

Layered Assembly of Organic Molecules and Host–Guest Interactions in a CAL-1 Chabasite-Type Precursor of H-SAPO-34 Catalysts**

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The first step in the preparation of molecular-sieve-based catalysts is the synthesis of a precursor comprising the inorganic framework in which the organic structure-directing agents (SDAs) are properly organized. Conversion to the final catalyst generally requires one further step, for example, the removal of the sacrificial SDAs. Owing to the high price of some SDAs, attempts have been made to decrease the costs of catalyst production by using two organic compounds: the less expensive one to increase the pH value and the other as a SDA. H-SAPO-34, an acidic silicoaluminophosphate with a chabasite-type structure (CHA),^[1,2] is used in the methanol-to-light-olefins (MTO) conversion, for which it is one of the best catalysts described to date. Its relevance is demonstrated by the large number of articles published and patents filled in the last ten years (230 research articles and 277 patents). Despite the considerable research effort, novel synthesis strategies are desired for tuning the acidity and morphology of H-SAPO-34. The nature of the SDA has a profound influence on the morphology of the crystallites. This issue is important, as the reactivation of the SAPO-34 catalyst by elimination of coke derived from the MTO process is facilitated in particles with high a surface/bulk ratio. Attempts to tune size and morphology of the particles have included dilution of the reaction mixture,^[3] addition of organic solvents to the reactants,^[4–6] and stirring^[7,8] the reaction mixture.

CAL-1 (CAmpinas-ALessandria) is a member of a novel family of aluminophosphates and is prepared using a combination of SDAs (*n*-butylammonium (*n*BA), and hexamethyl- enimine (HMI)), which are embedded in the solid after crystallization.^[9,10] The innovative synthesis starts from ALPO-*ntu*,^[11] a layered aluminophosphate that is structurally analogous to SiO₂ kanemite, which contains two fundamental components of the ALPO structure. This strategy led to a CHA-type solid with a peculiar layered morphology,^[10] which is unusual in that it contains both SDAs within the same cages. The solid is a precursor of acid H-SAPO-34 with tunable acidity features.^[10,12] The focus of this research is to obtain H-SAPO-34 with enhanced catalytic performance but also to lower the cost of the final product by using cheaper SDAs.

Herein, the fully solved structure of the novel CAL-1 was obtained by a combination of single crystal synchrotron X-ray diffraction and Fourier transform (FT) IR spectroscopy. This combined approach allowed for the first time the elucidation of the CAL-1 structure and the investigation of the interaction of the embedded SDAs with the inorganic framework.

The CAL-1 inorganic host lattice can be described as a CHA-type 3D framework that consists of corner-sharing TO₄ tetrahedra (T = Al, P, Si). The analogous structure of pure SiO₂ chabasite^[13] contains only one tetrahedrally coordinated species. Owing to the introduction of two T species with slightly different T–O bond lengths (the Al–O bond is about 0.2 Å longer than the P–O bond), the framework is slightly distorted from that of the pure SiO₂ chabasite. CAL-1 crystallizes in the space group *R* $\bar{3}$ and consists of three cages per unit cell, each of which hosts two organic entities. The threefold symmetry axis intersects the cavities of the host structure and leads to a disorder of the guest species within the framework (Figure 1).

While *n*BA can be arranged in one of three equivalent positions on a site, the center of gravity of the HMI rings is located on the rotation axis. This situation results in the formation of an approximately planar ring lying in the *ab* plane, which contains the disordered C and N sites of the HMI molecule.^[14] Buckled 2D guest-species layers in the *ab* plane were observed (Figure 1, top), with an *abc* stacking order in the crystal structure of this compound (Figure 1, bottom). Besides the organic entities, the guest species are composed of 0.56 water molecules per unit cell, which reside in the hexagonal prisms of the structure.

C and N atoms of the HMI ring could not be distinguished, and the H atoms of the guest species could not be refined, owing to the strong disorder. The absence of an ordered superstructure suggests that the two different amines are arranged in a random fashion within the CHA cages.

