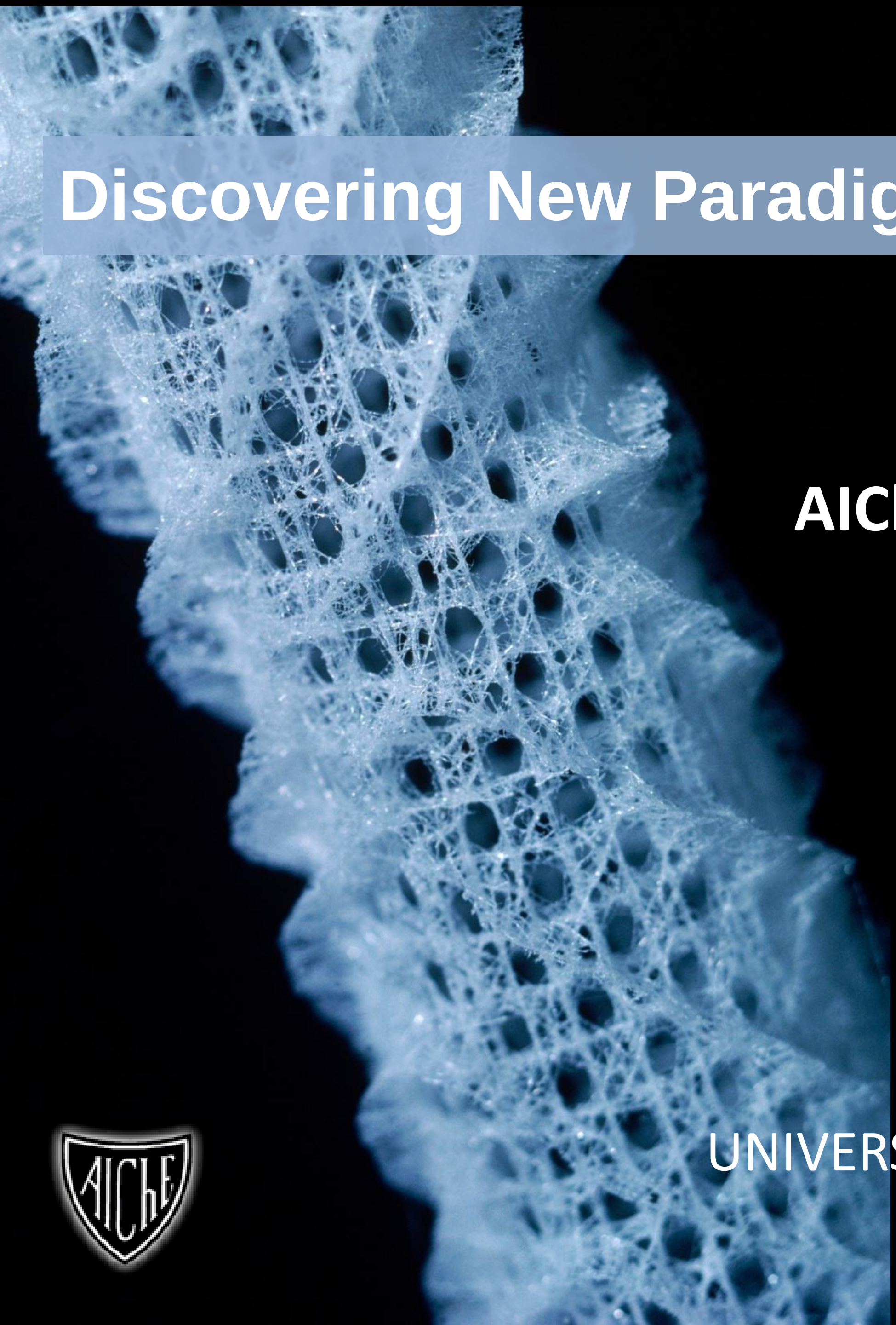


Discovering New Paradigms in Zeolite Synthesis
by Rational Design

AIChE South Texas Section
Houston, TX
December 9, 2014

STS
AIChE

Jeffrey D. Rimer

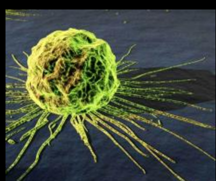
Ernest J. and Barbara M. Henley
Chemical Engineering Professor

UNIVERSITY of HOUSTON | ENGINEERING
Chemical & Biomolecular Engineering

AIChE

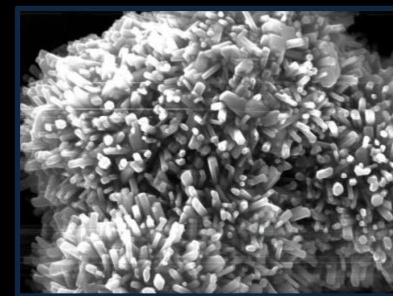
Biomineralization
(Health & Medicine)





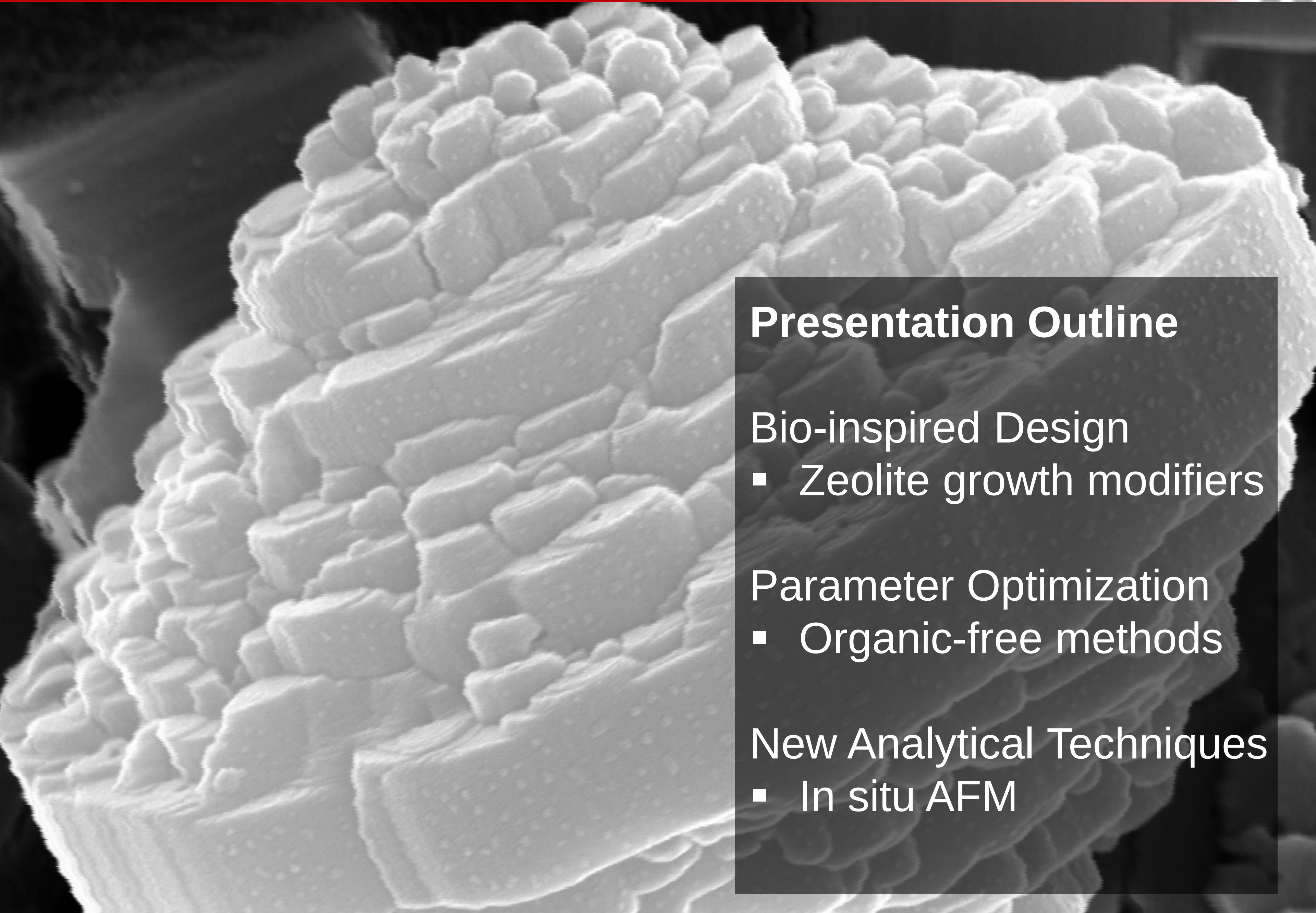

- ❑ Kidney stones (minerals)
- ❑ Malaria (heme)
- ❑ Cancer

Zeolite Catalysis
(Energy, Fuels & Chemicals)




- ❑ Catalyst synthesis
- ❑ Surface science (AFM)
- ❑ Catalytic testing
- ❑ Modeling (DFT, MD, MC)

Rational design of zeolite catalysts

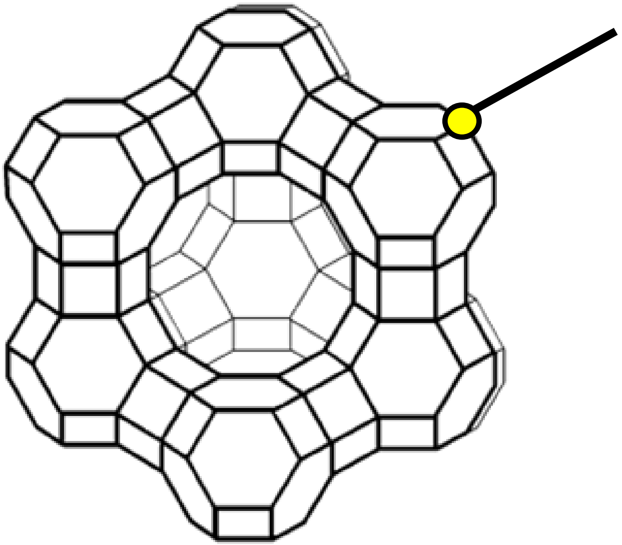


Presentation Outline

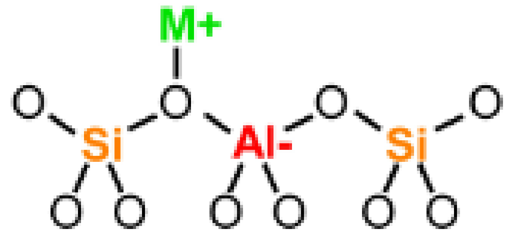
Bio-inspired Design
- Zeolite growth modifiers

