An in Situ Microcrystal X-ray Diffraction Study of the Synthetic Aluminophosphate Zeotypes DAF-1 and CoAPSO-44

Gavin Muncaster,[†] Gopinathan Sankar,[*,†] C. Richard A. Catlow,[*,†]
John Meurig Thomas,[*,†] Robert G. Bell,[†] Paul A. Wright,[‡] Simon Coles,[§]
Simon J. Teat,[§] William Clegg,[§,⊥] and William Reeve[#]

Davy Faraday Research Laboratory, The Royal Institution of GB, 21 Albemarle Street, London W1X 4BS, UK; School of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, UK; CLRC Daresbury Laboratory, Daresbury, Warrington, Cheshire WA4 4AD, UK; Department of Chemistry, University of Newcastle upon-Tyne, Newcastle, NE1 7RU, UK; and Clarenden Laboratory, University of Oxford, Parks Road, Oxford, OX1 3PU, UK

Received August 31, 1998

Microcrystalline diffraction techniques employing synchrotron radiation are used to obtain detailed structural information on two zeotype aluminophosphates. For DAF-1 a much improved description of the framework structure, especially relating to the Al−O, P−O bond alternation, has been obtained. A detailed in situ study of the structural changes occurring during the calcination of the template in the material CoAPSO-44 is reported. In situ FTIR spectroscopy yields a correlation between the decomposition of the template and the creation of framework Bronsted acid sites.

Introduction

Almost invariably, open-structure, aluminophosphate molecular sieve catalysts and their heteroatom-substituted analogues are prepared using a structure-directing organic template molecule, the function of which is to nucleate the inorganic framework around it so as to leave empty cages or channels when the template is then removed, usually by calcination in air or O_2. In this manner, a large and growing number of novel open framework aluminophosphate catalysts, in which desirable active centers (e.g., Co^{II}, Si^{IV}) are incorporated at synthesis into a small number of the tetrahedrally coordinated sites, have been prepared.[1−5]

The process of template removal sometimes yields empty cages or channels, with the framework itself undergoing only minor structural change. But it often happens that the removal of organic template leads to partial or complete collapse of the framework. In some cases exposure to water molecules can also destroy the microporous framework. The latter effect is important when exploiting the materials for use in the methanol dehydration reaction, where water is one of the byproducts. The reasons why some structures collapse and others not (or only partially) are unclear, and a deeper knowledge of the structural changes that ensue during the removal of template will help in the production of new open-structure frameworks that are of catalytic significance.

Here we investigate two systems, DAF-1[6] and CoAPSO-44, initially in their as-prepared states to elucidate the position of the template within the structures prior to calcination. At the very least, such studies yield a greater understanding of the way in which template species are oriented inside the framework. We then chart, by using in situ processes, the detailed structural changes that occur to both the template and framework during the calcination of CoAPSO-44.

DAF-1, structure type DFO, was originally synthesized as a Mg-substituted aluminophosphate, MgAPO, and has a structure with two parallel channels of circular pore apertures of ca. 6.1 and 7.5 Å respectively with interconnecting 8- and 10-ring channels. In this study the cobalt- and magnesium-substituted form is used, CoMgAPO. This form of the material has potential uses as both a solid acid and a redox catalyst, similar to the CoAPSO-44 studied here. Using single-crystal diffraction techniques which are feasible with microcrystalline samples (in this case with dimensions 25 × 10 μm) with synchrotron X-rays, we are able to determine the structure of DAF-1 in far greater detail than

---

[*] Authors to whom correspondence should be addressed.
[†] The Royal Institution of GB.
[‡] University of St. Andrews.
[§] CLRC Daresbury Laboratory.
[⊥] University of Newcastle upon-Tyne.
[#] University of Oxford.

(1) Barrer, R. M. *Zeolites and Clay Minerals;* Academic Press: New York, 1978.

(2) Breck, D. W. *Zeolite Molecular Sieves;* Wiley-Interscience: New York, 1974.

(3) Szostak, R. *Molecular Sieves: Principles of Synthesis and Identification*; Van Nostrand Reinhold: New York, 1989.

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

(5) Lewis, D. W.; Willock, D. J.; Catlow, C. R. A.; Thomas, J. M.; Hutchings, G. J. *Nature* **1996**, *382*, 604.

(6) Wright, P. A.; Jones, R. H.; Natarajan, S.; Bell, R. G.; Chen, J.; Hursthouse, M. B.; Thomas, J. M. *J. Chem. Soc., Chem. Commun.* **1993**, 633.

