamine.

$[Al_{3-x}Co_xH_{3+x+y}(PO_4)_{4-y}(SiO_4)_y]$. The AlPO forms synthesized ($x = 0$ and $y = 0$) were always contaminated with considerable amounts of amorphous aluminophosphate. Therefore, no results have been included in Tables I and II. The substitution mechanism for silicon in SAPO- and CoAPSO-SCS-22 is not yet clear. Both chemical analysis and ^{29}Si MAS NMR measurements (single peak around –94 ppm, typical of Si with four Al or with HO– and three Al in the first coordination shell) indicate that isolated silicon atoms (preferably) replace phosphorus atoms. However, two different types of phosphorus sites are observed by means of ^{31}P MAS NMR. In spite of the appearance of only a single resonance peak in the ^{29}Si MAS NMR spectrum, it is still possible that silicon could substitute for both phosphorus sites. Because of low Si concentrations in the samples and the much lower natural abundance of ^{29}Si as compared to ^{31}P, the spectral resolution could be insufficient to distinguish between crystallographically different sites.

The results in Table II and our proposed formula for SCS-22 suggest a stoichiometric ratio between (P + Si) and the alkylenediamine template (R). This ratio (P + Si):R = 4:1.5 (or (P + Si):NH_2 groups = 4:3) remains almost unchanged even if the framework charge is increased by isomorphous substitution. We assume that the amount of template cannot increase because of sterical reasons. However, it is likely that the NH_2 groups of the diamine interact with OH groups of the framework. It can be assumed that these OH groups and, hence, the hydrogen atoms are attached to phosphorus (and silicon) rather than to the metals since the ratio of tetrahedrally coordinated elements (P + Si):(Al + Co) = 4:3 indicates that Al and Co are four-connected while P and Si are three-connected. Moreover, the ^{31}P CP MAS NMR data suggest interaction between hydrogen atoms and phosphorus.

We have taken ^{13}C CP MAS NMR spectra of SCS-22 (sample CoAPSO-1) and, for comparison, of 1,8-octylenediamine in order to monitor possible interactions between the SCS-22 framework and the occluded organic material. It is obvious that the diamine occluded in SCS-22 gives a broader NMR spectrum (Figure 3). In particular, the signals of the α- and β-carbons (C1 and C2) are less intense, and their chemical shifts, as far as they can be determined accurately, have somewhat lower ppm values. This indicates that, indeed, the amine groups strongly interact with the framework of SCS-22, and the neighboring carbon atoms (in α- and β-position) are most affected by this interaction. The NMR signals of carbon atoms C3 and C4 in the middle part of the alkyl chain are much more intense and their high-field shift is negligible. Obviously, they merely "feel" the surrounding framework. The broadening of the corresponding signals is most probably caused by disorder, i.e. the middle part of the template chains can have somewhat different conformations and orientations. In sum, it can be assumed that the template molecules behave like mobile sticks which are fixed to the SCS-22 "framework" via the terminal amine groups.

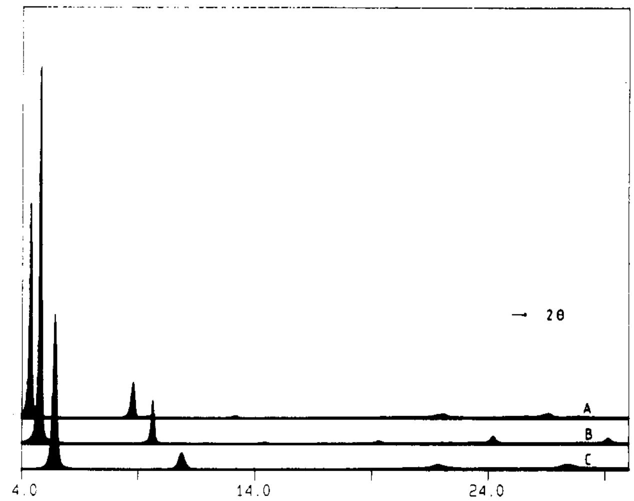

Figure 4. X-ray diffraction patterns of CoAPSO-SCS-22 synthesized with(A) 1,12-dodecylenediamine, (B) 1,10-decylenediamine, and (C) 1,8-octylenediamine.

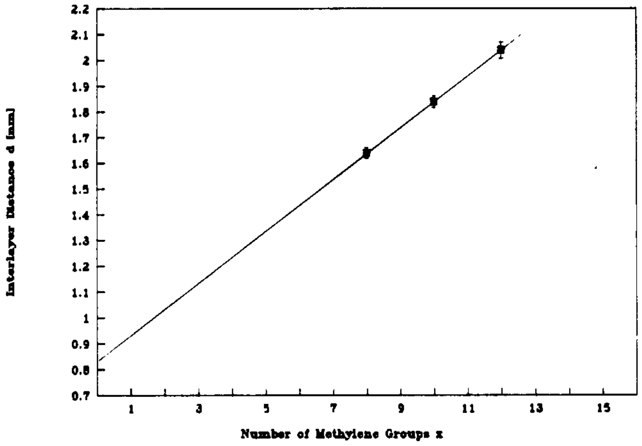

Figure 5. Interlayer distances of SCS-22 versus the number of methylene groups x in the diamine $H_2N(CH_2)_xNH_2$.