Parameter Optimization
- Organic-free methods

New Analytical Techniques
- In situ AFM



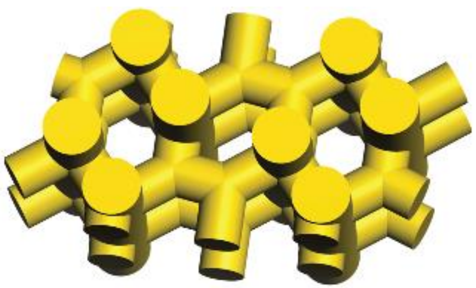
T-site, T = Si, Al, P, Ge, Sn,…

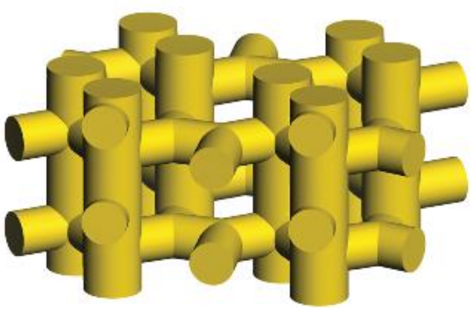


H^+ Brønsted Acid

M^+ Lewis Acid

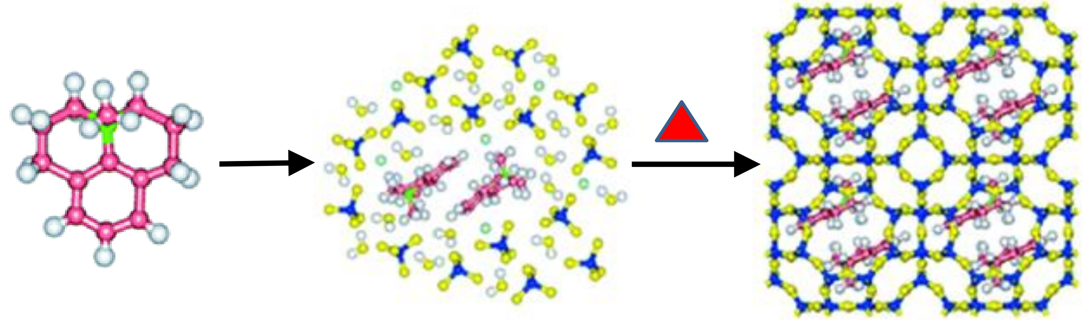
Dimensionality: 1D, 2D, 3D





Small pore (8-MR):	~0.4 nm
Medium pore(10-MR):	~0.6 nm
Large pore(12-MR):	~0.8 nm

Organic structure-directing agents (OSDAs)



NUCLEATION CRYSTALLIZATION

Corma, Nature Chem. 2012

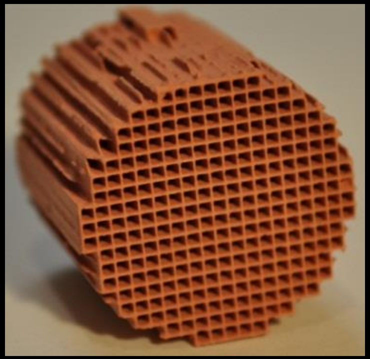
Zeolite applications

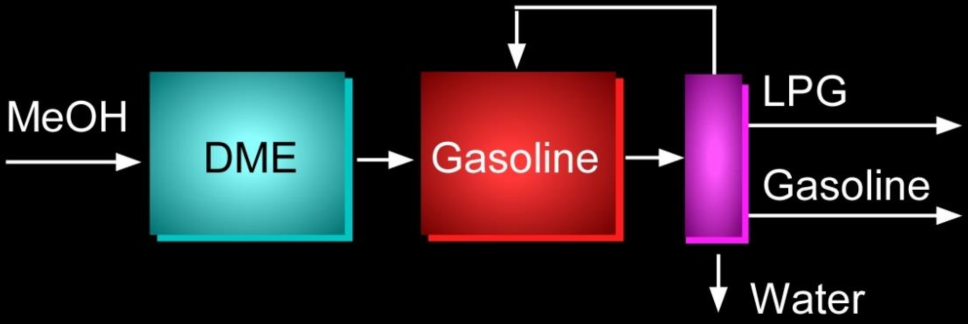
Catalysts

- ❑ Petroleum refining
- ❑ Chemicals
- ❑ Biofuels
- ❑ Methanol-to-hydrocarbons
- ❑ Emissions

Ion-Exchange



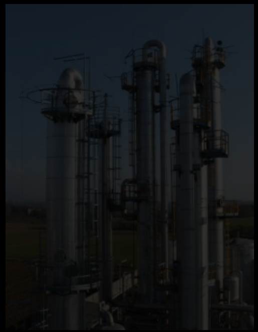


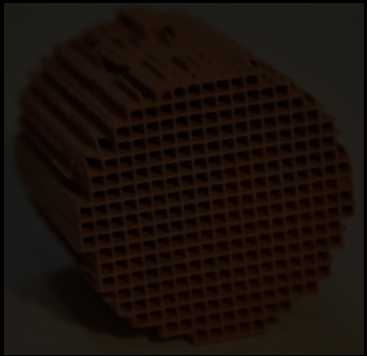


Olsbye et al., *Angew. Chem. Int. Ed.* 2012

Catalysts

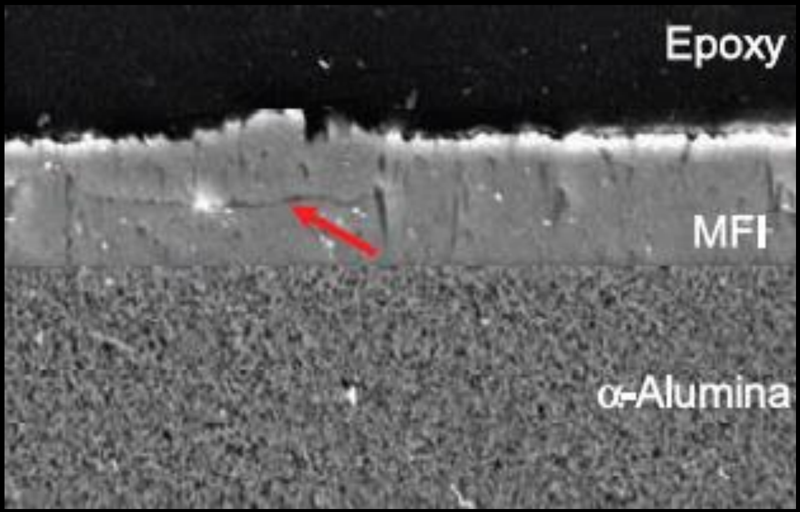
- Petroleum refining
- Chemicals
- Biofuels
- Methanol-to-hydrocarbons
- Emissions





Ion-Exchange

Selective Separations



Tsapatsis, *Science* 2009

Zeolite applications

Catalysts

- ❑ Petroleum refining
- ❑ Chemicals
- ❑ Biofuels
- ❑ Methanol-to-hydrocarbons
- ❑ Emissions