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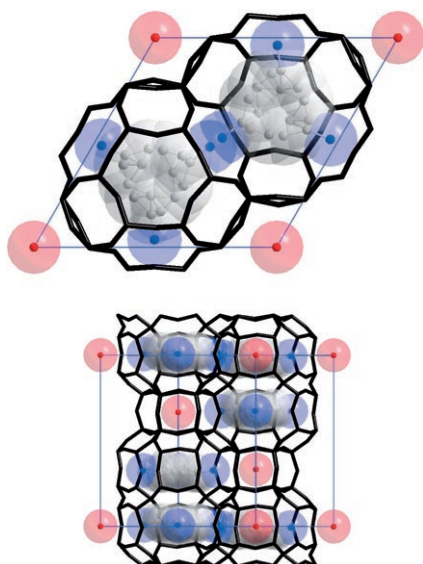


Figure 1. Assembly of the organic SDAs *n*BA and HMI (carbon and nitrogen atoms are represented as gray and blue spheres, respectively) in the CHA-type CAL-1 host framework. Oxygen atoms of water molecules are represented as pink spheres.

Figure 2 shows a possible arrangement of the two different guest species in a slab of the inorganic framework. For clarity, only one of the three possible positions of each molecule is displayed.

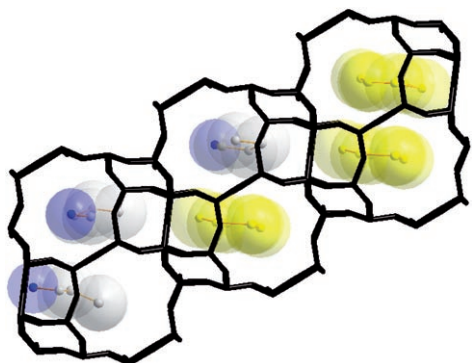


Figure 2. Random distribution of HMI and *n*BA SDAs in the CHA cages of the CAL-1 host structure.

Few crystalline framework systems that contain two different templating species are known, for example USH-8^[15] and sodalite.^[16] In these cases, one organic guest species is a decomposition product of the pristine organic template.

The nature of the host–guest interaction between SDAs and the CAL-1 framework was clarified by FT-IR spectroscopy (Figure 3). For comparison, the FT-IR spectra of *n*BA intercalated into the layers of ALPO-*ntu* and of HMI/HMIH⁺ embedded within MCM-49 zeolite^[17] were also recorded. When the low-frequency region is considered, it is clear that a mixture of *n*BA and HMIH⁺ (and possibly HMI) is found within the CAL-1 cages, in agreement with reported results of

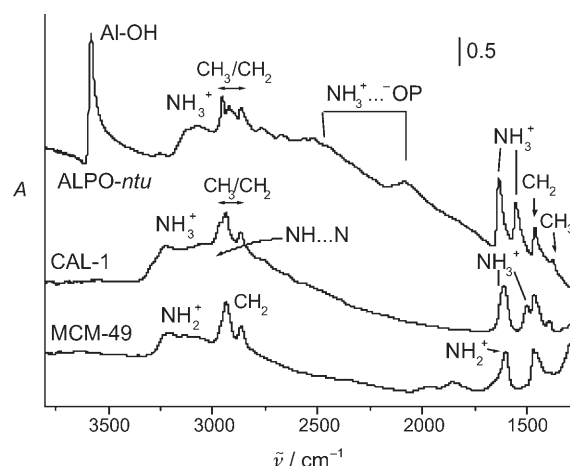


Figure 3. FT-IR spectra of *n*BA and HMI/HMIH⁺ in CAL-1 in comparison to *n*BA in ALPO-*ntu* and HMI/HMIH⁺ in MCM-49.

NMR spectroscopic investigations.^[10] In the CAL-1 spectrum, in fact, the deformation modes of *n*BA at 1612 and 1502 cm⁻¹ (NH₃⁺) and at 1394 cm⁻¹ (CH₃) are present along with CH₂ bending modes typical of the HMI and HMIH⁺ rings at 1470–1445 cm⁻¹.^[18]

