Synthesis of zeolite crystallites for diffusion measurements

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Main Activities in Previous Synthesis Research:
Synthesis, Modification, Characterization

- Synthesis of zeolite A:
  - various crystal sizes and restricted size distributions: 5, 10, 20, 40 µm;
- Synthesis of zeolite X:
  - various crystal sizes and restricted size distributions: 15, 50 and 80 µm;
- Synthesis of molecular sieve $AlPO_4$-5:
  - large crystal size up to 500 µm, but unsatisfactory size distribution;
- Synthesis of extra-large crystals of silicalite-1: 200 µm (W. Schmidt, Mülheim);
- Synthesis of large crystals of zeolite Y: 5 µm (R. Gläser, Stuttgart);
- Synthesis of extra-large crystals of ferrierite: 200 µm (R. Gläser, Stuttgart);
- Synthesis of the MOF maganese formate of controlled morphology and as film.

- Modifications of zeolites A and X:
  - Ion-exchange: Ca^{2+} in LTA, La^{3+} in FAU;
  - Magnification of surface barriers via liquid/vapor phase chemical deposition (LCD/VCD) of TEOS;
  - Removal of surface barriers via chemical etching with HF.

- Structural characterization:
  - SEM, TEM;
  - XRD, synchrotron XRD, neutron diffraction.

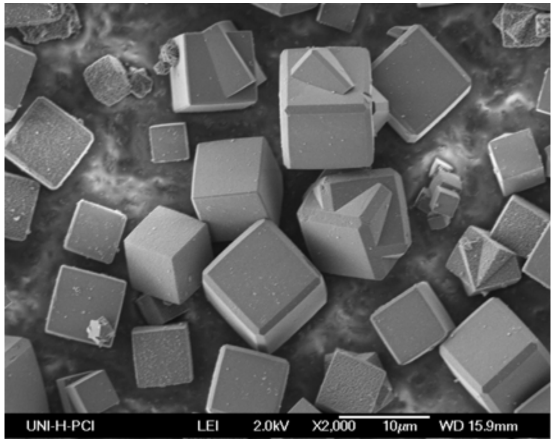
Highlights of Previous Synthesis Research:

Zeolite LTA

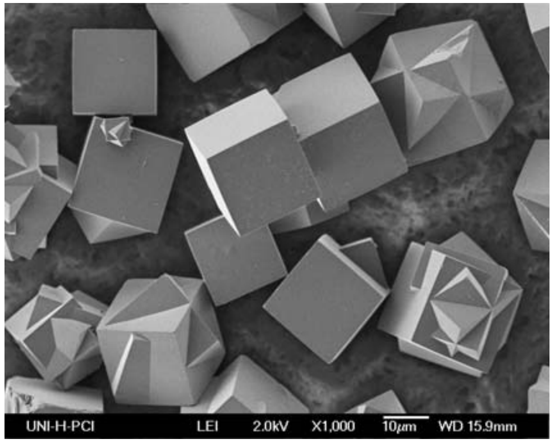
Standardized methods established for zeolites A of various crystal sizes and restricted size distributions.

X. Yang, D. Albrecht, J. Caro Micropor. Mesopor. Mater. 90 (2006) 53.

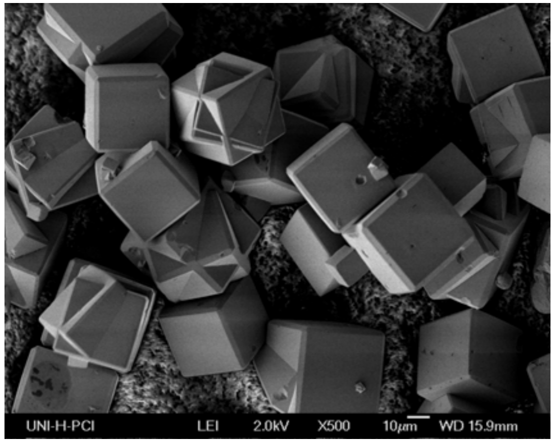
A. Möller, X. Yang, J. Caro, R. Staudt, CIT, submitted.



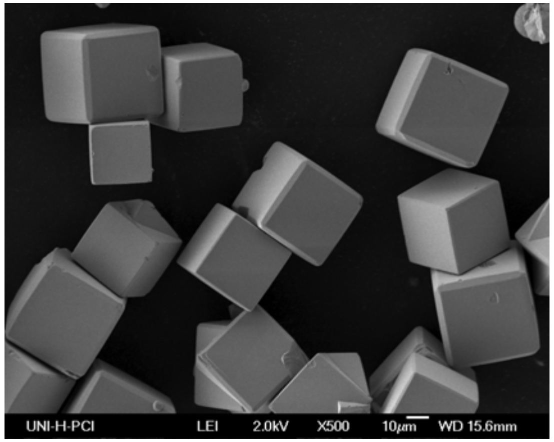
5 µm



20 µm



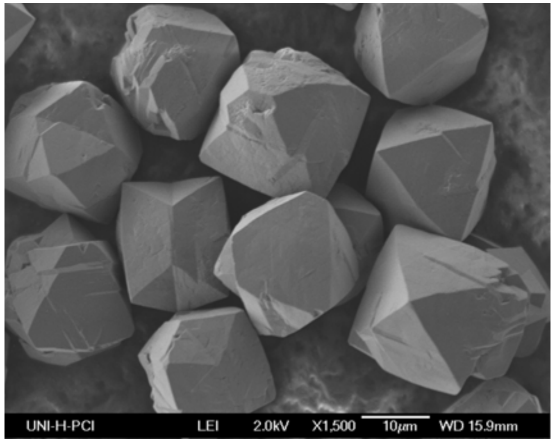
30 µm



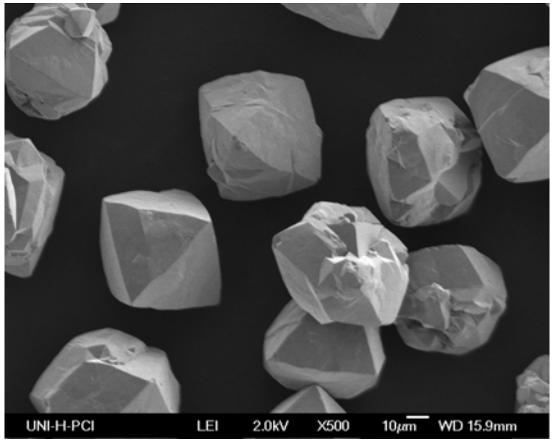
40 µm

Highlights of Previous Synthesis Research:
Zeolite FAU (X)

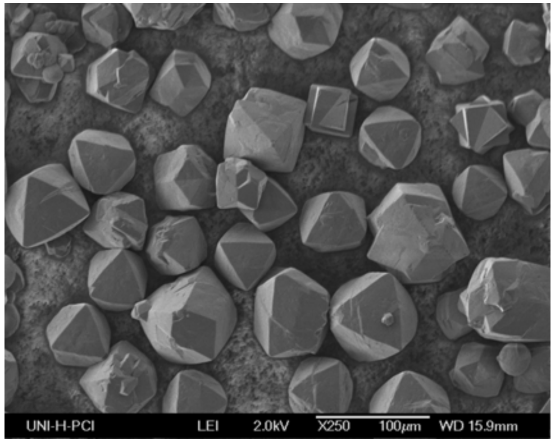
Standardized methods established for zeolites X of various crystal sizes and restricted size distributions.