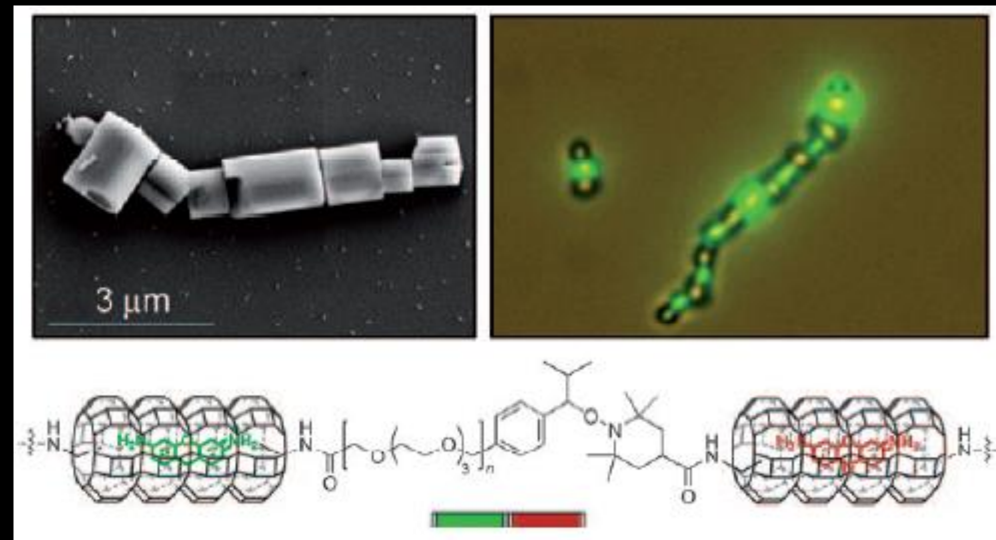
Ion-Exchange

Selective Separations

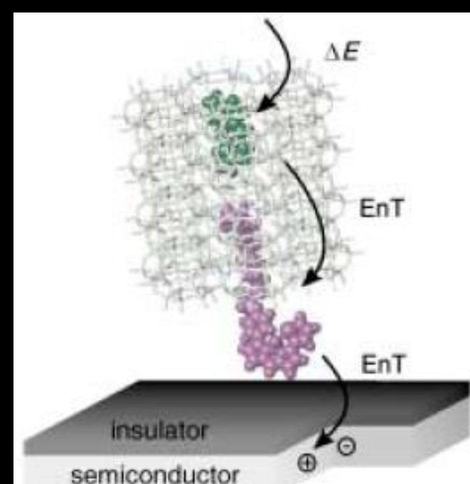
Drug delivery

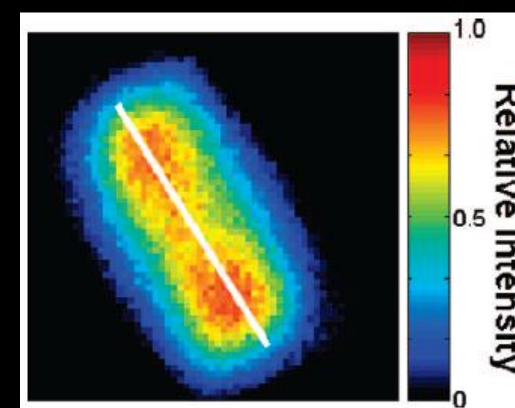
Sensors

- ❑ Photonic devices



De Cola, *Angew. Chem. Int. Ed.* 2010

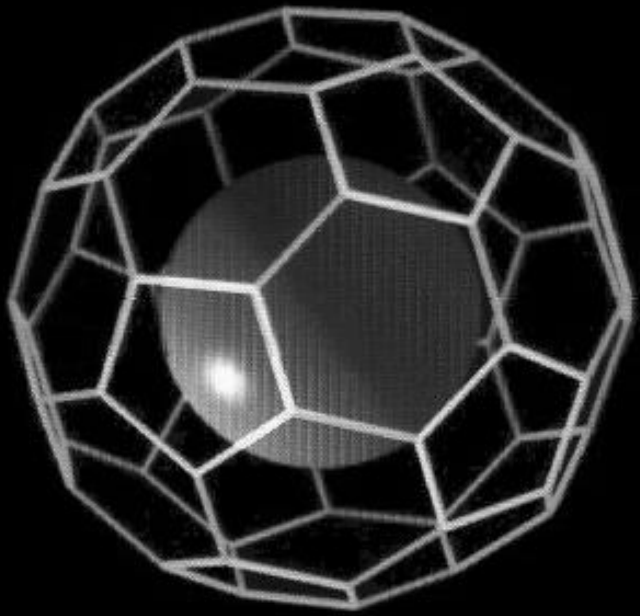




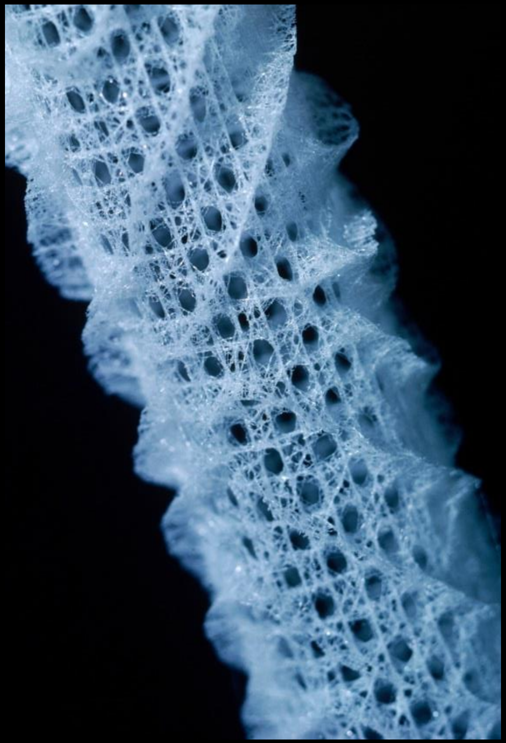
De Cola, *JACS* 2008

Calzaferri, *Angew. Chem. Int. Ed.* 2003

Multifaceted elements of catalyst design



SYNTHESIS



NATURE

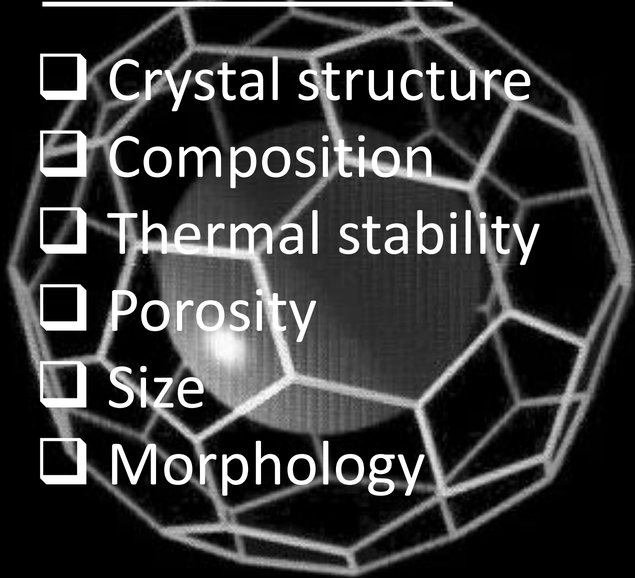
ARCHITECTURE

"A designer is an emerging synthesis of artist, inventor, mechanic, objective economist, and evolutionary strategist"

-R. Buckminster Fuller

Challenges in catalyst development

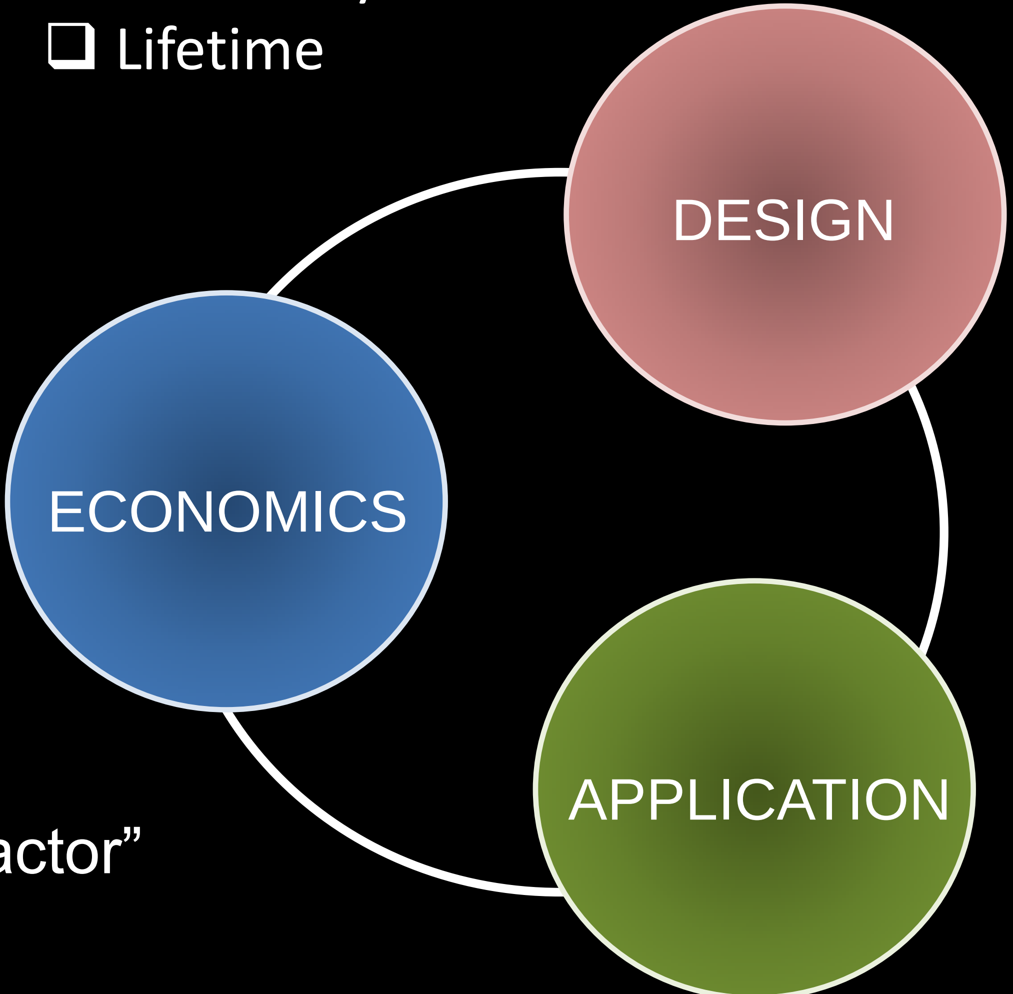
PROPERTIES



- ❑ Crystal structure
- ❑ Composition
- ❑ Thermal stability
- ❑ Porosity
- ❑ Size
- ❑ Morphology

PERFORMANCE

- ❑ Conversion (activity)
- ❑ Selectivity
- ❑ Lifetime



"From art to science"

"From benchtop to the reactor"

Challenges in catalyst development

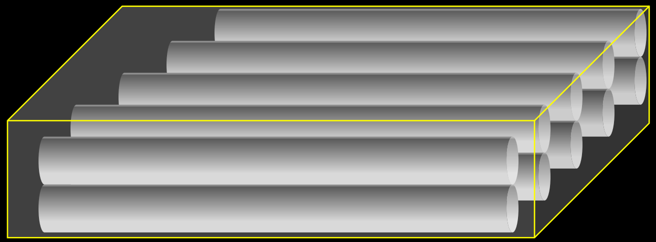
PROPERTIES

- ❑ Crystal structure
- ❑ Composition
- ❑ Thermal stability
- ❑ Porosity
- ❑ Size
- ❑ Morphology

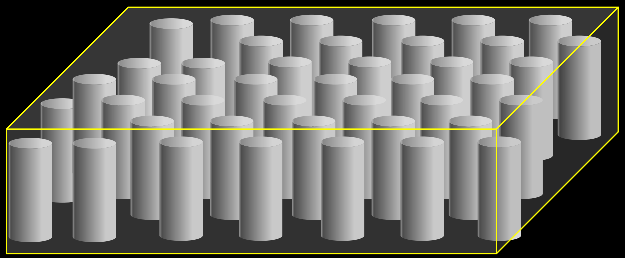
PERFORMANCE

- ❑ Conversion (activity)
- ❑ Selectivity
- ❑ Lifetime

Challenge: Predictive control of crystal habit



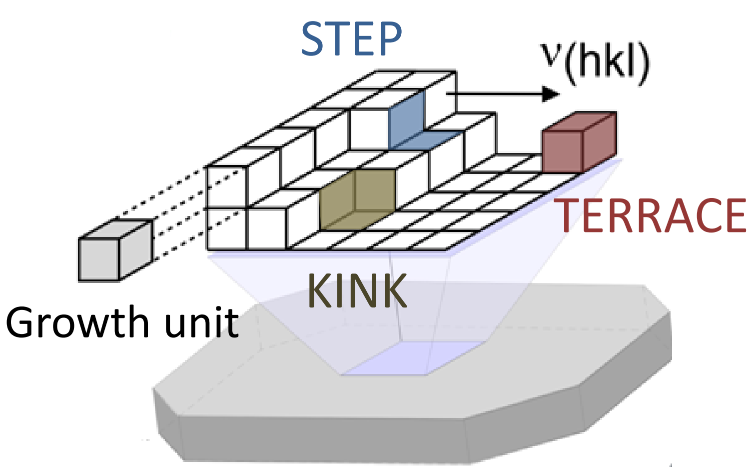
Poor Engineering

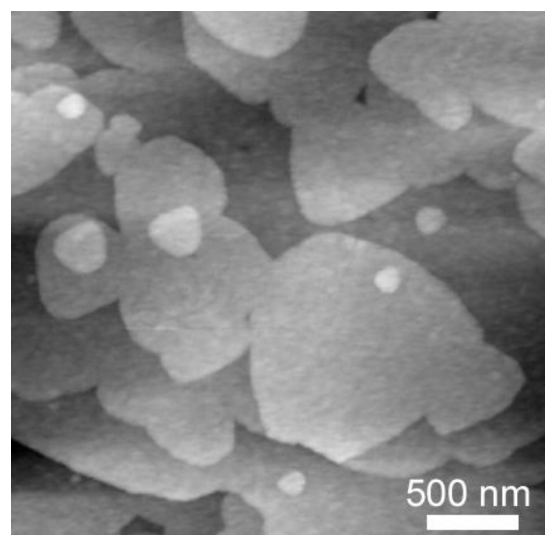


“Rational Design”