10.1021/cm980604q CCC: $18.00

was originally possible. A modified unit cell and space group permits more accurate assignment of discrete positions to the Al and P in the framework.

CoAPSO-44 is a cobalt- and silicon-substituted aluminophosphate with a structure similar to that of the natural mineral chabazite.[7] A few percent of the tetrahedrally coordinated Al^{III} and P^{V} have been substituted by Co^{II} and Si^{IV}, respectively, by adjusting the ingredients of the synthesis gel yielding a good solid acid catalyst. In addition to the in situ high-temperature micro-single-crystal diffraction employing synchrotron radiation,[8,9] diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was also employed. Together they yield in hitherto unequaled detail quantitative information about the location of the template and its remnants during the course of calcination.

The particular advantage of the synchrotron based microdiffraction technique is that it permits a single-crystal study, very rarely possible[10] in molecular sieve structural chemistry but occasionally feasible[11,12] in photochemical conversions of organic crystals. DRIFT spectra provide supplementary insights into the residual organic species retained in the framework during the course of calcination by recording the gradual changes in the intensity of peaks characteristic of the template molecule. Also, the DRIFT spectra allow us to chart the catalytic activation of the material by studying the growth of peaks that arise due to the Bronsted acid sites formed by charge-compensating protons that replace the template in this role upon calcination.

One of the aims of this work is to assess the degree of modification in the structure of the framework as the template is removed. Hitherto, such a question could be answered only by carrying out a structural investigation before and after thorough detemplatation, as was done by Koningsveld and co-workers in their work on the location and disorder of the tetrapropylammonium ions in the zeolite ZSM-5,[13-15] where, in relative terms, quite massive single crystals (230 × 200 × 150 μm) were available for conventional (CAD-4) diffractometry. With CoAPSO-44 reported here only minute crystals (30 × 30 × 30 μm) were available. Nevertheless, good quality single-crystal data have been obtained at various temperatures, and the respective structures at these temperatures are reported here.

Experimental Section

Each sample of DAF-1 and CoAPSO-44 was synthesized as pure, single phase, using the standard procedure of crystallization from an aqueous gel reacted under hydrothermal pressure. Details of both preparations have been published previously.[6,16] Phase purity and crystallinity of the samples was confirmed[7,8] using a Siemens D500 powder diffractometer.

Synthesis of DAF-1, containing both magnesium and cobalt, yields uniform blue hexagonal plates with a maximum dimension (across the hexagon) of ca. 35 μm and a maximum plate depth of ca. 15 μm, the average dimensions of the sample being 25 and 10 μm, respectively. A crystal of good quality, free from obvious defects, which appeared representative of the sample was selected for the study, with dimensions 25 × 10 μm.

The CoAPSO-44 preparation produced deep blue crystals with a cubic morphology which were comparable in size to the DAF-1 sample, the maximum dimensions being 35 × 35 × 35 μm. Again a representative crystal, free from obvious defects, was chosen for the study, dimensions 30 × 30 × 30 μm. In both systems, cobalt incorporation into the framework was confirmed by Co K-edge X-ray absorption spectroscopy,[17] Co−O distances were found to be ca. 1.94 Å, which is typical of cobalt in tetrahedral coordination.

Single-crystal data were collected on station 9.8 at the Daresbury SRS which operates at 2 GeV with a typical current in the range 150−250 mA. Data were collected using a CCD area detector, with typical data collection times of around 6−8 h. Details of the experimental facility have been reported elsewhere.[18] The crystals were mounted on a glass fiber, attached to a standard goniometer, using sodium silicate (water glass) as the adhesive. The DAF-1 and CoAPSO-44 data were collected at 150 K using an Oxford cryostream. For the in situ data collection, the cryostream was replaced by a custom-built heating system that operates by blowing air through the heater and directly over the sample. The CoAPSO-44 sample was then heated, in situ, without removing it from the diffractometer so that, once mounted, the same single crystal was used throughout the study. Data sets were collected at 150, 293, 473, 673, and 773 K and after cooling at 473 K. Collecting at this set of temperatures ensures that the whole process of calcination is covered. The crystal was held at each temperature for 30 min before recentering, and data collection was started. All structure solutions and refinements were carried out using the SHELXTL/SHELX-97 suite of programs.[19]

DRIFT data were collected (taking ca. 100 mg of finely ground sample) using a Perkin-Elmer 1725X FTIR spectrometer and a standard Spectra Tech DRIFT cell. The sample was heated in air, and the spectra were recorded at the same temperatures as for the single crystal.