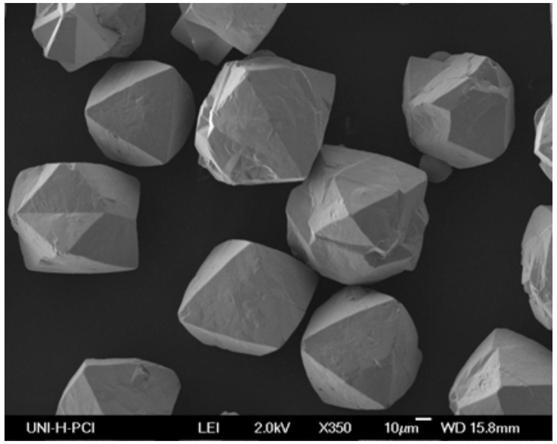
~15 µm



~ 50 µm



~50 µm



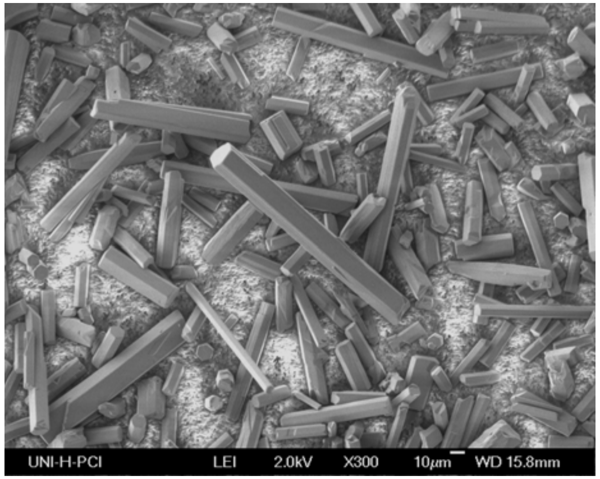
~80 µm

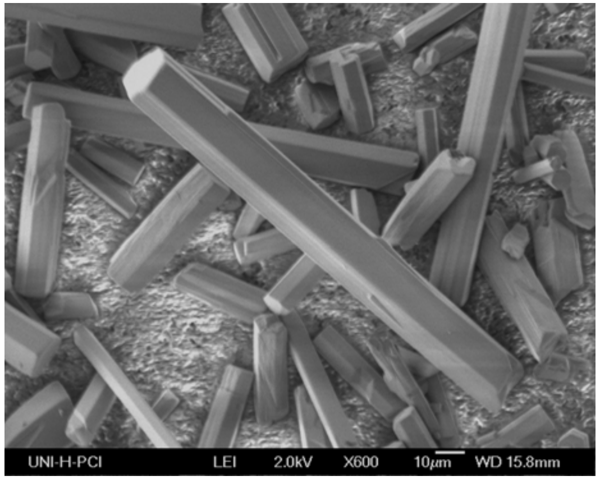
X. Yang, D. Albrecht, J. Caro
Micropor. Mesopor. Mater.
90 (2006) 53.

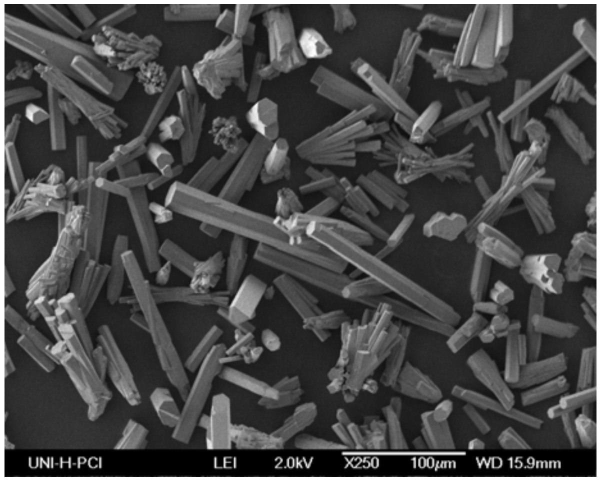
Highlights of Previous Synthesis Research:

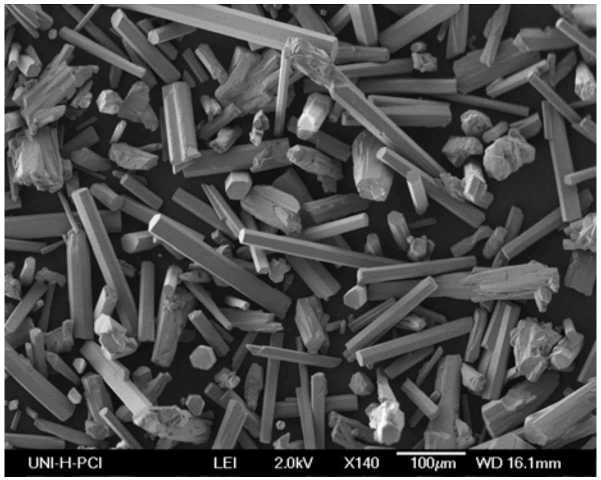
Aluminophosphate $AlPO_4$-5

$AlPO_4$-5: synthesis of crystals with shape of hexagonal prism of lengths ca. 500 µm has been achieved; Problems with broad distributions of crystal sizes and crystal intergrowth have to be solved.



