# Architecture of Hybrid Nanocrystalline Microporous Materials

Hybrid zeolites are well established as heterogeneous catalysts, ion exchangers, and molecular sieves with many different pore architectures


petrochemical industry

The synthesis of aluminosilicate hybrids with organic groups fused within a crystalline framework is a daunting mission which has eluded many workers. Hybrids add variable chemical modification to the repertoire of zeolites, which are well established as heterogeneous catalysts, ion exchangers, and molecular sieves with many different pore architectures.

Before 2008, when the crystalline aluminosilica-based hybrid

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| The challenge: | polycrystalline, beam sensitive & highly complex X-Ray diffraction pattern |
| Solution: | 3D diffraction tomography and precession electron diffraction, in combination with X-Ray refinement |

organic-inorganic porous materials -ECSs (eni carbon silicates)- were synthesized and analyzed, only hybrid materials made of amorphous siliceous were known. In 2012 a novel ECS structure was unrevealed: ECS-3. ECS-3 has textural properties typical of a crystalline microporous material (specific surface area 296 $m^2g^{-1}$, specific pore volume 0.13 $cm^3g^{-1}$, type I N2 adsorption isotherm).

The structure analysis of ECS-3 ($Na_{20.8}Si_{32}Al_{24}O_{96}C_{96}\cdot 32H_2O$) proved to be most challenging as the polycrystalline material is produced as small crystals (1 µm) and provides highly complex high-resolution X-ray powder diffraction (HR-XRPD) pattern, even from synchrotron beam line. Furthermore, the extremely fast deterioration of the structure under the electron beam of a transmission electron microscope does not allow the application of conventional methods.

3D diffraction tomography technique was the tool to surmount these obstacles. The benefits of diffraction tomography are that the reduced electron dose allows data collection on beam-sensitive materials and the collected data are less affected by dynamic scattering than conventional in-zone diffraction data, especially when beam precession is applied.

Analysis of diffraction tomography data collected on a small ECS-3 crystal under stable conditions provided a monoclinic unit cell. Based on intensities extracted from 3D electron-density data, a significant portion of the ECS-3 structure was readily obtained by using Cc space group in the SIR2004 software suite. The phenylene rings were completed with the specific routines of SIR2004, while the position of the extraframework species (Na/K and $H_2O$) were determined by analysis of the Fourier maps generated during the Rietveld refinement of the structure performed against the HR-XRPD data with GSAS software.

**Crystal Structure**

$Na_{20.8}Si_{32}Al_{24}O_{96}C_{96}\cdot 32H_2O$

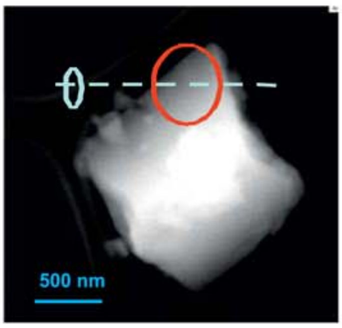
**Monoclinic Cc**
a=19.7 Å
b=27.7 Å
c=9.5 Å
β=102.78°

**Experimantal data**

tilt range: ±60° step: 1°
No ind. reflections: 2206
No ind. atoms: 62
R = 24.7 %

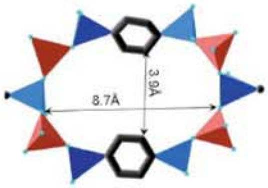
The intriguing crystal structure of ECS-3, whose framework contains 62 atoms in the asymmetric unit, is one of the most complex structures ever solved by electron diffraction, with a structural complexity comparable to zeolites. This is remarkable considering the high beam sensitivity of the sample, due to the phenylene rings. 3D diffraction tomography was indeed indispensable and could become widely utilized for structural investigation of hybrid nanocrystalline microporous materials.

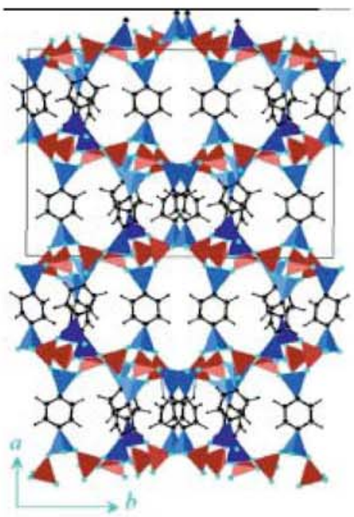
figure 1




ECS-3 Crystal & Tilted Area used 3D Diffraction Tomography

figure 2




Left: ellipsoidal ring of the sinusoidal channel snaking along [001].
Right: [001] projection of the ECS-3 framework structure.

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