Results

DAF-1. In the original structure determination of DAF-1, data were collected on a standard laboratory single-crystal diffractometer with a FAST area detector. Although there was sufficient information to solve the structure with unit cell dimensions $a = 22.351$ Å, $c = 21.639$ Å, and the space group $P6/mmm$, it was not possible to distinguish Al^{III} and P^{V} sites, and the structure was solved taking each tetrahedral site as an average of the two ions. It was noted at the time that a doubling of the c-axis may help to resolve this problem.

With the new synchrotron-based data there was clear evidence to support the earlier computational work,[20] i.e., the need to double the length of the c-axis, as indicated by a series of superlattice reflections. Subsequently in this work a unit cell of $a = 22.351$ Å and $c =$

---

(7) Calligaris, M.; Nardin, G.; Randaccio, L. *Zeolites* **1983**, *3*, 205.

(8) Noble, G. W.; Wright, P. A.; Lightfoot, P.; Morris, R. E.; Hudson, K. J.; Kvick, A.; Graafsma, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 81.

(9) Sankar, G.; Wyles, J. K.; Jones, R. H.; Thomas, J. M.; Catlow, C. R. A.; Lewis, D. W.; Clegg, W.; Coles, S. J.; Teat, S. J. *J. Chem. Soc., Chem. Commun.* **1998**, 117.

(10) Evans M. G. *Proc. R. Soc. London* **1934**, *A134*, 96.

(11) Nakanishi, H.; Jones, W.; Thomas, J. M.; Hursthouse, M. B.; Motevalli, M. *J. Phys. Chem.* **1981**, *85*, 3636.

(12) Thomas, J. M. *Nature* **1981**, *289*, 633.

(13) Van Koningsveld, H. *Acta Crystallogr.* **1987**, *B43*, 127.

(14) Van Koningsveld, H.; Jausen, J. C.; Van Bekkum, H. *Zeolites* **1990**, *10*, 235.

(15) Van Koningsveld, H. *Acta Crystallogr.* **1990**, *B46*, 731.

(16) Batista, J.; Kaucic, V.; Rajic, N.; Stojakovic, D. *Zeolites* **1992**, *12*, 925.

(17) Barrett, P. A.; Sankar, G.; Catlow, C. R. A.; Thomas, J. M. *J. Phys. Chem. Solids* **1995**, *56*, 1395.

(18) Cernik, R. J.; Clegg, W.; Catlow, C. R. A.; Bushnell-Wye, G.; Flaherty, J. V.; Greaves, G. N.; Burrows, I.; Taylor, D. J.; Teat, S. J.; Hamichi, M. *J. Synchrotron Radiat.* **1997**, *4*, 279.

(19) Sheldrick, G. M. University of Gottingen, 1997.

(20) Wright, P. A.; Sayag, C.; Rey, F.; Lewis, D. W.; Gale, J. D.; Natarajan, S.; Thomas, J. M. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 3537.

Table 1. Crystallographic Data for DAF-1

temp (K)	150
formula	$Co_{0.11}Mg_{0.11}Al_{0.78}PO_4$
fw, g mol^{-1}	149.36
Z, calcd density, mg/m^{-3}	1.776
a, Å	22.246(4)
c, Å	43.007(10)
V, Å^3	18432(7)
symmetry	hexagonal
space group	$P6/mcc$
λ, Å	0.68750
no. of unique reflections	5736
R_{int}	0.0462
no. of variables	315
R_1 for $I > 2\sigma(I)$	0.0950
wR_2 for $I > 2\sigma(I)$	0.2645
R_1 for all data	0.1382
wR_2 for all data	0.3102

43.007 Å was used. Also we found, with the $P6/mmm$ space group, as predicted, it was still not possible to assign framework positions to aluminum and phosphorus. When the complete structure is generated from the asymmetric unit, the eight-membered ring, as one example, contains Al−O−Al and P−O−P linkages, thus breaking the requirement of strictly alternating Al and P through the framework. Therefore, in the present study the symmetry was changed, and the appropriate space group found to be $P6/mcc$, again also predicted by calculations.[20] Using this new unit cell and space group, the Al and P atoms were assigned discrete positions in the framework, and the different bond lengths were immediately obvious (ca. 1.54 Å P−O and 1.7 Å Al−O) as opposed to an average distance of ca. 1.62 Å obtained based on earlier structure solution.