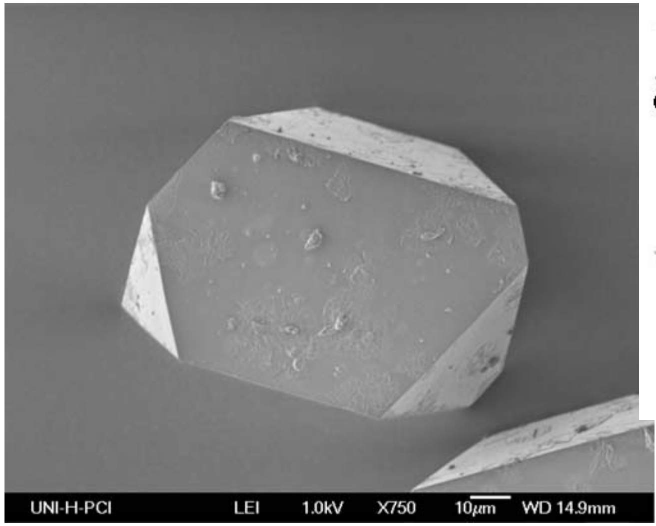


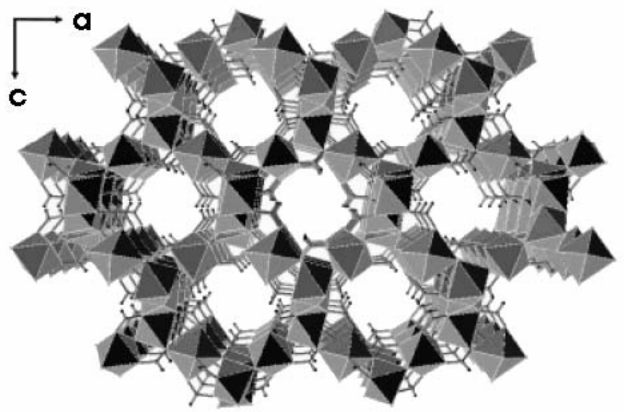




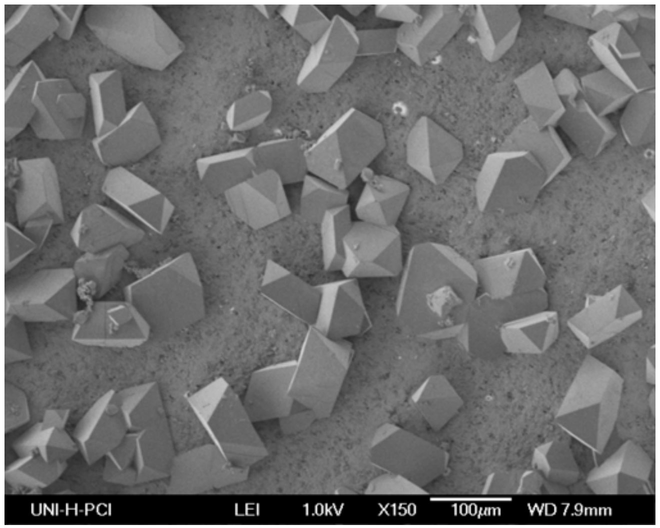
Highlights of Previous Synthesis Research:

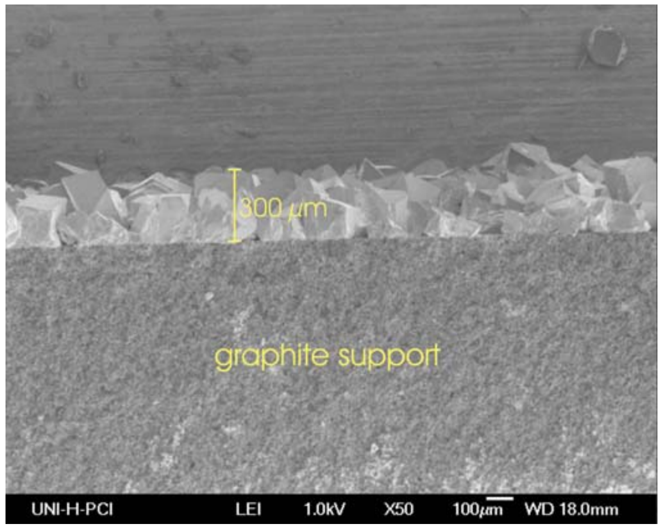
MOF Manganese Formate: Crystals and Film





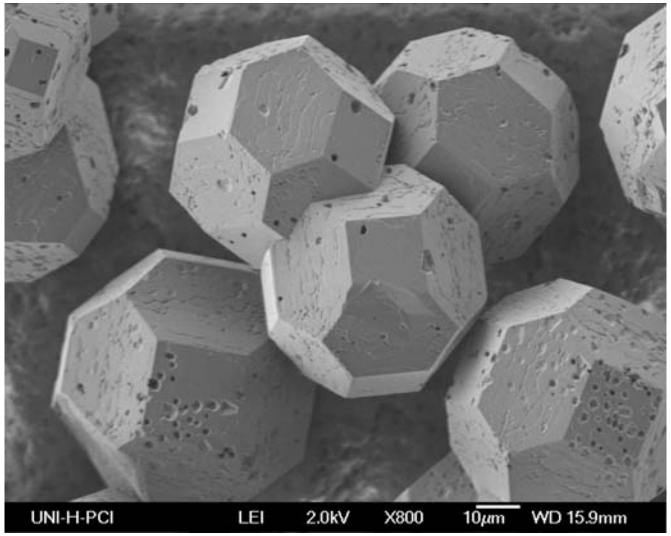
M. Arnold, P. Kortunov, D.J. Jones, Y. Nedellec, J. Kärger, J. Caro, Europ. J. Inorg. Chem., in press.



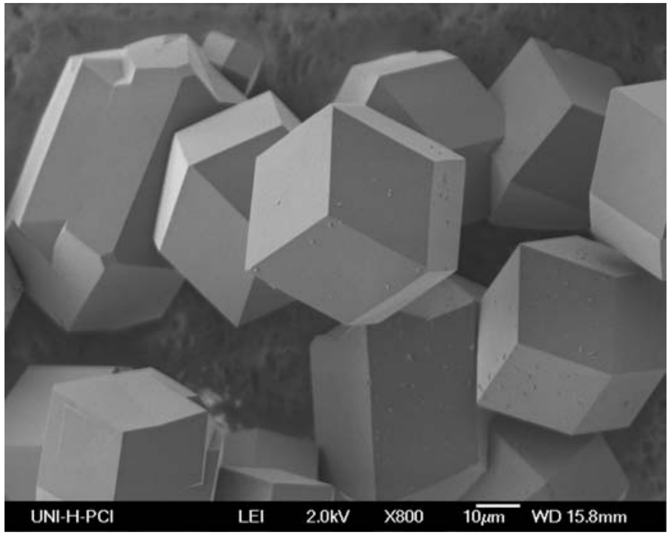


Highlights of Previous Synthesis Research:
Germanosilicate Sodalite

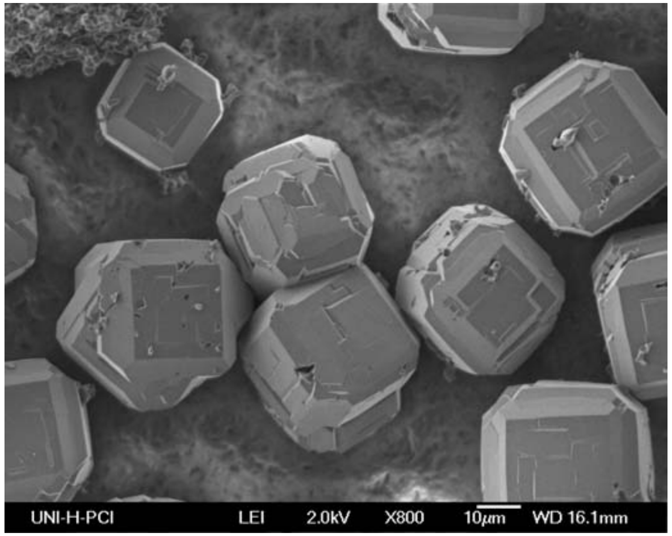
X. Yang, D. Albrecht, J. Caro, Micropor. Mesopor. Mater., accepted.