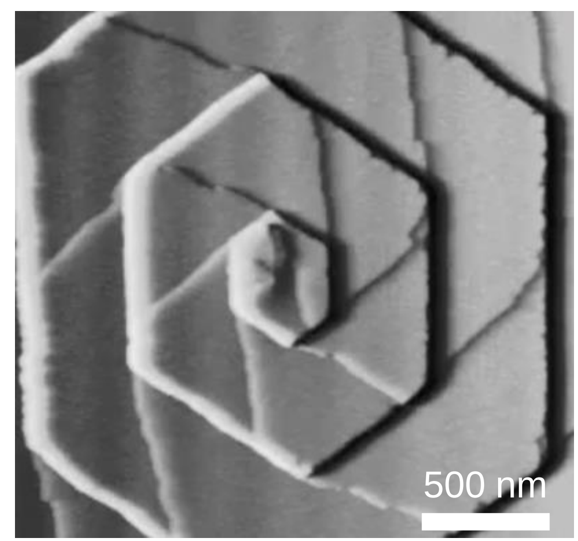
Classical crystallization mechanisms

Crystal growth





Lupulescu and Rimer, *Submitted*



Rimer et al., *Science* 2010

Controlling kinetics of crystallization

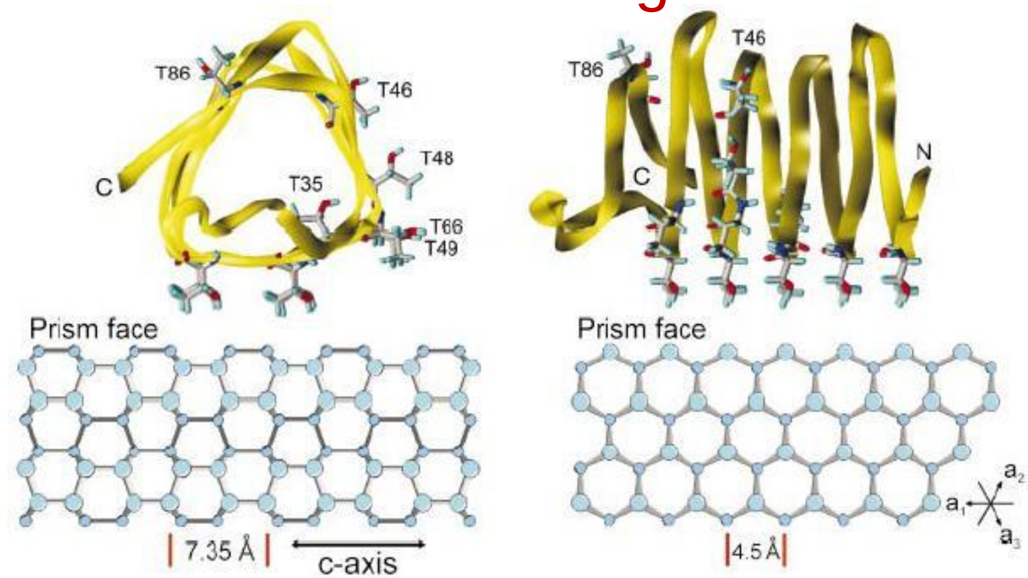
Lahav et al., *Science* 1991

Growth Modifiers:

- Minerals
  - $CaCO_3$, CaC_2O_4, …
  - $BaSO_4$
- Amino acids
- Organic crystals
- Metal oxides
- Metals
- Ice *(antifreeze proteins)*

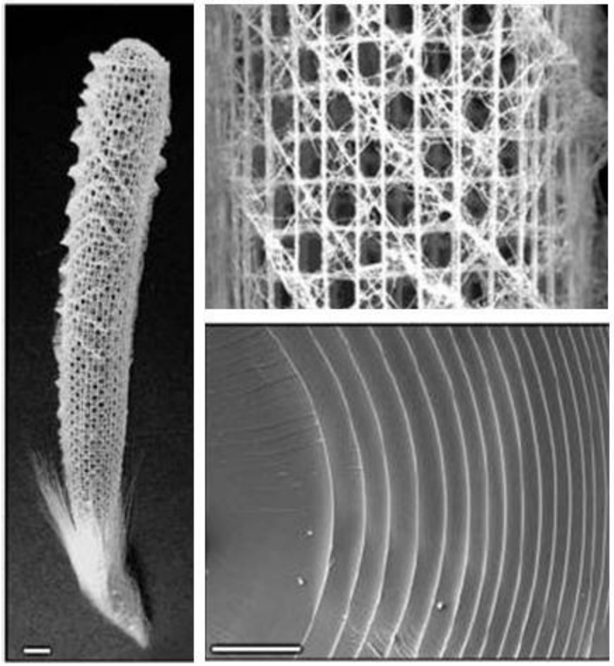
STEP
KINK
Growth unit

Molecular Recognition

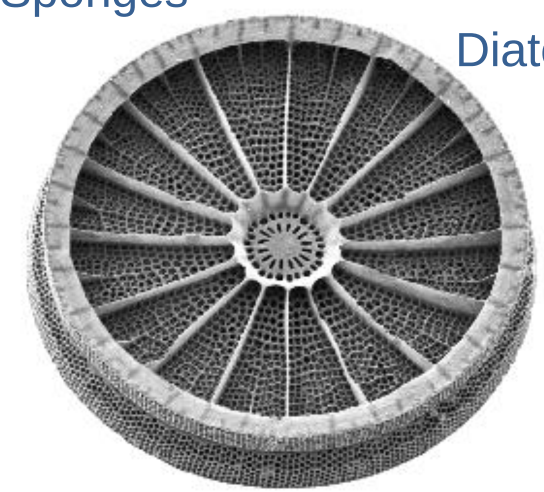


Marshall et al., *Nature* 2004

Bio-inspired zeolite synthesis

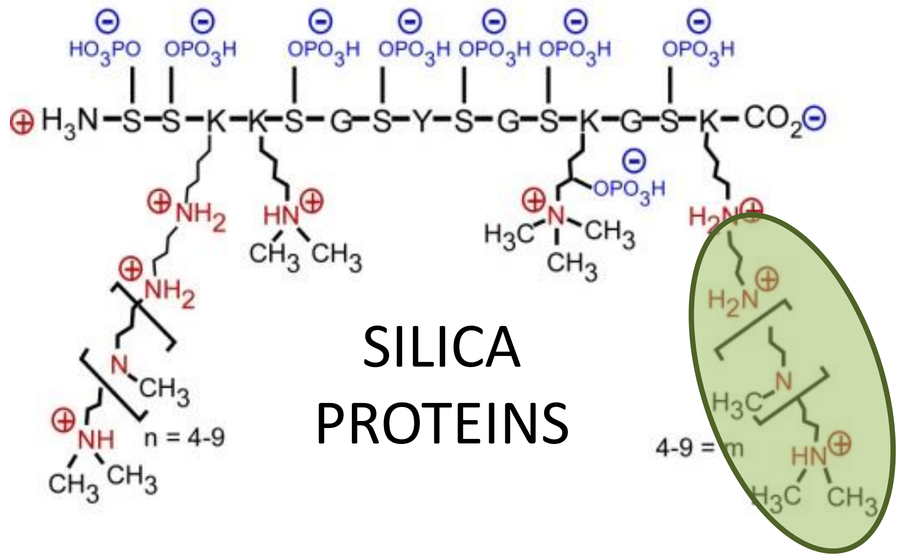


Sponges

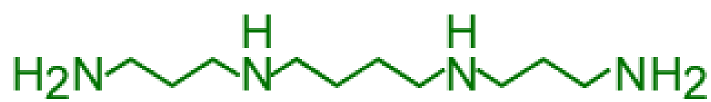


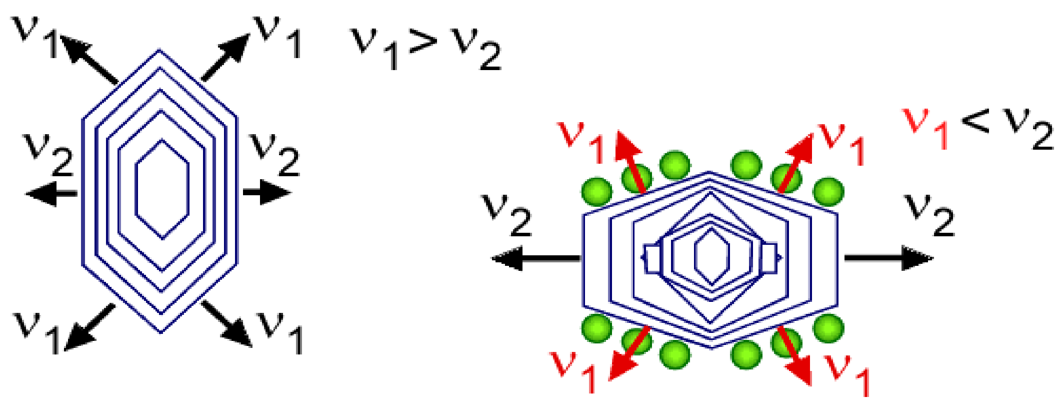
Diatoms

Inspired by unicellular organisms



Zeolite Growth Modifier

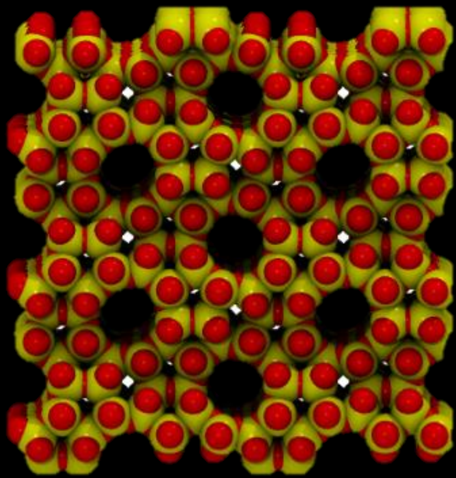




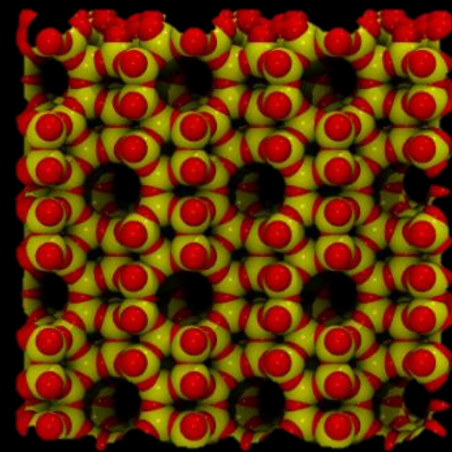
Aizenberg et al., *Science* 2005

MFI crystal topology and habit

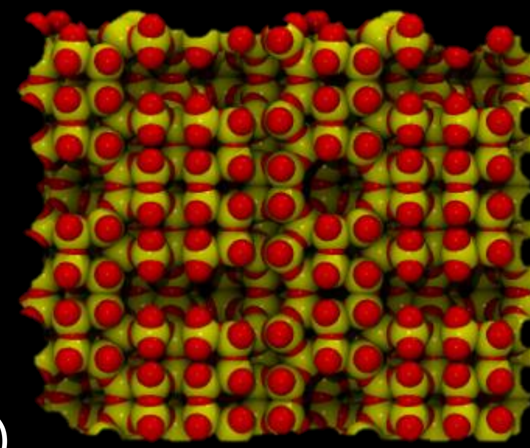
(010)