The template for DAF-1 is decamethonium hydroxide with two relatively bulky amine groups at either end of a 10-carbon chain. From the single-crystal data it is possible to locate the amine groups in the center of the small channel. However, although there is a large amount of electron density in the channel between two amine groups, it is so disordered that a definitive location of the chain is impossible. There is considerable electron density in the larger channels, but here again the extensive disorder prevents us from assigning even the bulky end groups of the template. The final R-factor for the framework, without assigning any electron density to the decamethonium hydroxide other than the amine groups at either end of the molecule in the smaller channel, is 9.5% ($R = 0.095$). Crystallographic details are given in Table 1. Despite the difficulty in the location of the template, it is apparent that the organic molecule is less disordered in the small, 6.1 Å channel (see Figure 1a) than in the larger 7.5 Å one (see Figure 1b). An earlier computational study from our laboratory indeed predicted such a possibility.[20] The structure derived from this single-crystal data is shown in Figure 2.

It is highly desirable to study, in situ, the detemplatation of DAF-1 as ex situ methods are unsuitable, since the calcined material loses its microporous structure in the presence of water molecules. However, the in situ study did not provide adequate information on the nature of template decomposition and the generation of an active catalyst due to the large disorder in the orientation of the template molecule.

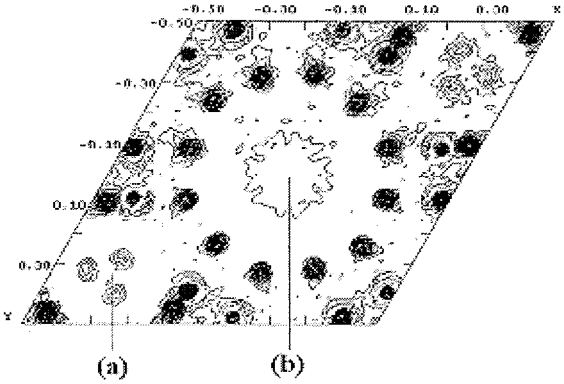

Figure 1. Comparison of the electron density distribution in the two channels of DAF-1 where in the smaller channel (a) there appears to be an ordering of the decamethonium hydroxide template molecule and in the larger channels (b) the electron density indicates a more disordered configuration.

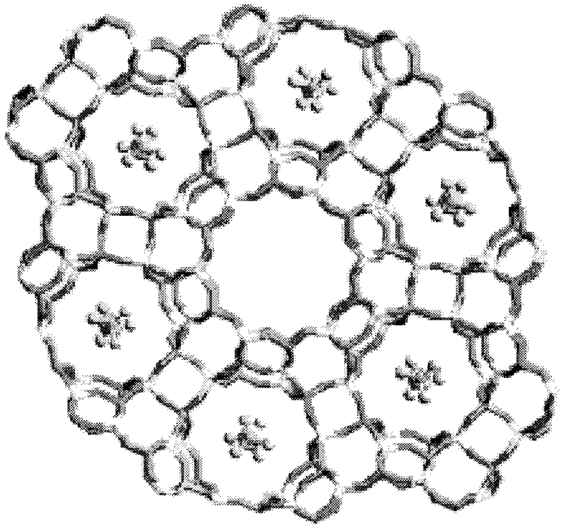

Figure 2. Computer graphic representation of DAF-1 generated from the crystal structure information presented in Tables 1 and 2. The partial ordering of fragments of the template within the smaller channels is shown, whereas in the larger channel no such species could be located.

CoAPSO-44. As mentioned in the Experimental Section, single-crystal diffraction data were collected at 150, 293, 473, 673, and 773 K and, after cooling, again at 473 K. With the template restricted by the cages, it is much more ordered,[21] and indeed it is possible to solve and refine the position and orientation of the molecules (see Figure 3). The detailed crystal structure information obtained using the data collected at 150 K is given in Table 2. Hydrogen atoms of the template are given idealized positions and refined using isotropic temperature factors. All the other atoms were refined with anisotropic temperature factors with no constraints, except in the 473 K structure where restraints on the thermal parameters of the template molecule were necessary. The final structure derived from the data collected at 150 K shows clearly the presence of highly ordered template, with two molecules occupying each cage as shown in Figure 3. Each molecule of the template has 3-fold rotational disorder through the center of the cage with each of the three amine positions having $^1/_3$ occupancy. It is interesting to note that the bulky amine groups are always projected toward the

---

[21] Bennett, J. M.; Marcus, B. K. *Stud. Surf. Sci. Catal.* **1987**, *37*, 269.