The NH₃⁺ deformation modes of *n*BA in CAL-1 are at significantly lower frequencies than those of the ion intercalated in ALPO-*ntu*, which were found at 1634 and 1555 cm⁻¹. This result is a clear indication that *n*BA ions are bound to the frameworks of the two solids in different ways. NH₃⁺ groups interact with oxygen atoms of the host lattice through hydrogen bonds, as indicated by the presence of broad bands in the NH stretching region at approximately 3120 and 3075 cm⁻¹ for ALPO-*ntu* and at 3290 and 3230 cm⁻¹ for CAL-1. The difference in the frequencies of both stretching and bending modes of the NH₃⁺ groups for *n*BA ions intercalated in ALPO-*ntu* or embedded in CAL-1 suggests that these vibrations are very sensitive to the chemical environment of the host framework. The positive charge of the NH₃⁺ groups, in fact, balances the negative charge of [Si-O-Al]⁻ and P-O⁻ groups in CAL-1 and ALPO-*ntu* respectively, and the lower basicity of the [Si-O-Al]⁻ groups should lead to the formation of weaker hydrogen bonds. Weaker interactions, in accordance with the hydrogen-bond theory,^[18,19] lead to higher-wavenumber values of stretching vibrations and lower values of bending vibrations, as is the case for *n*BA ions embedded in CAL-1.

Additional information on host–guest interactions of *n*BA ions embedded in CAL-1 and intercalated into ALPO-*ntu* was derived from the distances of the NH₃⁺ groups to framework oxygen atoms. For CAL-1, as measured in the fully solvated structure, N...O distances are found between 3.28(6) and 3.59(7) Å. In the case of ALPO-*ntu*, a combined FT-IR spectroscopic and DFT study^[20] suggests that N...O distances (2.62–2.82 Å) are much shorter than in CAL-1. These results fully confirm the spectroscopic data.

Whilst the N positions of the disordered *n*BA molecules could be determined, HMI had to be described using a simplified model. The C and N atoms could not be distinguished, and N...O distances between HMI and the host

framework were found in the 3.61(6)–4.30(7) Å range using the C1 site.

The FT-IR spectrum of CAL-1 shows a very broad band at 3150–2600 cm⁻¹, which overlaps with the CH₂ and CH₃ stretching modes at 3000–2800 cm⁻¹ and is absent in the spectrum of ALPO-*ntu*. This band may be assigned to NH...N bonds in *n*BA–HMI complexes, in agreement with a N...N(C1) distance of 2.48 Å found in the refined structure.^[21] The absorption at 3150–2600 cm⁻¹ indicates the presence of patches of supramolecular organic guest structures within the host CHA framework.

It is concluded that the novel CAL-1 structure displays a layered organization of the SDAs, which may be responsible for the crystal morphology. The layered SDA assembly in synergy with host–guest interactions probably drives the crystallization of the layered morphology of the CAL-1 particles, which is unusual for a CHA-type solid. It is predicted that the morphology of the SAPO-34 final product can be designed, along with the acid strength and catalytic site distribution, by tuning the supramolecular organization of the SDAs.

Experimental Section

The structure of CAL-1 was determined from single crystal synchrotron diffraction. A transparent crystal (40 × 30 × 30 μm) was measured at SNBL (ESRF, Grenoble) using a MAR345 image-plate detector (λ = 0.7111 Å). The data were collected at 100 K at a crystal-to-detector distance of 120 mm. 101 images were collected with a 1.5° step. Diffraction images were treated with CrysAlis software.^[22] Intensities were integrated in a rhombohedral cell with *a* = 13.736(3) and *c* = 15.170(2) Å. The structure was solved and refined in the space group *R*3̄ using the SHELX-97 program package.^[23] Analysis of bond distances^[24] showed that Si atoms were present at both T sites in the aluminophosphate framework. Microprobe analysis was used to define the composition of single crystals used for X-ray diffraction study.^[25] The resulting percentages for Al, P, and Si were used for the refinement of the crystal structure. Both T positions were described as mixed T/Si sites with Σsof = sof(T) + sof(Si) = 1.

Standard values for T...O distances were taken from the literature.^[26] Difference Fourier map analysis, which was performed after locating the atoms of the inorganic framework, showed that both *n*BA and HMI were present in the CHA cages. Calculations performed at an intermediate stage, in which the relative positional occupancies of the interstitial atoms were refined, revealed the strong disorder of the organic guest species.^[14] Final *R* indices obtained by the use of 1001 reflections, 80 refined parameters, and 78 restraints were: *R*₁ = 0.0605, *wR*₂ = 0.1531 for [*I* > 2σ(*I*)] and *R*₁ = 0.0674, *wR*₂ = 0.1573 for all data.^[21]

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[1] H. O. Pastore, S. Coluccia, L. Marchese, *Annu. Rev. Mater. Res.* **2005**, *35*, 351–395.