Synthesized in anhydrous EG solution, Si/Ge~5



Synthesized in anhydrous EG solution, Si/Ge~3



Synthesized in EG solution with fluoride ions and small amount of water, Si/Ge~3

Highlights of Synthesis Research:

Help from Partners silicalite-1, zeolite Y, ferrierite

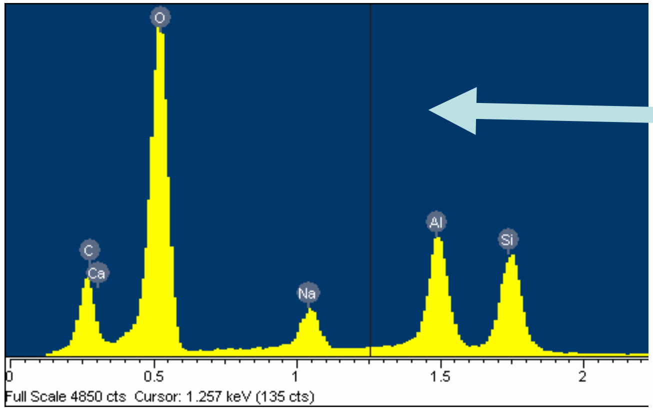
Great help from partners: Extra-large crystals of

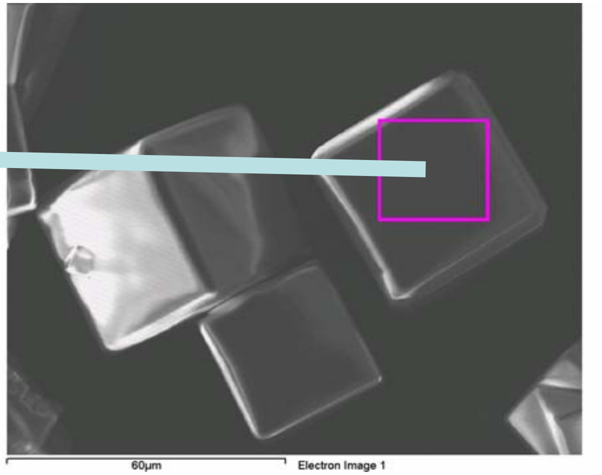
• silicalite-1 (200 µm in length) :	W. Schmidt, Mülheim
• zeolite Y (5 µm diameter):	R. Gläser, Stuttgart
• ferrierite (200 x 50 x 10 μm^3):	R. Gläser, Stuttgart

Highlights of Synthesis Research:

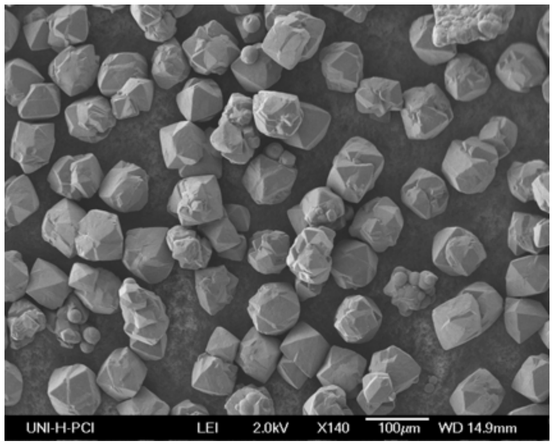
Post-synthesis Modifications

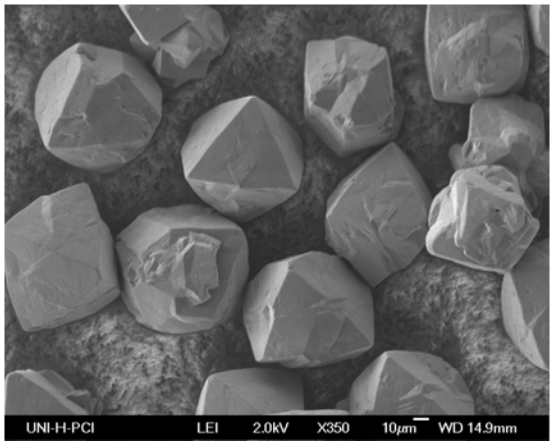
Ca^{2+}-exchange of zeolite NaA: Quantitative determination of Ca-content by SEM/EDX





CaNaA, edge-length ~ 40 µm





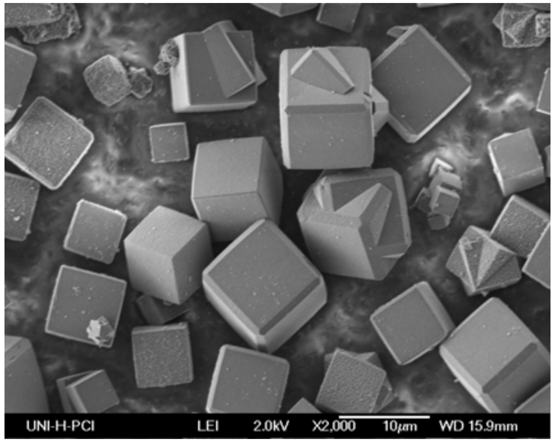
LaNaX, edge-length ~ 70 µm

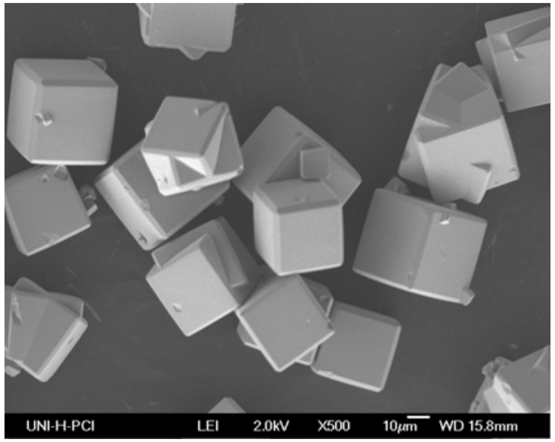
After 3 times La^{3+}-exchange of zeolite NaX: SEM shows crystals are un-damaged

Highlights of Synthesis Research:

Strengthen surface barriers for diffusions through LCD/VCD of TEOS

Before TEOS coating

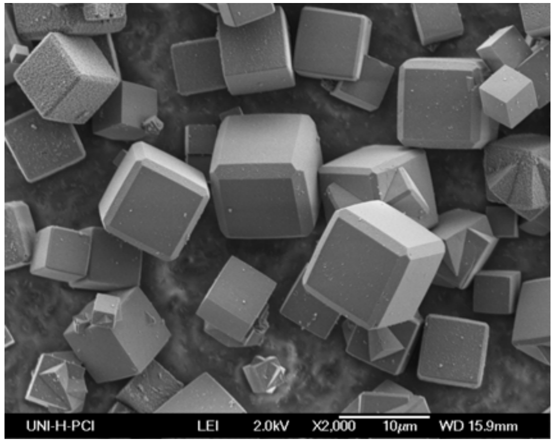


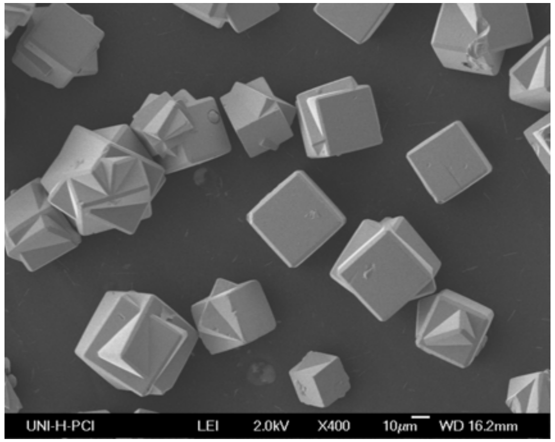


5 µm

35 µm

After TEOS coating



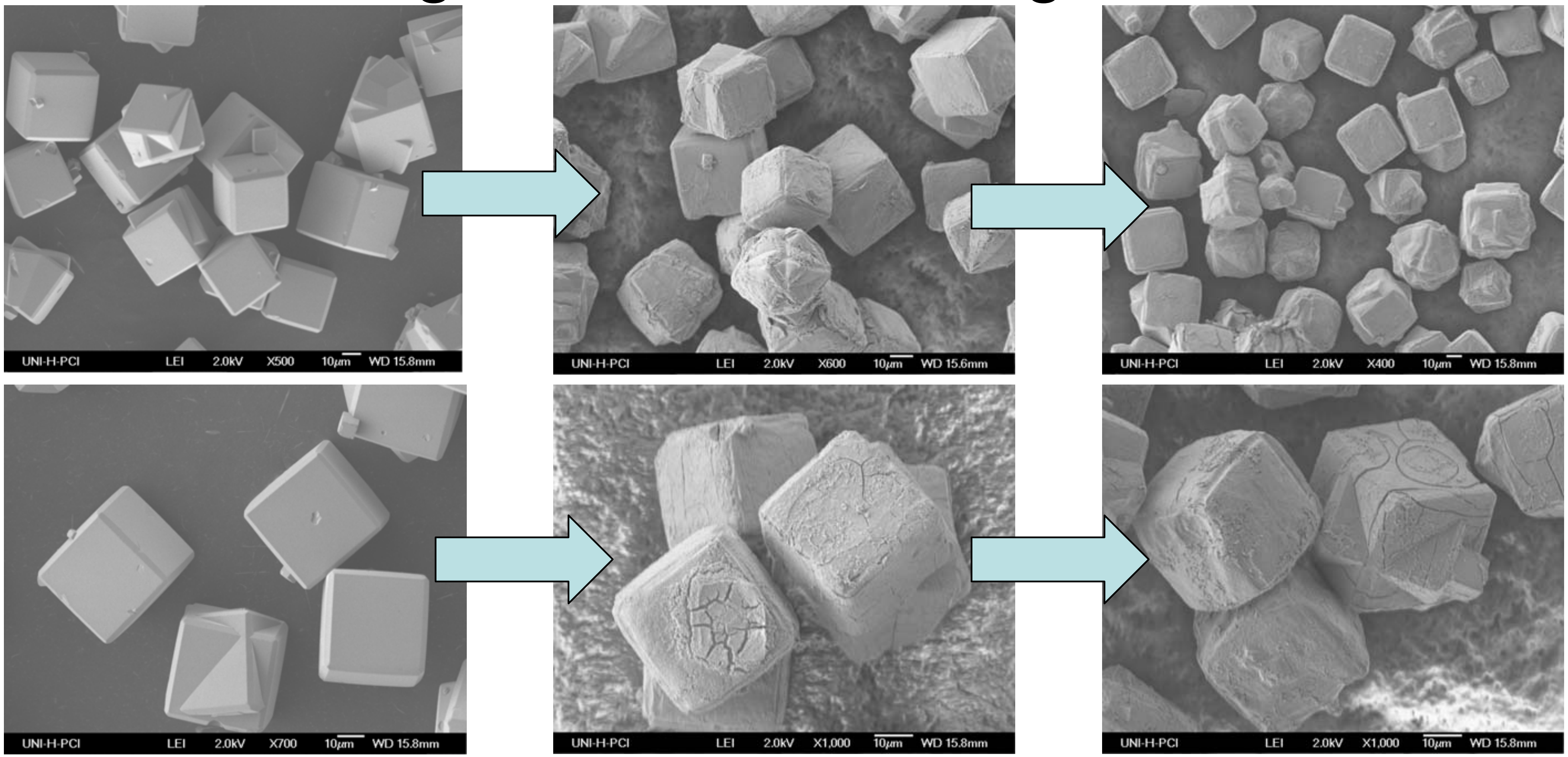


No foreign particles are formed (silica)

Homogeneous silica coating

Highlights of Previous Synthesis Research:

Removal of surface barriers for diffusions through chemical etching with HF



Stirred in 1 g 39% HF+12 g acetone for 5 min.

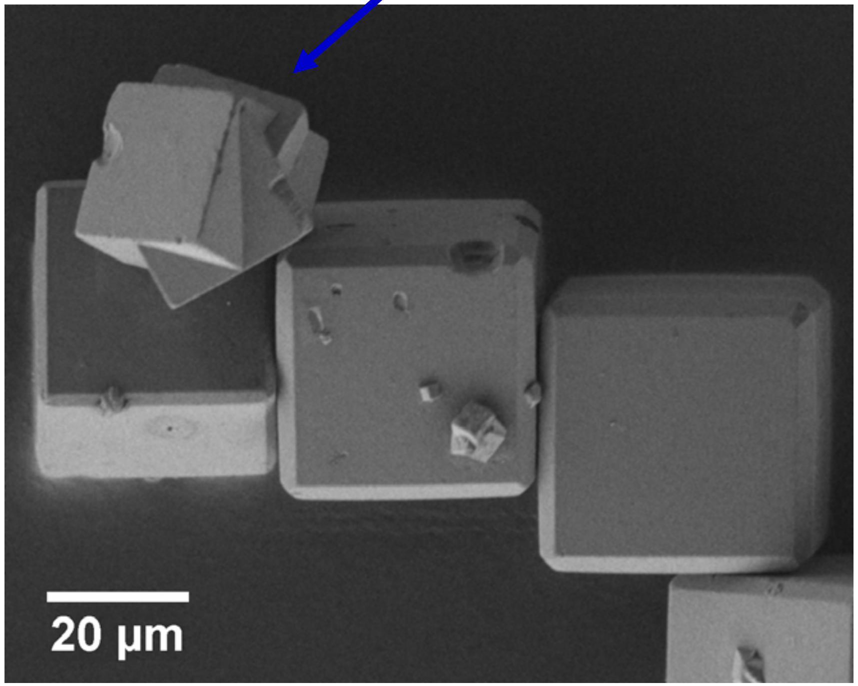
Stirred in 1 g 39% HF+12 g acetone for 10 min.

Starting: XY293_1 CaNaA
1 g, calcined at 500° C.
Exposed to n-C_6 at RT for 1 week

1. Loss of ~1/2 total weight
2. Shape and size of the recovered crystals unchanged
3. Serious internal damages/voides/pores.