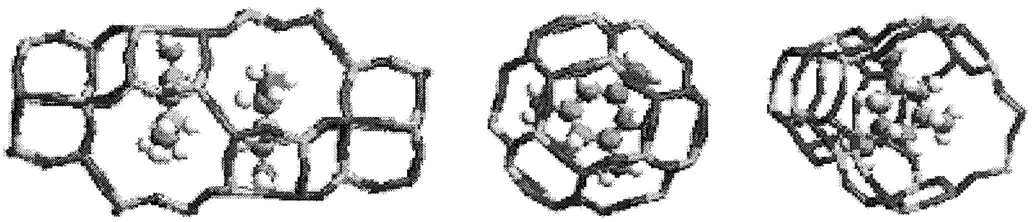

Figure 3. CoAPSO-44 structure solved using the data collected at liquid nitrogen temperature. As expected, two cyclohexylamine template molecules occupy the cages, and more interestingly the amine group is oriented toward the eight-membered-ring window.

Table 2. Fractional Coordinates and *U*(eq) for DAF-1

atom	*x*	*y*	*z*	*U*(eq)	occupancy
P1	0.4718(8)	0.3877(8)	0.1015(4)	0.028(4)	1
P2	0.3836(9)	0.1221(9)	0.0645(4)	0.031(5)	1
P3	0.4369(9)	0.1462(9)	0.1593(4)	0.031(5)	1
P4	0.2880(9)	0.2101(9)	0.1265(5)	0.034(5)	1
P5	0.4695(10)	0.0819(10)	0.2868(4)	0.034(5)	1
P6	0.2992(14)	0.2207(13)	0.0000	0.034(6)	1
Al1	0.3909(9)	0.4696(9)	0.1042(5)	0.024(5)	1
Al2	0.3036(14)	0.0811(13)	0.0000	0.026(6)	1
Al3	0.4352(10)	0.2866(10)	0.1575(5)	0.028(5)	1
Al4	0.4706(10)	0.0799(11)	0.2137(5)	0.032(5)	1
Al5	0.3777(11)	0.2569(10)	0.0644(5)	0.029(5)	1
Al6	0.2144(10)	0.2930(10)	0.1257(5)	0.027(5)	1
O1	0.4231(3)	0.4134(3)	0.1110(14)	0.045(14)	1
O2	0.4498(3)	0.1337(3)	0.1929(12)	0.044(13)	1
O3	0.2572(3)	0.1318(2)	0.1300(13)	0.042(13)	1
O4	0.3456(3)	0.2478(3)	0.1499(14)	0.051(14)	1
O5	0.2303(3)	0.2263(3)	0.1329(13)	0.041(12)	1
O6	0.3590(3)	0.0947(3)	0.0323(14)	0.056(16)	1
O7	0.4811(3)	0.3483(3)	0.1278(13)	0.046(13)	1
O8	0.5422(2)	0.4486(2)	0.0927(13)	0.041(13)	1
O9	0.3602(3)	0.1025(3)	0.1525(14)	0.049(14)	1
O10	0.4113(3)	0.2002(2)	0.0656(13)	0.041(13)	1
O11	0.2746(4)	0.1435(4)	0.0000	0.055(2)	1
O12	0.3257(3)	0.0863(3)	0.0882(14)	0.053(15)	1
O13	0.4599(3)	0.2225(2)	0.1554(13)	0.041(13)	1
O14	0.4435(3)	0.3415(3)	0.0729(12)	0.046(13)	1
O15	0.4785(3)	0.1278(3)	0.1374(14)	0.049(15)	1
O16	0.4610(4)	0.0940(3)	0.2528(12)	0.057(16)	1
O17	0.3432(3)	0.2555(3)	−0.0280(14)	0.062(17)	1
O18	0.3140(3)	0.2312(3)	0.0936(13)	0.050(15)	1
O19	0.5429(3)	0.0983(3)	0.2928(16)	0.057(16)	1
O20	0.4426(3)	0.1093(3)	0.0729(13)	0.054(15)	1
O21	0.2368(4)	0.2310(4)	0.0000	0.051(2)	1
O22	0.4194(3)	0.0070(3)	0.2951(15)	0.055(15)	1
O23	0.4534(3)	0.1297(3)	0.3059(13)	0.055(16)	1
O31	0.5000	0.5000	0.0000	0.225(15)	1
C1	0.6009(10)	0.2766(10)	0.1000(5)	0.159(7)	1
C2	0.6470(6)	0.3120(6)	0.1643(14)	0.220(4)	0.33
N1	0.6667	0.3333	0.1146(5)	0.096(6)	1

