Large Cage Zeolite Structures with Multidimensional 12-ring Channels

What is the goal? (they have identified) A material composed of:

a. A zeolite with large porous channels that travel in all 3 directions of the structure.

What is the motivation? (in what terms?)

Known large pore zeolites (VPI-5, AlPO4-8) have channels with large pore sizes that travel in only one direction. → Leads to diffusional limitations.

Strategy?

Frameworks with high charge density.
Why?

Tetrahedral atoms with different charges are made available during the structure formation,

which allows *Charge Density Matching*

Figure of large cage of UCSB 8

Authors: Bu, X; Feng, P.; Stucky, G.D.

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UCSB-6, UCSB-8, UCSB-10

Table 1

<u>Host-Guest Charge Density Matching</u>: If T_h atoms with different charges are made available during the assembly, the inorganic framework can adjust to match the charge of the organic cation.

The template-framework species interaction is N-H ···O

How were these synthesized? How were they characterized?

<u>Metal Substituted,</u> $Al^{3+} \rightarrow M^{2+} + M^{+}$ (ammonium cation), $[(C_2H_{10}N_2^{2+})_2][Co_4P_4O_{16}]$

→ framework has increasing negative charge with increasing … ? Range?

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Figure 1

Figure 2,3

All three zeolites are constructed from similar secondary ‘building blocks’

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Figure 4

Figure 5

UCSB-8

UCSB-10

Future: Pore geometry and charge density can be predicted (to a certain extent).

→ Even larger cages?

Materials with Open Frameworks

What is the motivation? (in what terms?)

Interest in creating structures with cavities and channels that can be used in catalysis separations, sensors, optoelectronics, etc.

Supertetrahedral Sulfide Crystals with Giant Cavities and Channels

Hailian Li, Aaron Laine, M. O'Keeffe,* O. M. Yaghi*

What is the goal?

a. To make sulfide-based porous materials, based on TS_4 tetrahedra, which tend to favor more condensed structures.

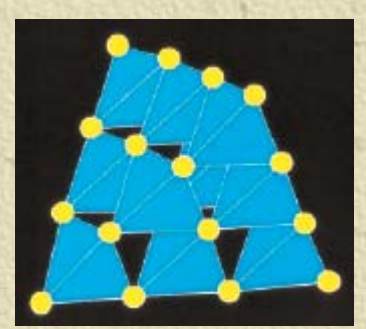
Strategy:

Fulfill 3 conditions:

1) Utilize supertetrahedra

2) Should have large cavities even in their contracted forms

3) Framework should not interpenetrate



Metal Sulfides with Open Frameworks

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'Building Units'

Figure 1

Hydrothermal Synthesis:

In + S + Ligand →

$In_{10}S_{18}\cdot L_6(H_2O)_{15}$

$In_{10}S_{18}\cdot L_3(H_2O)_7$

$In_{10}S_{20}$ shares 4 sulfide vertices,
so $In_{10}S_{16}S_{4/2}^{6-}$

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Figure 3

ASU-31 – 25.6A cavity

ASU-32 – 14.7A cavity

Figure 2

The supertetrahedra are sharing vertices to form similar frameworks as known for simple tetrahedra, except on a different size scale.

Metal Sulfides with Open Frameworks

Table 1

~80% space

→ Organic cation ligands completely exchanges with Na+

→ 2 useful measures of cavity size:

1) Maximum size of sphere in the largest cavity

2) Maximum size of sphere to freely move along channels.

InS → Semiconductor → Nanopores in a semiconductor framework, an 'antidot'

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Discussion Points

How did the scientists go from fundamental idea → research?

What new useful knowledge was gained?

Was this scientific paper fully convincing in its conclusions?

What other knowledge might be interesting to know? (future research hypotheses?)