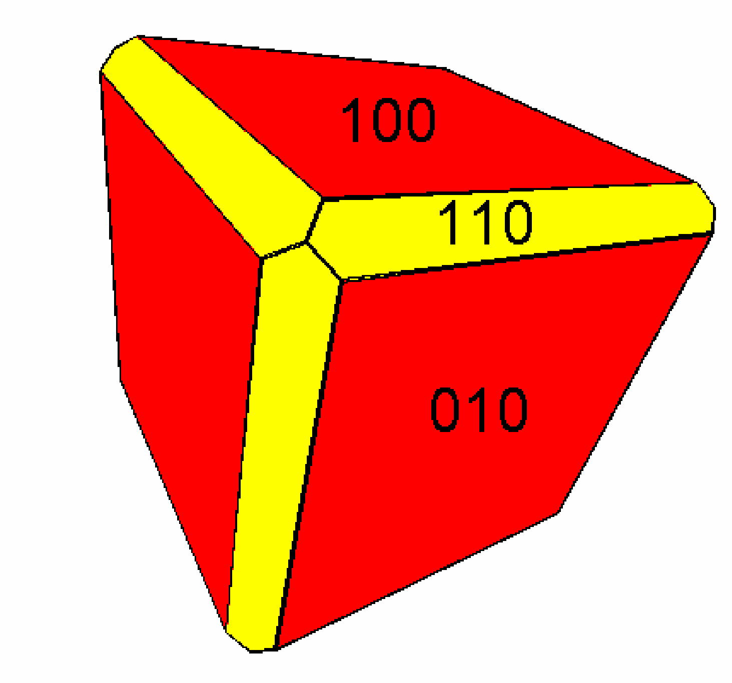
Highlights of Synthesis Research:
Characterization by SEM

• occassionaly intergrown twins



XY293_1

SEM Characterization: CaNaA



• cubes with truncated edges

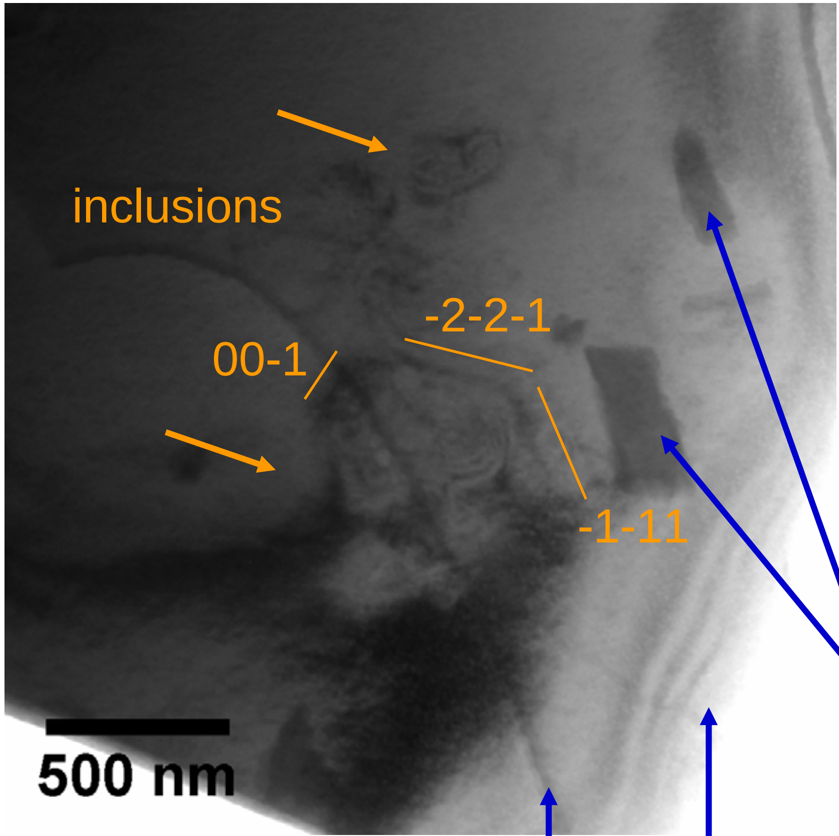
6 faces of the type (100): A_{100} = 80 %

12 faces of the type (110): A_{110} = 20 %

$$\Rightarrow \frac{A_{100}}{A_{110}} = 4$$ (estimated by SEM)

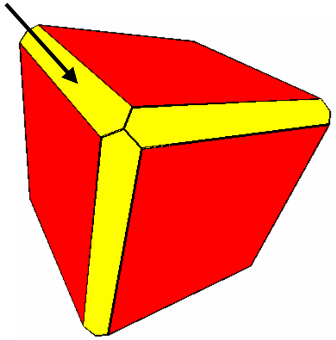
Highlights of Synthesis Research:

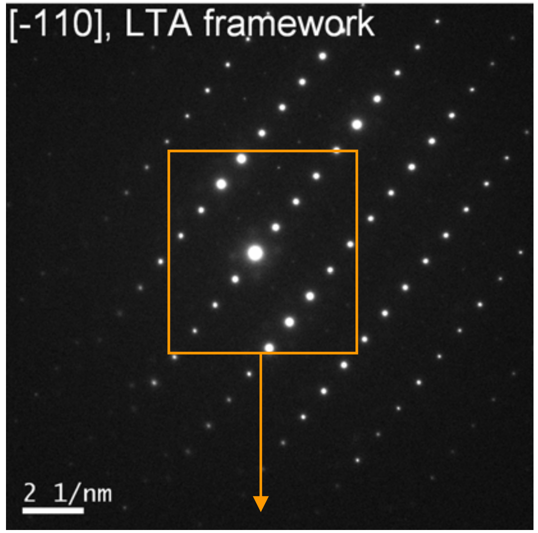
Characterization by TEM

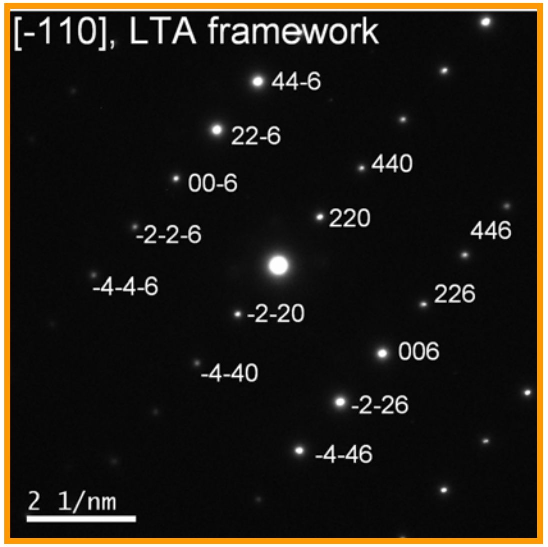


XY293_1

TEM view along
a normal of
a truncated edge







deposited
fragments due to
sample crushing

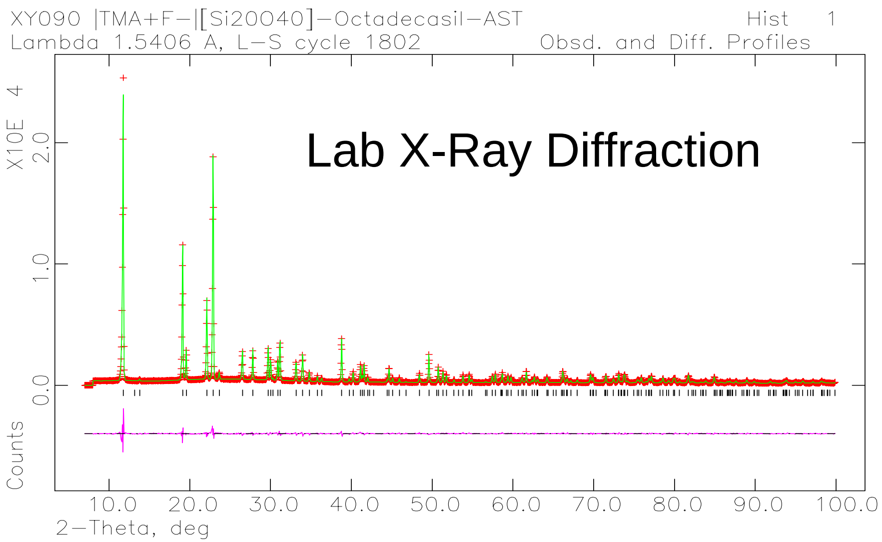
thickness fringes at
the edge of the crystal