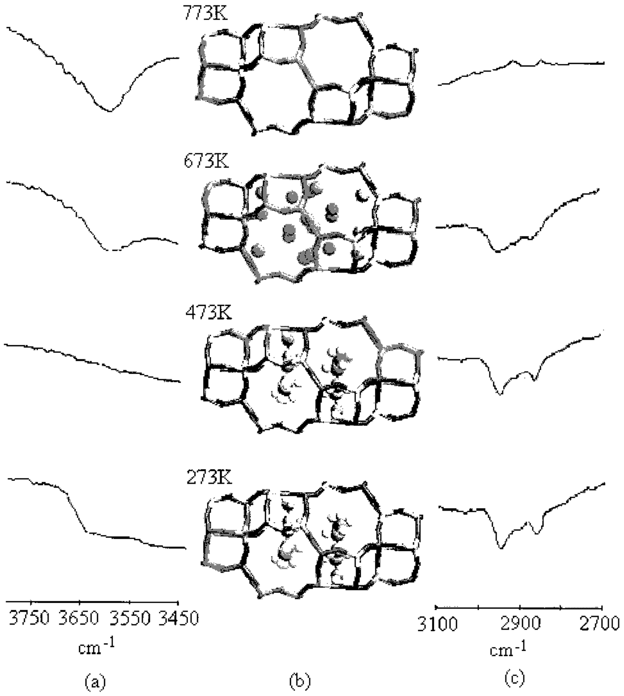

Figure 4. Sequence of final structures derived from the single-crystal data recorded at 293, 473, 673, and 773 K in (b). Corresponding IR data are also shown in this figure. For clarity, we have shown only the O−H (a) and C−H (c) stretching regions.

8-ring channel, which intersects the cages. This may imply that there are some intercage template−template interactions. The same can be seen in the 293 and 473 K data (Figure 4), with the template still ordered even at these elevated temperatures. At 673 K the template has lost much of its structural integrity, but fragments of organic species are still visible inside the cage as shown again in Figure 4. One of the most important features indicating the decomposition of the template molecule is that some of the derived C−N and C−C distances are much higher (ca 1.75 Å) than those seen at lower temperatures (ca 1.55 Å). The final two structures, solved using the data collected at 773 K and after cooling to 473 K (postcalcination), showed no trace of organic species, indicating the complete removal of the template, with the framework remaining unchanged and the cages now empty (Figure 4, 773 K). Analysis of bond distances and angles shows that there is only minor change in cage size upon calcination. Crystallographic details are given in Table 3, and the fractional coordinates and *U*(eq) of as-prepared CoAPSO-44 are given in Table 4 and for the calcined sample in Table 5.

Previous work on this system had shown that there were certain reflections in the as-prepared spectra that violated the $R\bar{3}$ symmetry of the pure CoALPO-44 analogue and other chabazitic structures.[21] Subsequently, the CoAPSO-44 structure was refined in $P\bar{1}$ symmetry. However, we found no such evidence for the extra reflections in any of our data and were able to solve and refine in $R\bar{3}$ for all the data sets. Attempts were made to refine in $P\bar{1}$, but no satisfactory *R*-factors were achieved. As pointed out in the Experimental Section, our preparation of CoAPSO-44 contained no K^+ ions, compared to the sample used in the previous study.[21] This may therefore be the cause for the reduction in symmetry they observed previously.

As can be seen in Table 3, all of the *R*-factors achieved are acceptable. As expected, the high-temperature structures have larger *R*-factors because of the combination of thermal motion of the framework and template molecules (present until 673 K).