- [2] L. Smith, L. Marchese, A. K. Cheetham, J. M. Thomas, P. A. Wright, J. Chen, R. E. Morris, *Science* **1996**, *271*, 799–802.
- [3] US Patent 6,685,905, **2004**.
- [4] World Patent WO 01/036328, **2001**.
- [5] World Patent WO03/048042, **2003**.
- [6] European Patent EP-A-185525, **1985**.
- [7] European Patent EP-A-541915, **1992**.
- [8] World Patent WO 00/06493, **2000**.
- [9] H. O. Pastore, G. A. V. Martins, M. Strauss, L. G. Pedroni, G. B. Superti, E. C. de Oliveira, G. Gatti, L. Marchese, *Microporous Mesoporous Mater.* **2007**, DOI: 10.1016/j.micromeso.2007.04.022.
- [10] H. O. Pastore, E. C. de Oliveira, G. B. Superti, G. Gatti, L. Marchese, *J. Phys. Chem. C* **2007**, *111*, 3116–3129.
- [11] S. F. Cheng, J. N. Tzeng, B. Y. Hsu, *Chem. Mater.* **1997**, *9*, 1788–1796.
- [12] G. A. V. Martins, G. Berlier, S. Coluccia, H. O. Pastore, G. B. Superti, G. Gatti, L. Marchese, *J. Phys. Chem. C* **2007**, *111*, 330–339.
- [13] M. J. Díaz-Cabanas, P. A. Barrett, M. A. Cambor, *Chem. Commun.* **1998**, 1881–1882.
- [14] Owing to their vicinity, not all of these 21 disordered atom positions could be resolved; nevertheless, a satisfying structural model was obtained using a hexagon composed entirely of carbon atoms. The occupancy of these atoms was set to obtain a total electron count equivalent to a cyclic C₇ unit. The vicinity of the *n*-butyl group of the *n*BA to the threefold symmetry axis led to an overlap of two C positions. These two nonequivalent atoms were described using one atom site (C5) with a doubled site occupancy factor. The percentage of both guest species in the sample was taken from reference [9].
- [15] X. Wang, J. Huang, A. J. Jacobson, *J. Am. Chem. Soc.* **2002**, *124*, 15190–15191.
- [16] M. Fechtelkord, *Microporous Mesoporous Mater.* **1999**, *28*, 335–351.
- [17] A. L. Santos Marques, J. L. F. Monteiro, H. O. Pastore, *Microporous Mesoporous Mater.* **1999**, *32*, 131–145.
- [18] W. O. George, R. Lewis in *Handbook of Vibrational Spectroscopy, Vol. 3* (Eds.: J. M. Chalmers, P. R. Griffiths), Wiley, Chichester, **2002**, p. 1919.
- [19] G. C. Pimentel, A. L. McClellan, *The Hydrogen Bond*, Freeman, San Francisco, **1960**.
- [20] M. D'Amore, C. Bisio, G. Talarico, M. Cossi, L. Marchese, unpublished results.
- [21] CCDC-653576 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [22] CrysAlis Software Package, Oxford Diffraction, Oxfordshire, UK, **2004**.
- [23] G. M. Sheldrick, SHELXL-97: Program for crystal structure refinement, University of Göttingen, **1997**.
- [24] A. Martucci, A. Alberti, G. Cruciani, A. Frache, S. Coluccia, L. Marchese, *J. Phys. Chem. B* **2003**, *107*, 9655–9661.
- [25] Microprobe analysis of CAL-1 single crystals was performed using an ARL-SEMQ microprobe at the Department of Earth Sciences, University of Modena, Italy. Measurements were carried out at 15 kV and 10 nA. The beam diameter was 1 μm, the acquisition time was 10 s on peak and 5 s on background. Aluminosilicates and synthetic apatite were used as standards. Measurements were averaged over 19 single crystals with a diameter of 20 μm.
- [26] R. D. Shannon, *Acta Crystallogr. Sect. A* **1976**, *32*, 751–753.