edge of the carbon support film

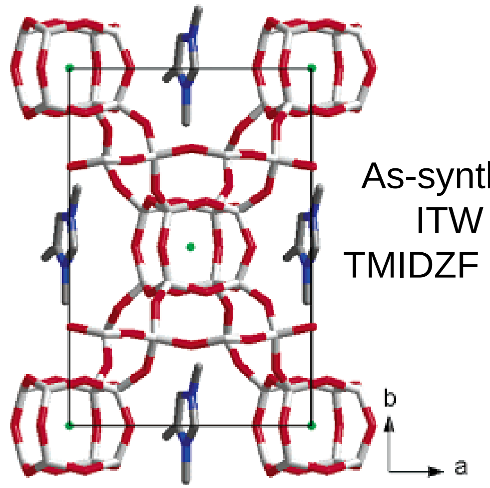
electron diffraction
shows crystallinity

TEM
Characterization:
CaNaA

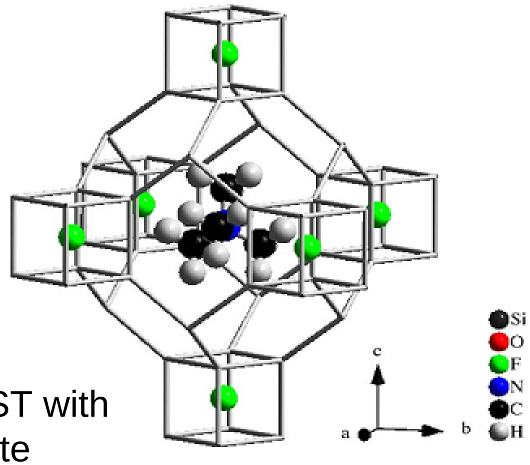
Highlights of Synthesis Research: Crystallographic characterization of zeolitic host/guest systems



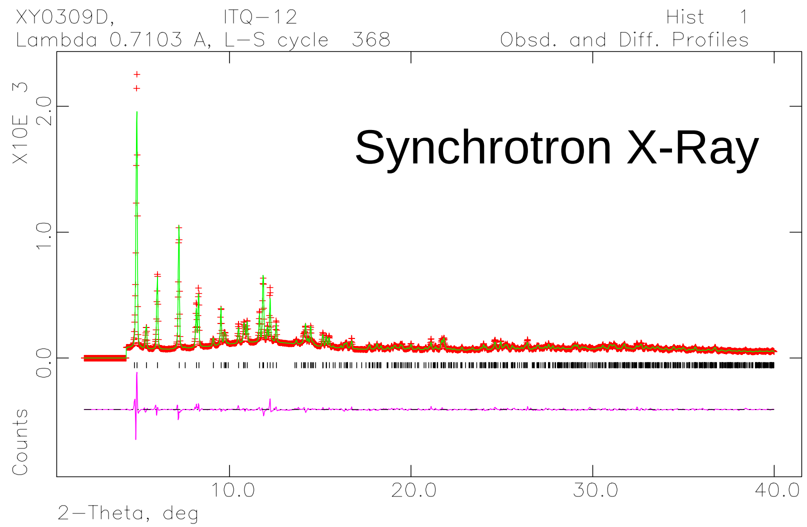
As-synthesized zeolites



As-synthesized ITW with TMIDZF template



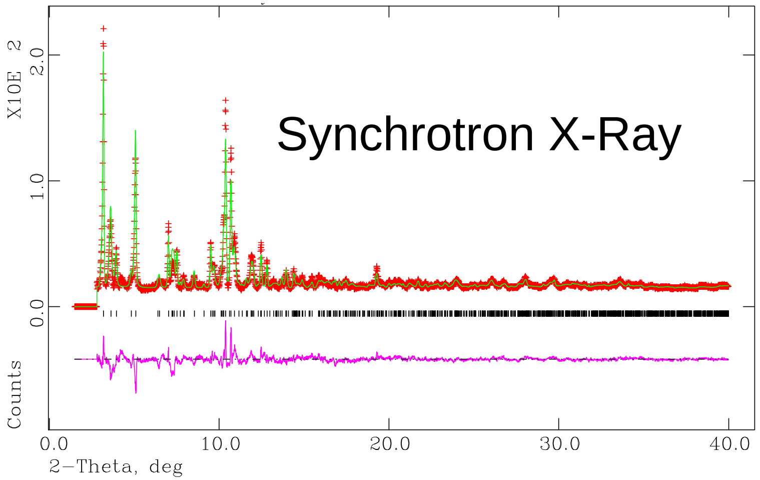
As-synthesized AST with TMAF template

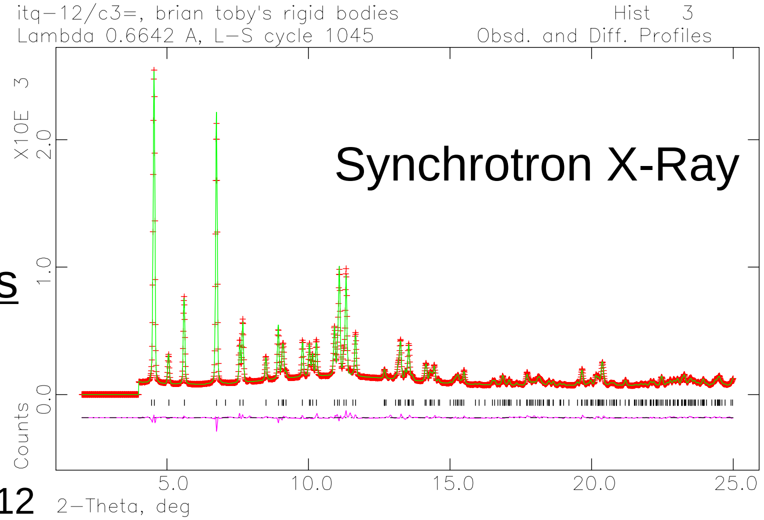


X. Yang, Materials Research Bulletin, 41 (2006) 54.

X. Yang, M.A. Camblor, Y. Lee, H. Liu, D.H. Olson, J. Am. Chem. Soc., 126 (2004) 10403.

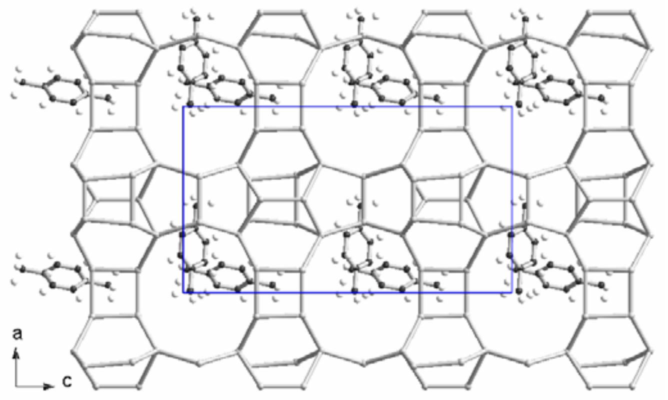
Highlights of Synthesis Research: Crystallographic characterization of zeolitic host/guest systems