To establish the presence of the template molecule or its fragments at 673 K, DRIFT spectra were recorded at the same temperatures as that of the single-crystal

Table 3. Crystallographic Details for CoAPSO-44

	temperature (K)					
	150	273	473	673	773	473
formula[a]	F^1	F^1	F^1	F^2	F^3	F^4
fw, g mol^{-1}	156.91	156.91	156.91	154.79	127.04	125.89
Z, calcd density, mg/m^{-3}	18, 1.931	18, 1.931	18, 1.927	18, 1.890	18, 1.558	18, 1.557
a, Å	13.5494(3)	13.5494(4)	13.534(2)	13.6592(13)	13.731(3)	13.6888(7)
c, Å	15.2795(5)	15.2795(5)	15.3446(18)	15.1479(12)	14.930(3)	14.8893(11)
V, Å^3	2429.29(11)	2429.29(11)	2434.0(6)	2447.6(4)	2437.8(8)	2416.2(2)
symmetry	hexagonal	hexagonal	hexagonal	hexagonal	hexagonal	hexagonal
space group	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$
λ, Å	0.68490	0.68490	0.68490	0.68490	0.68490	0.68490
no. of unique reflections	1200	1163	1067	1024	917	1177
R_{int}	0.0370	0.0313	0.0349	0.0219	0.0989	0.0366
no. of variables	85	83	79	71	59	59
R_1 for $I > 2\sigma(I)$	0.0428	0.0433	0.0813	0.0549	0.0758	0.0438
wR_2 for $I > 2\sigma(I)$	0.1445	0.1348	0.2118	0.1582	0.2311	0.1600
R_1 for all data	0.0459	0.0490	0.0901	0.0598	0.0844	0.0537
wR_2 for all data	0.1471	0.1384	0.2251	0.1614	0.2369	0.1645

[a] $F^1 = Co_{0.06}Al_{0.96}P_{1.0}O_4C_2N_{0.33}H_{4.33}$, $F^2 = Co_{0.06}Al_{0.96}P_{1.0}O_4C_2N_{0.33}Na_{0.1}$, $F^3 = Co_{0.06}Al_{0.96}P_{1.0}O_4Na_{0.14}$, and $F^4 = Co_{0.06}Al_{0.96}P_{1.0}O_4Na_{0.09}$.

Table 4. Fractional *x*, *y*, and *z* Coordinates and *U*(eq) for As-Prepared CoAPSO-44 (Data Recorded at 150 K)

atom	x	y	z	U(eq)	occupancy
Al(1)	0.0973(1)	0.6621(1)	0.0695(1)	0.013(1)	1
Co(1)	0.0973(1)	0.6621(1)	0.0695(1)	0.013(1)	1
P(1)	0.3283(1)	0.8979(1)	0.0630(1)	0.015(1)	1
O(1)	0.2160(2)	0.7896(2)	0.0436(1)	0.031(1)	1
O(2)	0.1259(2)	0.5528(2)	0.0520(1)	0.031(1)	1
O(3)	−0.0102(2)	0.6496(2)	0.0019(1)	0.031(1)	1
O(4)	0.0539(2)	0.6607(2)	0.1773(1)	0.029(1)	1
O(5)	0.3333	0.6667	0.1667	0.020(4)	0.667
C(1)	−0.2668(4)	0.4573(4)	0.1906(5)	0.089(2)	0.667
C(1′)	−0.2668(4)	0.4573(4)	0.1906(5)	0.089(2)	0.333
N(1)	−0.2056(9)	0.5828(9)	0.1755(11)	0.092(5)	0.333
C(2)	−0.2106(5)	0.3907(5)	0.1837(6)	0.0107(2)	1

Table 5. Fractional *x*, *y*, and *z* Coordinates and *U*(eq) for CoAPSO-44, Calcined at 773 K and Data Recorded at 473 K[a]

atom	x	y	z	U(eq)	occupancy
P(1)	0.7708(1)	−0.0039(1)	0.1073(1)	0.021(1)	1
Al(1)	0.7734(1)	−0.2305(1)	0.1016(1)	0.022(1)	1
Co(1)	0.7734(1)	−0.2305(1)	0.1016(1)	0.022(1)	1
O(1)	0.7605(2)	−0.1169(2)	0.1323(2)	0.041(1)	1
O(2)	0.6921(2)	0.0154(2)	0.1681(2)	0.040(1)	1
O(3)	0.8931(2)	0.0890(2)	0.1216(2)	0.046(1)	1
O(4)	0.7357(3)	−0.0044(2)	0.0097(2)	0.045(1)	1

[a] Sodium silicate, water glass was used as the high-temperature adhesive, and it was found that Na^+ ions were present in the crystal after calcination. The coordinates of this are $x = 1.0000$, $y = 0.0000$, and $z = 0.1705$ and U(eq) $= 0.065(5)$. This is located between the double six-membered ring.