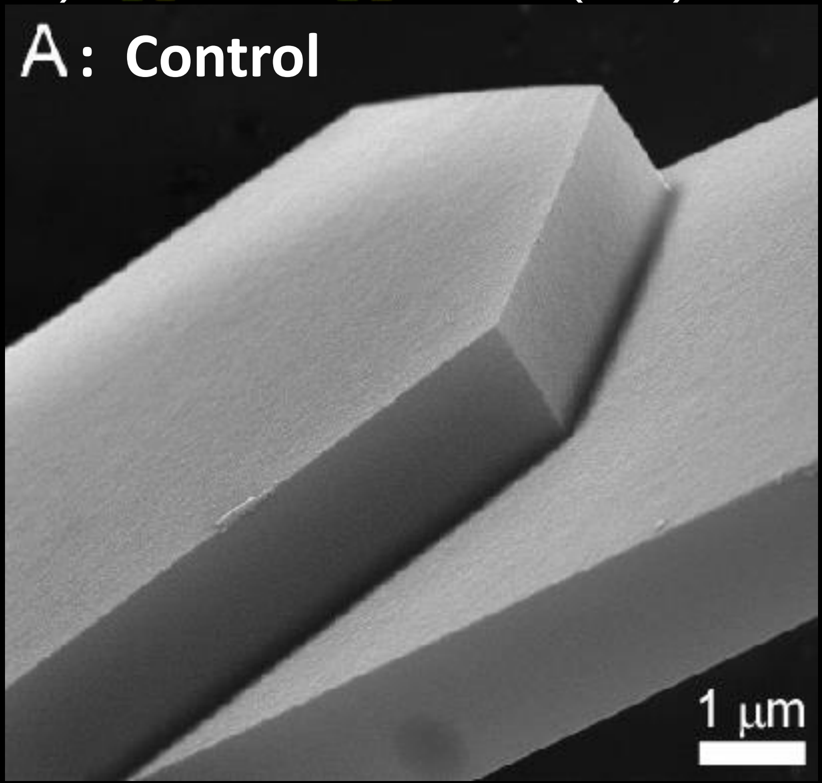


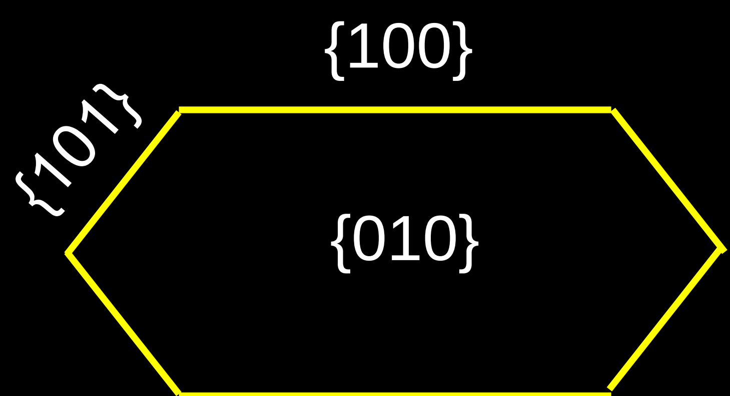
(100)



(101)





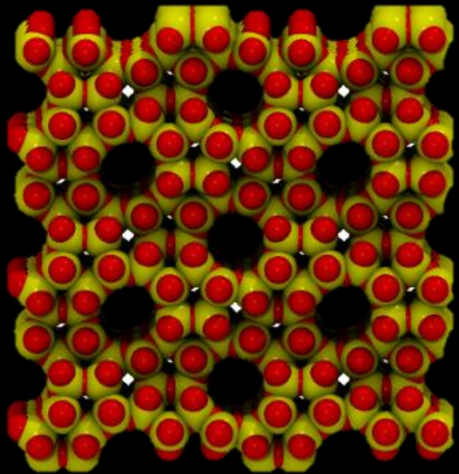


Design targets:

Ultrathin (010) platelets

Large surface area

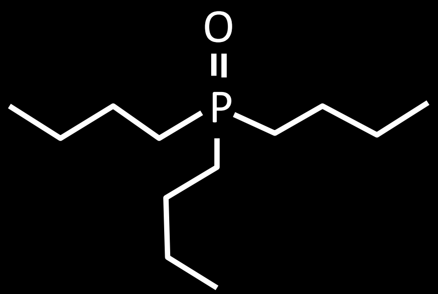
Modification of MFI [010] growth

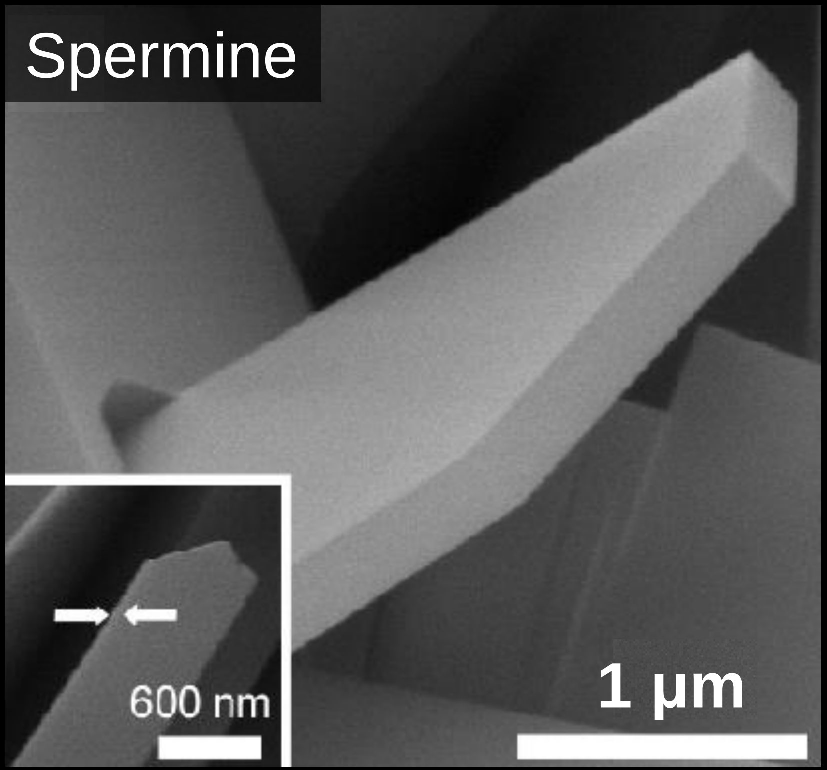


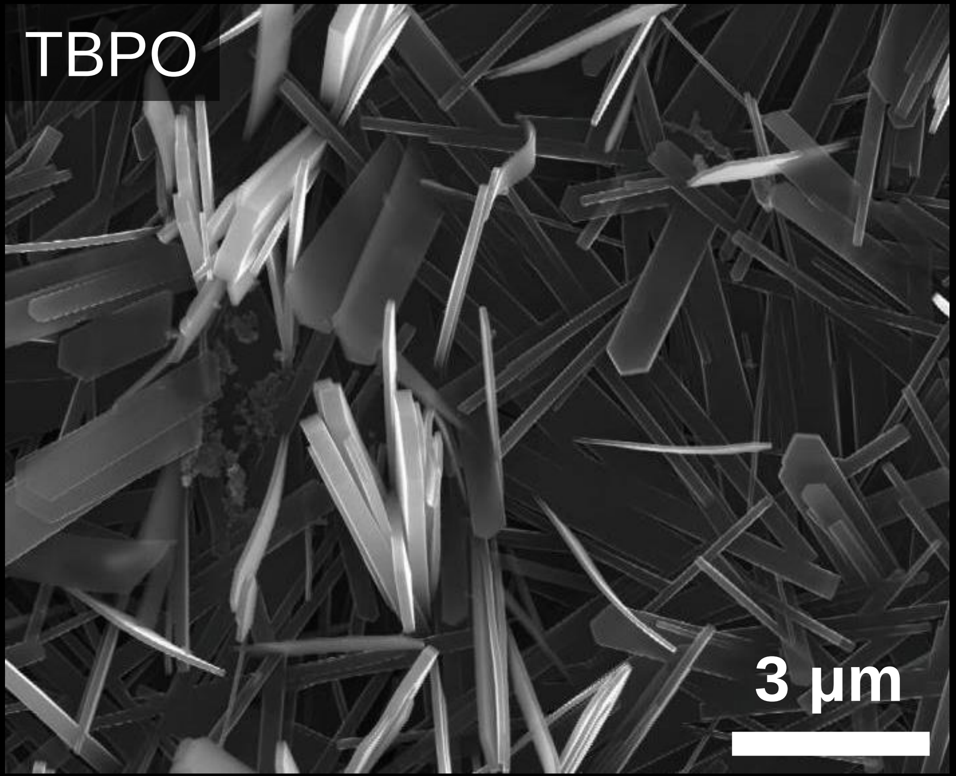
(010)