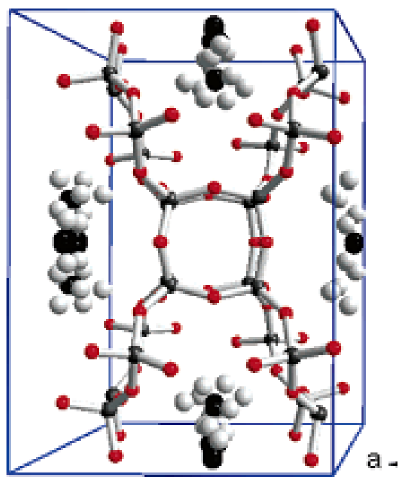


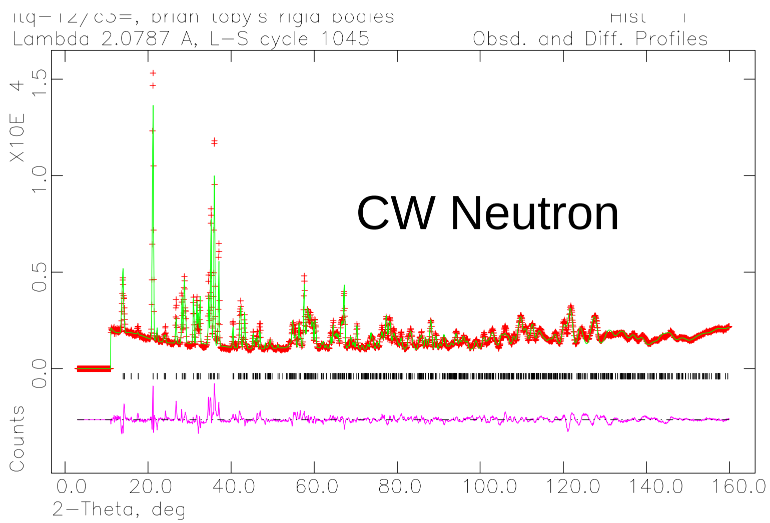
Adsorption Sites in zeolites

Propene in ITQ-12



P-Xylene in ITQ-13





X. Yang, B.H. Toby, M.A. Camblor, Y. Lee, D.H.Olson,
J. Phys. Chem. B, 109 (2005) 7894.
D.H. Olson, X. Yang, M.A. Camblor, J. Phys. Chem. B, 108 (2004) 11044.

Planned Activities vis. Achieved Results in the previous project 2004-2006

Planned	Achieved	Remark
NaCaA	NaA and NaCaA, 5-40 µm	Hannover, successful
Cation Free A	Not achived	Guth‘s AlPO-LTA, or Corma‘s ITQ-29
Silicalite-1/ZSM-5	Extra-large crystals	Mühlheim
NaX	Extra-large crystals 15, 50 and 80 µm	Hannover, successful
NaY	Large crystals 5 µm	Stuttgart
$AlPO_4$-5	Up to 500 µm	Crystal size distribition unsatisfactory
Ferrierite	Extra-large crystal	Stuttgart

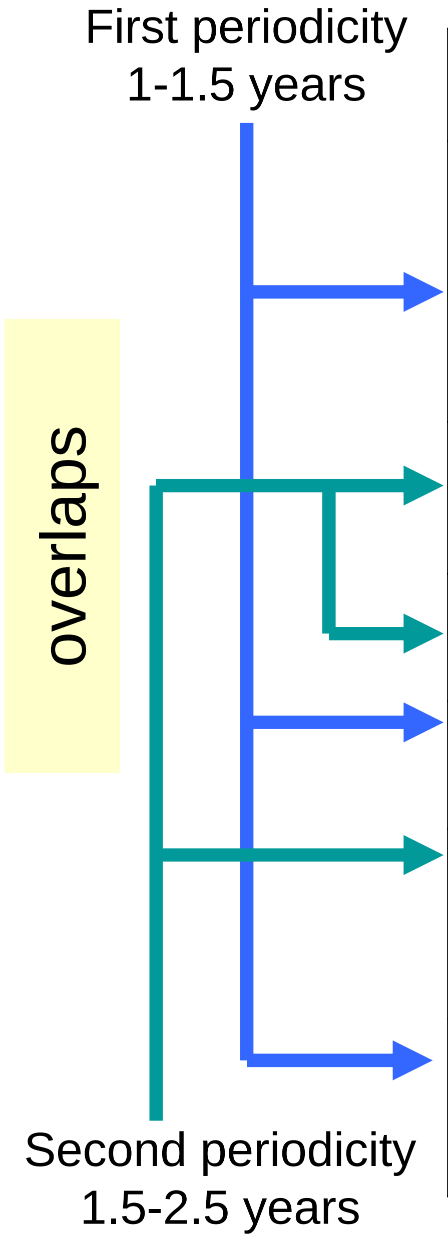
Aims of the Synthesis Work in the Second Period

- Synthesis of materials of the same framework types but of different chemical compositions;
- Control of crystal sizes and size distributions;
- Modification of surface and bulk microstructures.

Targets:

- Self-diffusivity measurements;
- Multi-component diffusion.

Working Programme Second Period



Framework Type	Material	Remark	Pore Dimension
LTA	Aluminosilicate = Linde type A (optional: ZK-4 and zeolite alpha with Si/Al up to 5)	Variable Si/Al ratio	3D, 8-ring
	Pure SiO_2 = ITQ-29	Corma's LTA	
	Aluminium phosphate	Guth's $AlPO_4$	
MFI	Pure SiO_2 = silicalite-1	Pentasil	3D, 10-ring
	(optional: Aluminosilicate = ZSM-5)		
(optional: **MEL)**	Pure SiO_2 = silicalite-2		
	Aluminosilicate = ZSM-11		
FAU	Aluminosilicate Zeolite X	Variable Si/Al ratio	3D, 12-ring
	Aluminosilicate Zeolite Y		
FER	Pure SiO_2 ferrierite	Gies' invention	2D, 8 and 10-ring
	(optional: Aluminosilicate ferrierite)	Vaughan's work in 1966	
AFI	Aluminium phosphate = $AlPO_4$-5	Caro's standard	1D, 12-ring
	Aluminosilicate SSZ-24	Zones' invention	

Resources

Available in the Institute:

- SEM and TEM for microstructure analysis;
- Powder XRD with heatable sample stage for phase identification;
- Other instruments for chemical and physical (thermal) analyses, etc.

Purchased in the first period:

- Autoclaves for conditional experiments, 5 X 23 mL, 10 X 45 mL, 5 X 100 mL;
- Autoclave (mini-reactor) for scale-up, 1 X 300 mL.

Needed for the second period:

- Heating blocks, 2 X for 100 mL autoclaves, 5000 €;
- Autoclaves for conditional experiments, 10 X 100 mL, 20 000 €;
- Autoclave for scale-up, 1 X 1000 mL,
  with stirring and heating accessories, 29 000 €.