

STRUCTURE OF INTRIGUING MESO-MICROPOROUS ZEOLITES

Zeolite with small and medium-sized pores acts like a funnel, enhancing its catalytic properties

Zeolites are crystals that are mainly created from aluminum and silicate. They have small pores which make them interesting for the field of energy and environmental technology due to their potential use as adsorbers, ion exchangers or catalysts. In water treatment, they can help to filter out heavy metals; in the oil and gas industry, their introduction was like a mini revolution for crude oil cracking. We also encounter them in our everyday lives inside washing

The challenge:

nanocrystalline powder with very poor X-ray diffraction pattern; crystal degradation at ambient temperature

Solution:

3D diffraction Tomography & precession electron diffraction with a cryo- holder

powders .

As catalysts, Zeolites are not effective for processing large molecules as these cannot enter inside the pores. To overcome this obstacle several strategies have been considered, such as increasing the pore dimensions and increasing the ratio of the external to internal surface by decreasing the crystallite size or by preparing monolayered zeolites . Another approach is to generate mesopores within the zeolite crystallites, yielding a network of connected mesopores and micropores. Such networks can improve the activity and selectivity of catalysts for cracking and hydrocracking of vacuum gasoil.

Avelino Corma and his research group from the Technical University of Valencia synthesized a zeolite with small and medium-sized pores, the combination of which acts like a funnel, thereby further enhancing its catalytic properties. The zeolite ITQ-43 that features a structurally hierarchical system of connected mesopores and micropores, was synthesized as a silicogermanate.

Due to large cell parameters, data resolution of X-ray Powder Diffraction was reduced by severe peak overlap even at low 2q values ($d_{min} > 1.8 \text{ \AA}$). In combination with the low stability of the calcined sample, this precluded the extraction of an appropriate set of intensities for structural determination using powder data. Thus, 3D diffraction tomography strategy in combination with beam

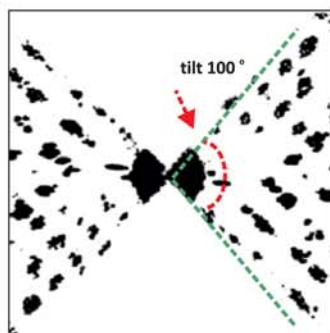
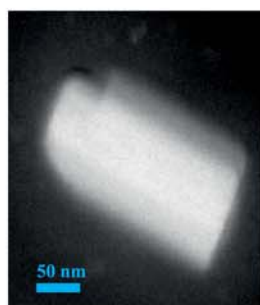
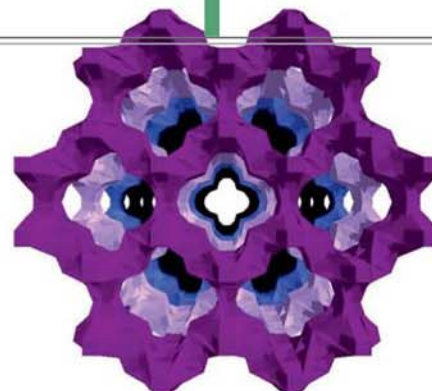


figure 1

ITQ-43 CRYSTAL AND THE CORRESPONDING 3D REFLECTION RECONSTRUCTION MAP

meso-microporous ITQ-43



precession was applied for structure solution of the ITQ-43 zeolite.

Diffraction tomography data was collected from two different crystals by cooling the sample down to liquid N₂ temperature (~100 K). The three-dimensional reconstructed volume revealed only extinctions due to C-centering. Reflection intensity symmetry was consistent with Laue class Cmmm, confirming the orthorhombic setting (R_{sym}= 24%). ITQ-43 has a very open structure, with a framework density as low as 11.4 tetrahedral atoms per 1000 Å³. The most notable characteristic of ITQ-43 is the leaf-like channels formed by 28-rings (units of 28 tetrahedral atoms) presence of clover along the c axis, with pore diameters in the range of the mesopore (21.9 Å × 19.6 Å). This mesoporous system is also connected by 12-ring

channels of 6.8 Å × 6.1 Å along the a axis, and two additional sets of 12-ring channels along (a + b) and (a - b), related by symmetry, with apertures of 7.8 Å × 5.7 Å.

Even though the combination of HRTEM, electron diffraction, and XRPD data provides an important step toward the solution of complicated zeolitic structures, *ab initio* structure solution by direct methods based on pure electron diffraction data may be a faster and more reproducible path applicable to any class of catalytic porous materials.

Crystal Structure

Orthorhombic Cmmm
a=26.09 Å
b=41.87 Å
c=12.84 Å

Structural data

tilt range: ±50° step: 1°
No ind. reflections: 2735
No ind. atoms: 39
R = 34%

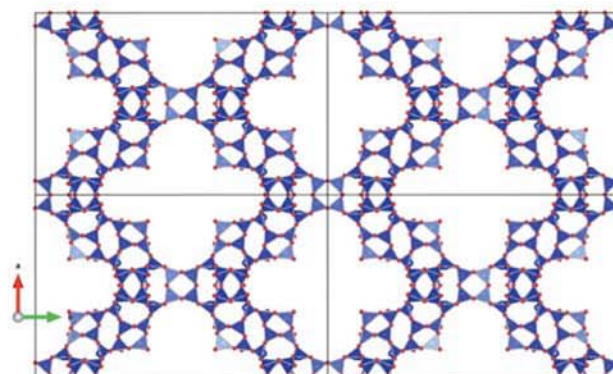


figure 2

CRYSTAL STRUCTURE OF ITQ-43