Spermine

TBPO

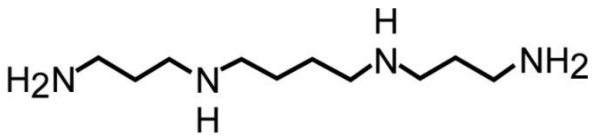




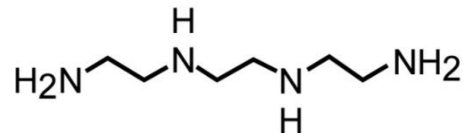


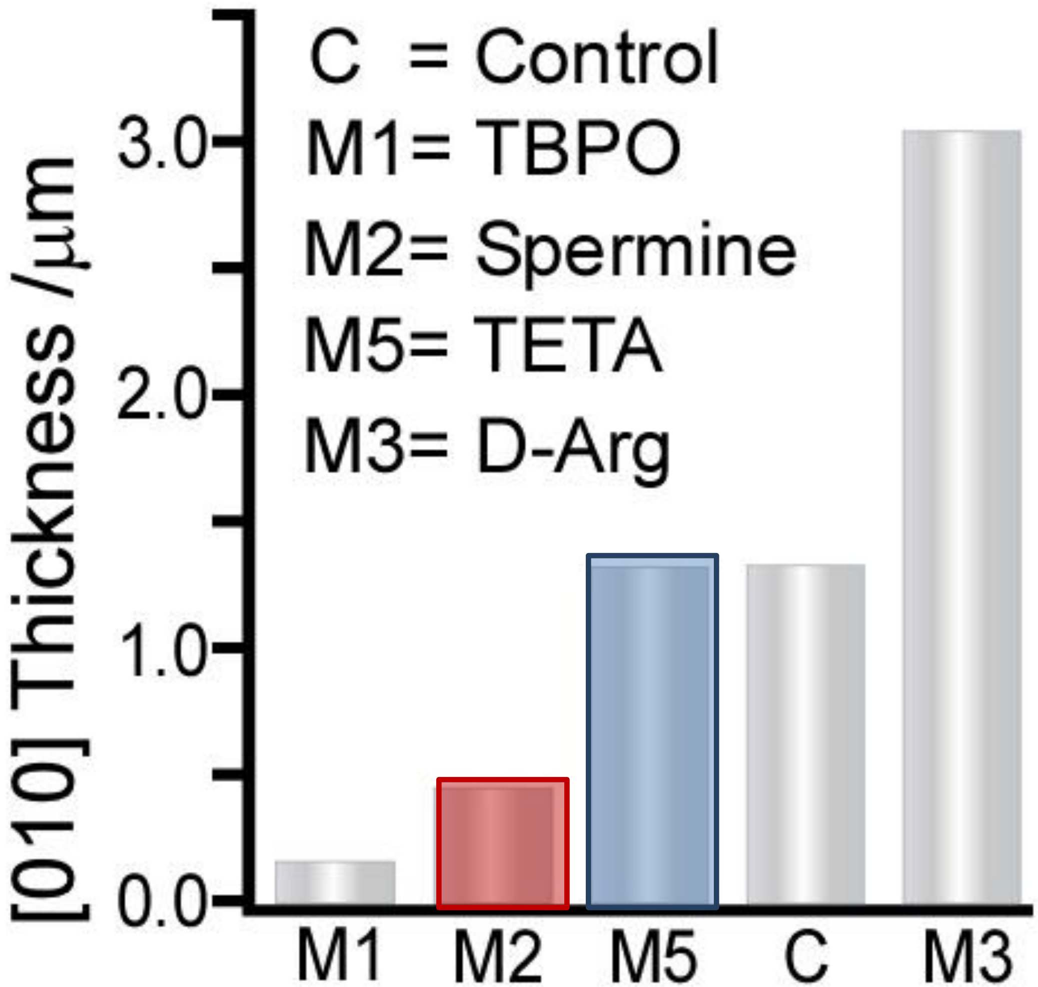
Tailoring thickness of MFI platelets

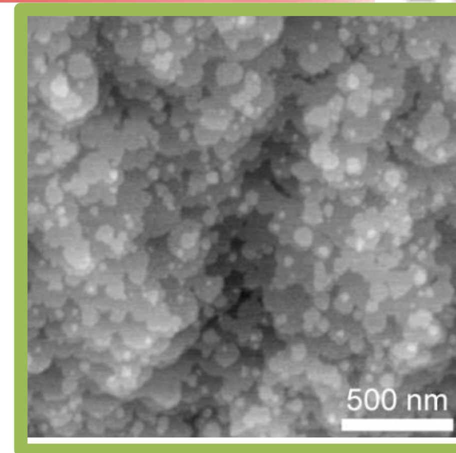
Spermine

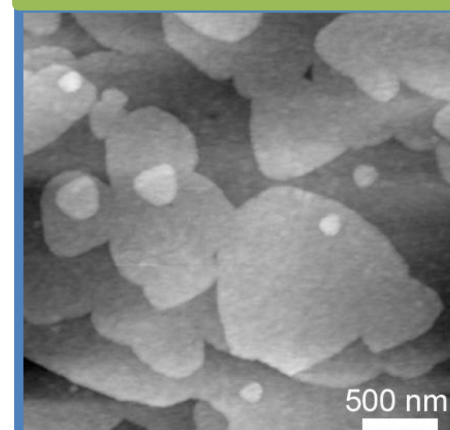


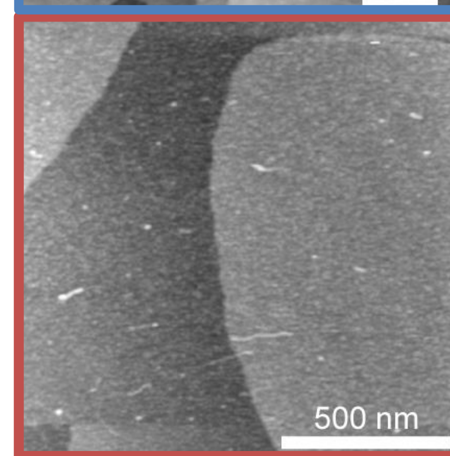
Triethylenetetramine (TETA)





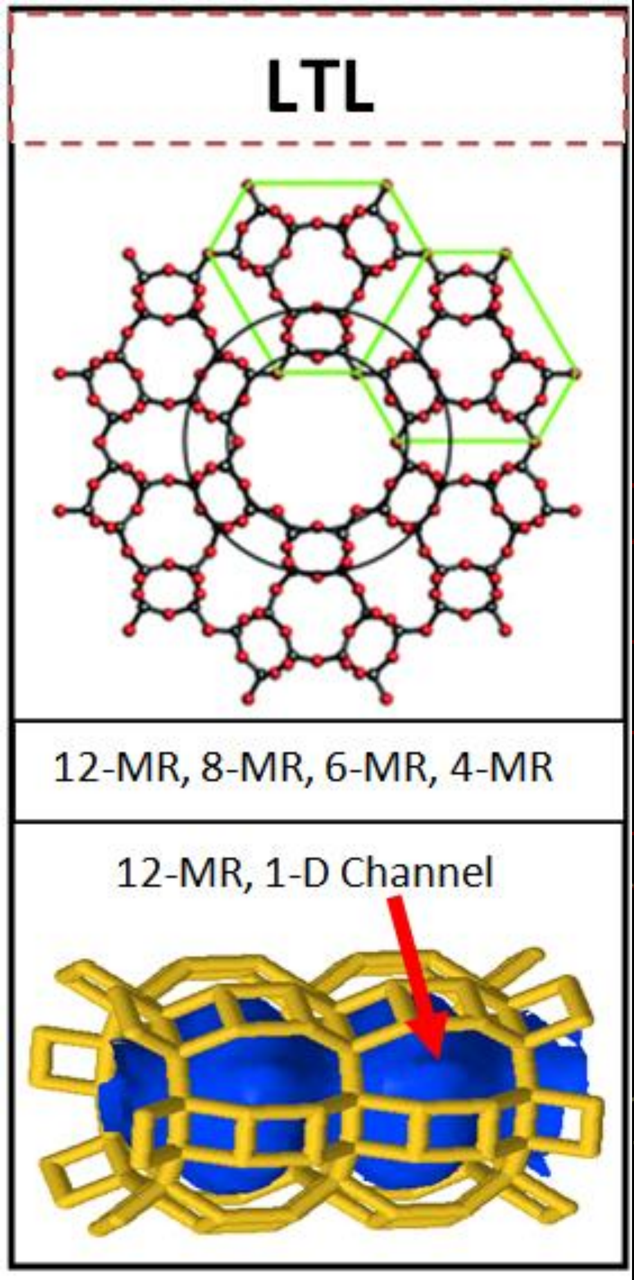




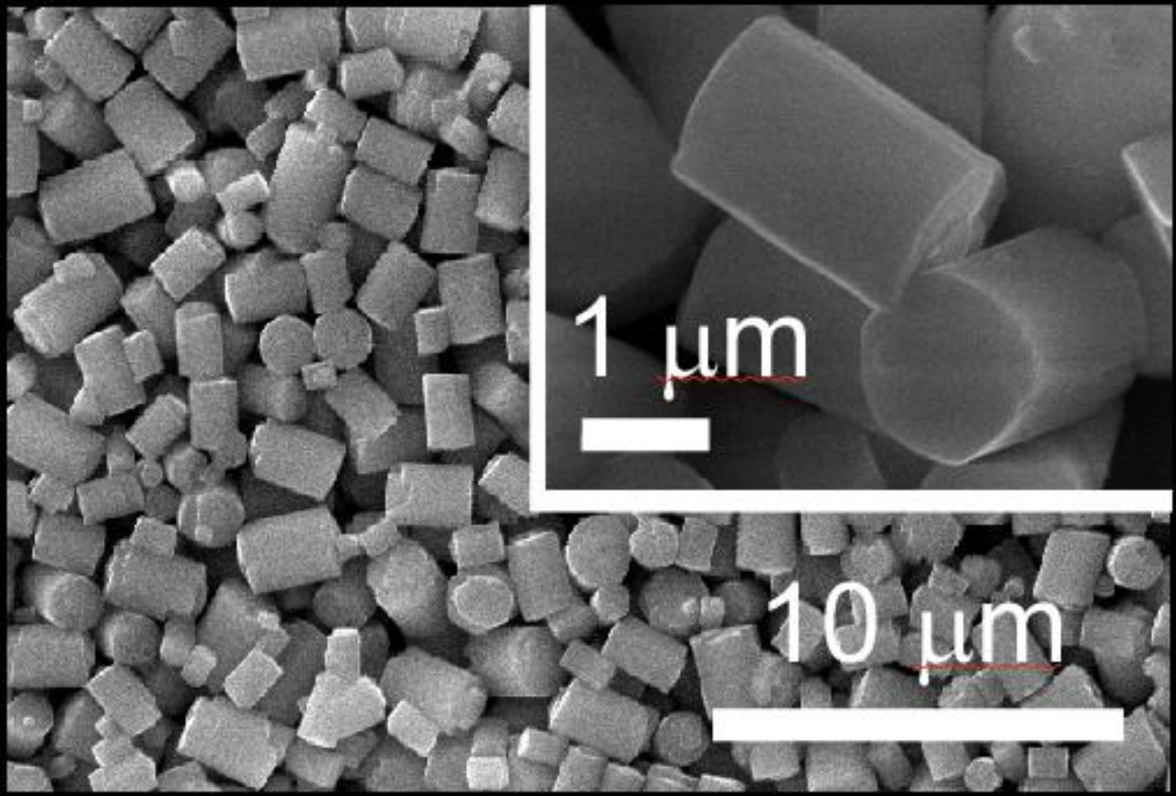


Lupulescu and Rimer, *Angew. Chem. Int. Ed.* 2012

Zeolite L (LTL type)