Both the chemical composition and the ^{13}C CP MAS NMR data strongly suggest that SCS-22 exhibits not a three-dimensional but rather a two-dimensional framework in which an AlPO-based sheet structure is intercalated by diamine chains. Evidence for this hypothesis is given by the X-ray diffraction data. Figure 4 shows the XRD patterns of SCS-22 samples prepared with diamines of different chain lengths, viz. 1,8-octylenediamine (C_8-DN), 1,10-decylenediamine (C_{10}DN), and 1,12-dodecylenediamine (C_{12}DN). A striking feature of these spectra is the strong dominance of [00*l*] lines, especially the [001] reflection, over the other lines, which is typical of layered structures. Furthermore, it can be observed that the 2Θ values decrease with increasing chain length of the template.

As shown in Figure 5, the change in 2Θ values can be translated into a linear increase of the interlayer distance of 0.1 nm for each additional methylene group ($-CH_2-$) in the alkyl chain. Extrapolation towards zero carbon atoms and subtraction of two amine groups (ca. 0.1–0.12 nm each) would yield a thickness of

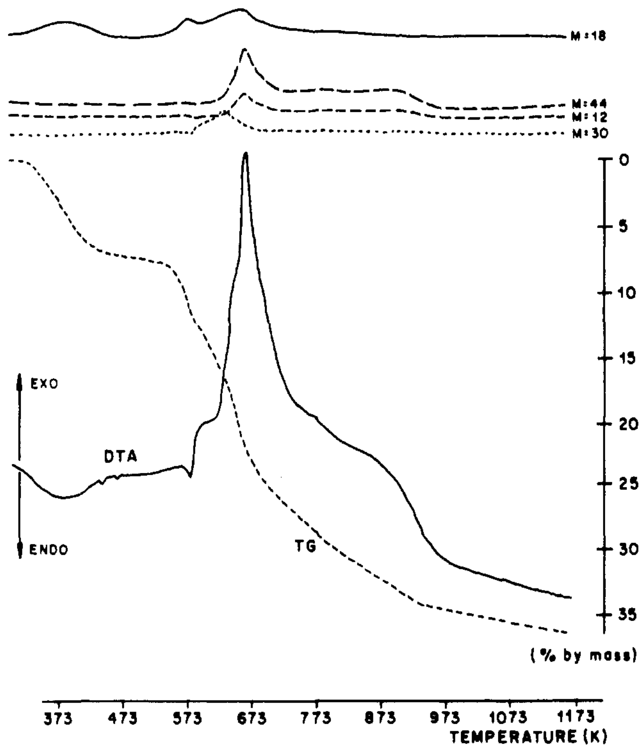

Figure 6. Thermogravimetric analysis of SCS-22 in combination with mass spectrometry.

the SCS-22 layer of 0.6 to 0.65 nm. This value is very close to the layer thickness of α-zirconium phosphate (0.63 nm). When α-zirconium phosphate was intercalated with alkylenediamines, an increase in interlayer distance by ca. 0.11 nm per methylene group in the alkyl chain was observed.[8] This value, too, is very close to that found in SCS-22, giving further evidence of a layered structure of SCS-22. The increment from a methylene group in an all-trans alkyl chain is 0.127 nm. The lower values in SCS-22 and in α-zirconium phosphates indicate that the diamines are not arranged perpendicular to the phosphate sheets but must adopt instead an oblique configuration. For α-zirconium phosphates, it has been calculated that the diamines are at an angle of about 60° to the sheet.[8] Thus, in the case of SCS-22 the angle must have a similar value.

A thermogravimetric analysis of CoAPSO-SCS-22 containing 1,8-octylenediamine is depicted in Figure 6. The first weight loss occurs at about 373 K and is caused by the endothermic evolution of physisorbed water. The template combustion starts at 573 K with the oxidation of part of the hydrogen and the formation of water. In a highly exothermic reaction starting at about 623 K, H_2O, NO_x, and CO_2 are successively evolved. The major part of the carbon atoms, however, are oxidized at temperatures above 723 K.

The structural changes upon template decomposition (in vacuo) have been studied by means of variable-temperature X-ray diffraction. It should be noted, however, that the powder sample had to be moistened in order to facilitate its fixing to the probe. As can be seen in Figure 7A, the moist sample at ambient temperature appears to be "swollen", i.e., signals are shifted toward lower values of 2Θ. After heating at 373 K and evacuation, the signals are shifted back (Figure 7B) toward values typical of SCS-22 containing 1,8-octylenediamine as a template. The patterns taken at 473 and 573 K did not indicate any further changes. In the XRD pattern recorded at 673 K (Figure 7C), however, signals are broadened, peak positions are shifted, and a background signal stemming from amorphous material emerges, which indicates the breakdown of the ordered structure. With increasing temperature signals continue to broaden, and at 873 K the sample is almost completely amorphous.