data. Spectra are presented in Figure 4. For clarity only two regions are shown: that of the O−H stretching region, 3750−3450 cm^{-1} (in Figure 4a), and C−H stretching of the template molecule, 3100−2700 cm^{-1} (in Figure 4c). It is clear that at 673 K there is a considerable decrease in the intensity of the band corresponding to the C−H stretch of the template. Some residual intensity remains as would be expected from the fragments of the organic species seen in the single-crystal data (Figure 4b, 673 K). In the region of OH stretching frequency, a new band at 3610 cm^{-1} appears at 673 K, which is due to the bridging hydroxyl species[22] (Bronsted acid site) which provide charge compensation after the breakdown of the template molecule. Indeed, the IR data recorded at 773 K clearly showed the absence of any organic species and the presence of only the Bronsted acid sites, thus complementing the structure solutions derived from single-crystal studies (Figure 4b).

Discussion

The initial structure of the microporous material DAF-1 was incompletely resolved owing to the nature of the data available at the time. Using the superior intensity of synchrotron-based X-rays, we have been able to solve the structure in much greater detail. The increased quality of our data allowed us to measure superlattice reflections, showing the need to double the *c*-axis and consequently assign aluminum and phosphorus in the framework, which up until now has not been possible. We also found the need to change the symmetry group from *P*6/*mmm* to *P*6/*mcc* in order to accommodate the strict alternation of aluminum and phosphorus tetrahedra when the complete structure is generated from the asymmetric unit. The amine groups of the template could be located in the smaller (6.1 Å) channel, but the rest of the molecule could not be reliably assigned because of the high level of disorder. In the larger channels the presence of considerable electron density is detected, but owing to the high degree of disorder, no template species can be assigned. Thus, it was not possible to track the breakdown of the template and the formation of the solid acid by this method. Our experimental results clearly agree with the computationally predicted *P*6/*mcc* symmetry and doubling of the *c*-axis.

In contrast to the decamethonium template molecules in DAF-1, cyclohexylamine in CoAPSO-44 is highly ordered and could easily be located and refined, not only at 150 K but also at 293 K and even at 473 K. Because of this ordering we have been able to chart accurately and in situ the structural details that characterize the activated, open framework structure of CoAPSO-44 under operating conditions. For the data collected at 673 K, the observed increase in some of the C−C and C−N bond distances (ca 1.7 Å) suggests that the template molecule started decomposing to smaller fragments, which is a more likely explanation than the occurrence

---

(22) Barrett, P. A.; Sankar, G.; Catlow, C. R. A.; Thomas, J. M. *J. Phys. Chem.* **1996**, *100*, 8977.

of large thermal motion of the organic molecule due to the data collection at elevated temperature. The reasons being, first, our IR data show the formation of bridging hydroxyl species associated with Bronsted acidity at 673 K, which is clearly the result of the absence of charge-compensating organic template molecules, which are replaced by protons. Such proton transfer has been noted previously in both aluminosilicate and CoAlPO materials.[23,24] Second, several reported TGA experiments on microporous aluminophosphates have shown that the template is lost in the temperature range 300–400 °C.[25,26] The study revealed that there is little effect on the framework throughout the process and that Bronsted acid sites form immediately as the template begins to decompose. The integrity of the cage structure has also been shown, a factor that is crucial when designing a shape selective catalyst

The present study provides a new, in situ, approach to the fundamental investigations of catalytically important microporous materials that are formed, in many cases, with crystal sizes smaller than 30 μm. Our study clearly shows some of the major advantages that synchrotron-based microcrystalline diffraction can offer to structural chemistry and in particular to in situ studies of solid-state materials which require a very high level of structural detail.

Acknowledgment. We thank EPSRC for financial support and synchrotron beam time and CCLRC for other facilities at Daresbury Laboratory.

CM980604Q

---

(23) Koller, H.; Lobo, R. F.; Burkett, S. L.; Davis, M. E. *J. Phys. Chem.* **1995**, *99*, 12588.

(24) Sankar, G.; Thomas, J. M.; Greaves, G. N.; Dent, A. J. *J. Phys. IV* **1997**, *7*, 871.

(25) Montes, C.; Davis, M. E.; Murray, B.; Narayana, M. *J. Phys. Chem.* **1990**, *94*, 6425.

(26) Lohse, U.; Parlitz, B.; Muller, D.; Schreier, E.; Bertram, R.; Fricke, R. *Microporous Mater.* **1997**, *12*, 39.