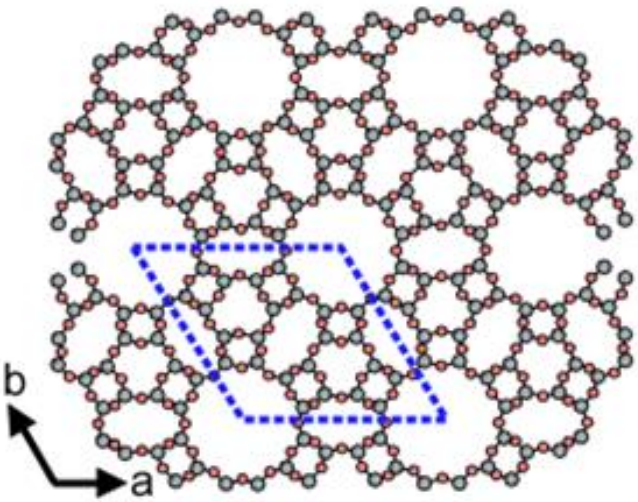


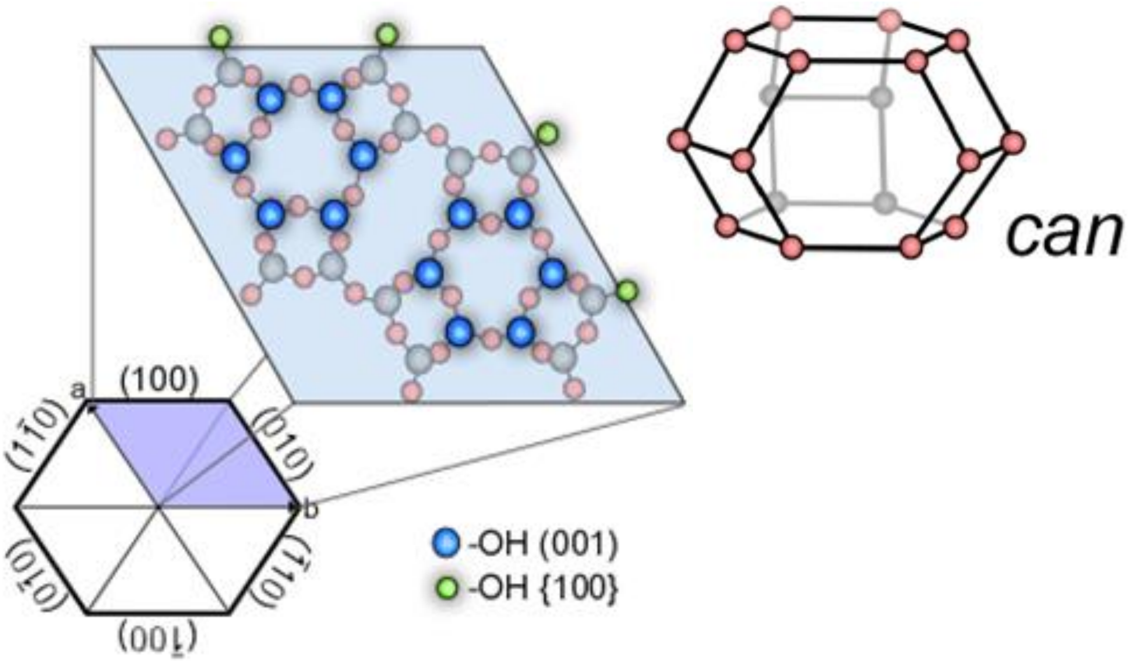
- Large pore zeolite (~0.7 nm)
- Long diffusion path length (axial)
- Targets: Large (001) surface area
  ZGM site specificity for {001)



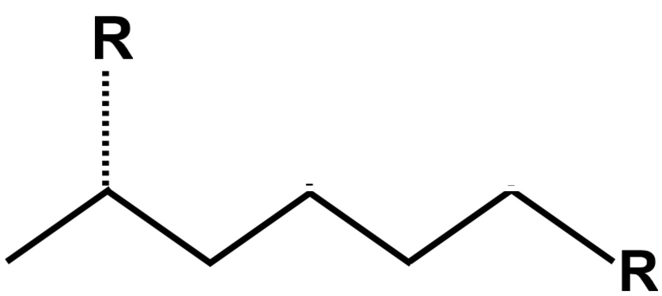
Systematic investigation of ZGMs

LTL (001) Surface





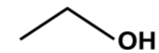
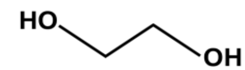
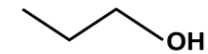
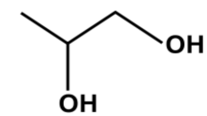
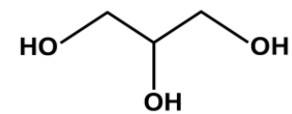
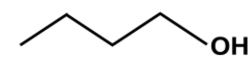
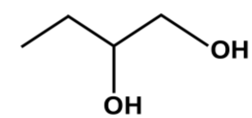
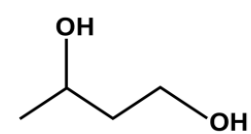
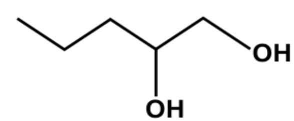
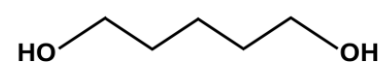
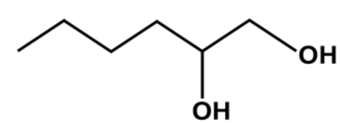
Polyol Modifiers



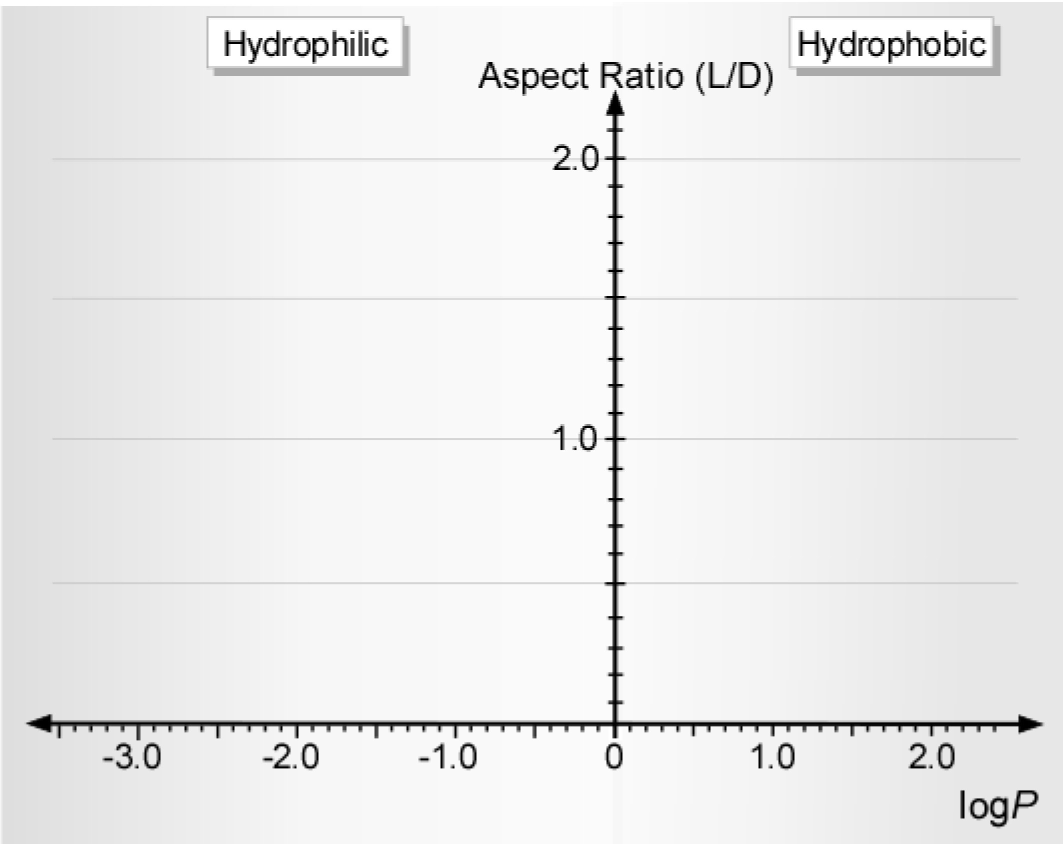
Systematic Investigation of…

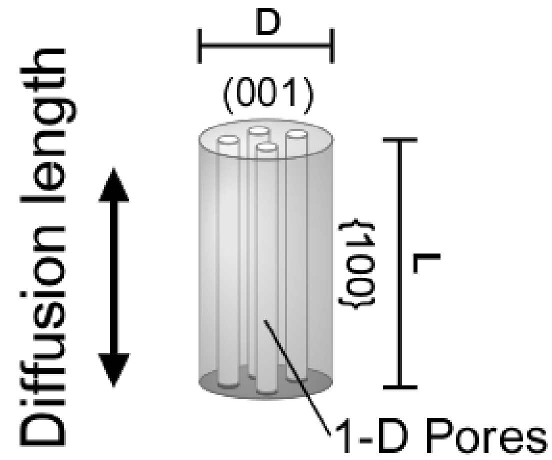
- ❑ Spatial positioning of OH groups
- ❑ Hydrogen-bonding
- ❑ Hydrophobic interactions

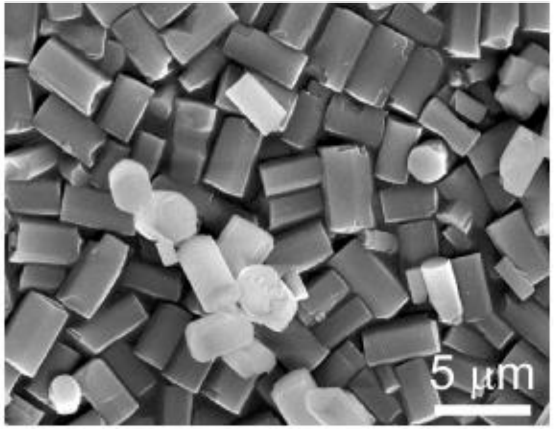
Polyol ZGMs

Symbol	Name	Formula	MW ($gmol^{-1}$)	Structure
Alcohols: primary (P), diols (D), and triols (T)				
P2	ethanol	C_2H_6O	46.07	
$D2_{1,2}$	ethylene glycol	$C_2H_6O_2$	62.07	
P3	n-propanol	C_3H_8O	60.10	
$D3_{1,2}$	1,2-propanediol	$C_3H_8O_2$	76.09	
$T3_{1,2,3}$	glycerol	$C_3H_8O_3$	92.09	
P4	n-butanol	$C_4H_{10}O$	74.12	
$D4_{1,2}$	1,2-butanediol	$C_4H_{10}O_2$	90.12	
$D4_{1,3}$	(R/S)1,3-butanediol	$C_4H_{10}O_2$	90.12	
$D5_{1,2}$	1,2-pentanediol	$C_5H_{12}O_2$	104.15	
$D5_{1,5}$	1,5-pentanediol	$C_5H_{12}O_2$	104.15	
$D6_{1,2}$	1,2-hexanediol	$C_6H_{14}O_2$	118.17	

Reducing internal diffusion (L/D aspect ratio)