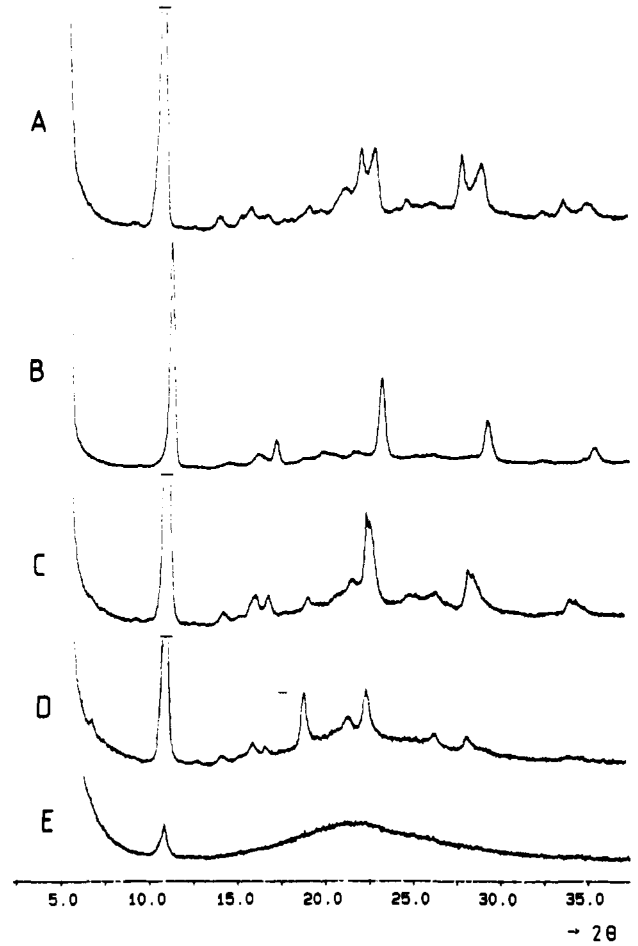

Figure 7. Variable-temperature XRD spectra of SCS-22: (A) 298 K; (B) 373 K; (C) 673 K; (D) 773 K; (E) 873 K. All were recorded in vacuo.

It is obvious from the comparison of thermoanalytic results and variable-temperature XRD that decomposition/combustion of the template and structural changes occur in the same temperature range. The concurrence of template removal and structural collapse further supports the hypothesis that SCS-22 belongs to a novel group of layered aluminophosphates structures, in which the diamine molecules are intercalating.

Conclusions

SCS-22 belongs to a novel group of aluminophosphate-based compounds which combine the properties of the AlPO-based molecular sieves with those of layered zirconium phosphates.

In terms of the coordination of the framework elements, SCS-22 shows more similarity with the three-dimensional molecular sieves than with the layered structures. Aluminium and phosphorus are tetrahedrally coordinated, and the mechanisms of isomorphous substitution, i.e., Co for Al and Si predominantly for P, are the same as in AlPO-based molecular sieves. In zirconium phosphates or related layered phosphates $M(HPO_4)_2$, the metal (M = group IV metal, e.g. Zr, Ti, Hf, Ge, Sn, etc.) is always octahedrally coordinated.

The chemical composition of SCS-22, however, indicates a major difference from molecular sieves in that the (P + Si):(Al + Co) element ratio is not smaller than unity but rather 4:3. The composition of, for instance, nonsubstituted SCS-22 can be expressed as $R_{3/2}[Al_3H_3(PO_4)_4]$. Taking the coordination and number of sites as derived from NMR (and UV–vis) into account, we can propose the following structural formula: $R_{3/2}[AlO_{4/2}]_3[HO{-}PO_{3/2}]_3[O{=}PO_{3/2}]$. This expression suggests aluminium (and substituting cobalt) to be four-connected, while tetrahedral phosphorus is three-connected. Three-connected

[HO–$SiO_{3/2}$] groups could substitute for both types of phosphorus sites.

Chemical composition, as well as spectroscopic results and XRD data of SCS-22 containing diamines of different chain lengths, strongly points to a layered structure. The precise determination of the structure of the inorganic layers by means of diffraction techniques has not yet been achieved. However, from the linear relationship between the interlayer distance and the number of carbon atoms in the diamine chains, it is possible to calculate the inclination angle of the diamine with respect to the sheets as well as the thickness of the AlPO sheet itself.

As to the arrangement of the organic molecules between the inorganic layers, we observe a close similarity between α-Zr(HPO_4)$_2$ intercalated with alkylenediamines and SCS-22. Amine groups of the template interact with P–OH (and Si–OH) groups at the sheet surfaces. In zirconium phosphates these P–OH groups provide exchange capacity. The protonated amine intercalates, for instance, can be exchanged against cations or cationic complexes. The exploration of possible ion-exchange properties of SCS-22 could, therefore, be an interesting subject for further studies, in particular, since the introduction of inorganic "pillars" by means of ion-exchange might enhance the thermostability.