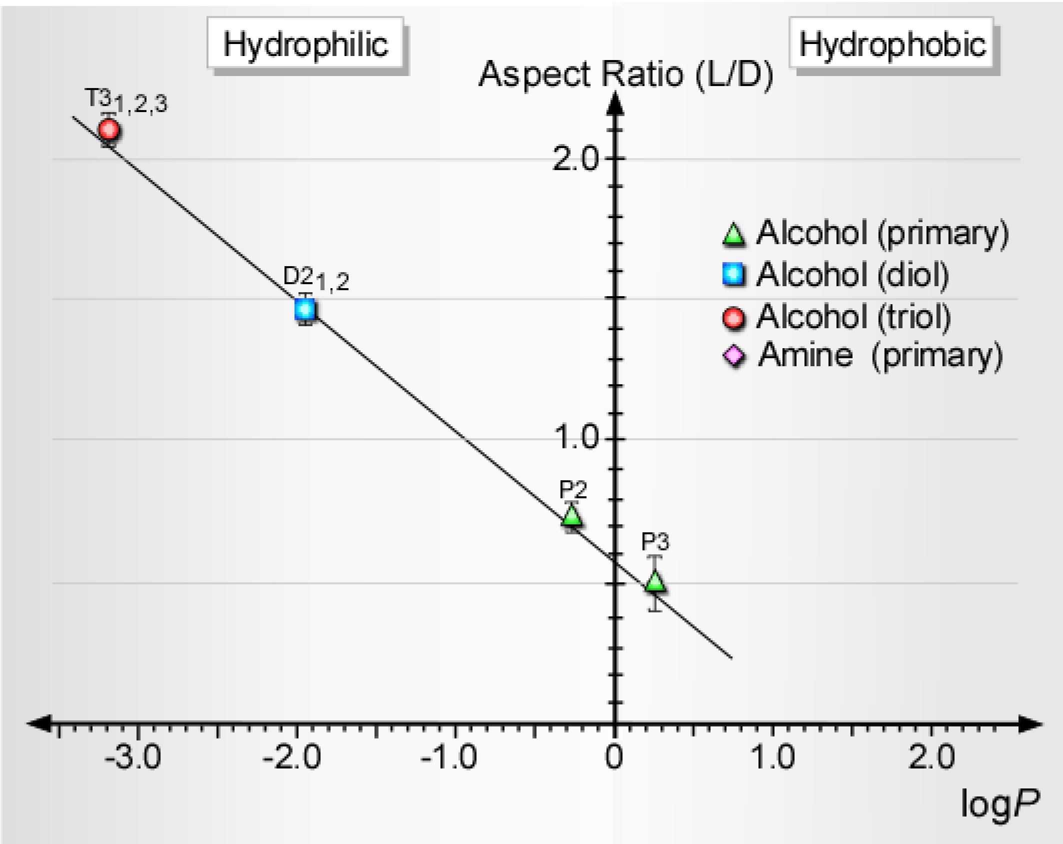


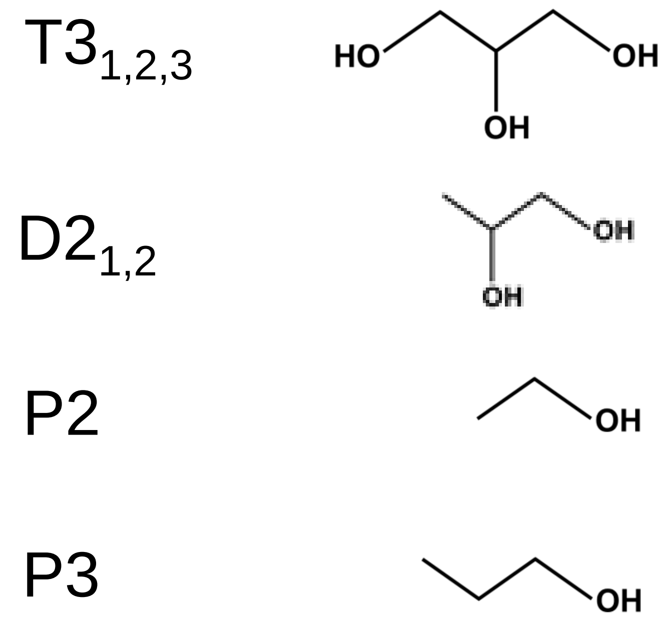


log*P* = logarithm of the octanol-water partition coefficient

$$\log P_{\text{octanol/water}} = \log\left(\frac{[solute]_{\text{octanol}}}{[solute]_{\text{deionized water}}}\right)$$

Reducing internal diffusion



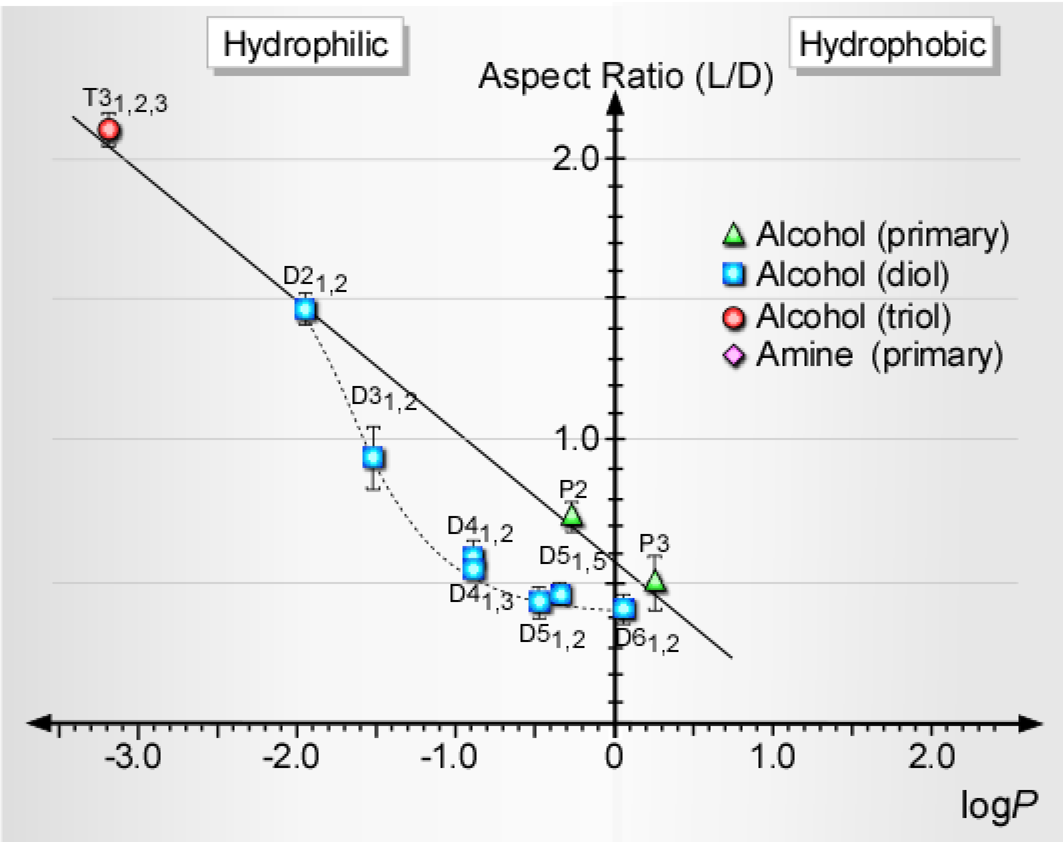


- ❑ Molecules exhibit linear dependence on hydrophobicity
- ❑ Qualitatively consistent with thermodynamic studies

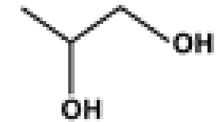
Xiong, Sandler, Vlachos, *Langmuir* 2012

Mallon et al., *J. Phys. Chem. B* 2011

Reducing internal diffusion

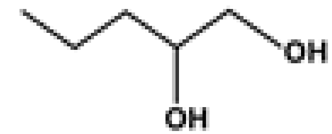


$D2_{1,2}$

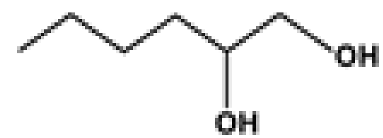


$D4_{1,2}$

$D5_{1,2}$

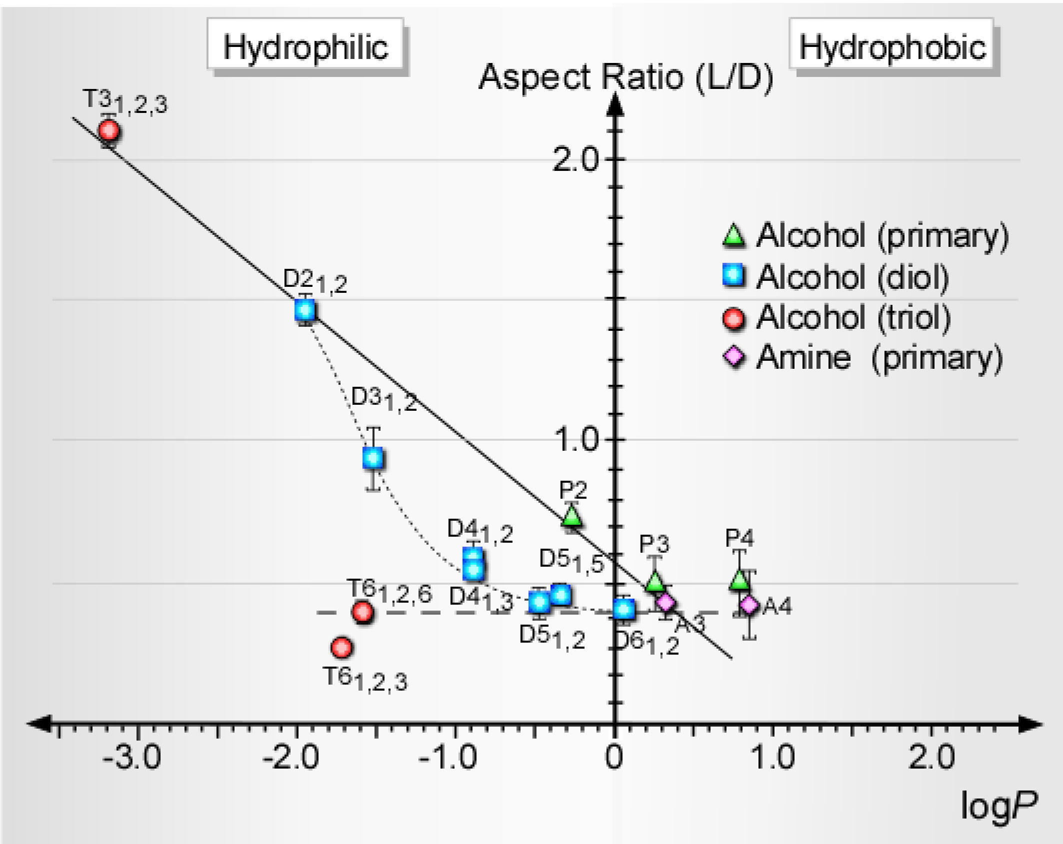


$D6_{1,2}$

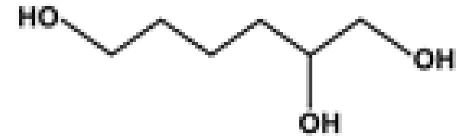


- ❑ Shift from linear trend for C_3 and C_4 modifiers
- ❑ Efficacy improves with $(CH_2)_n$ and $n \geq 3$

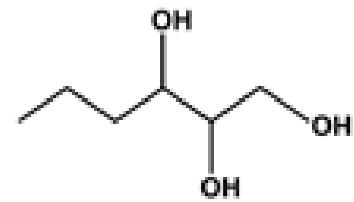
Reducing internal diffusion



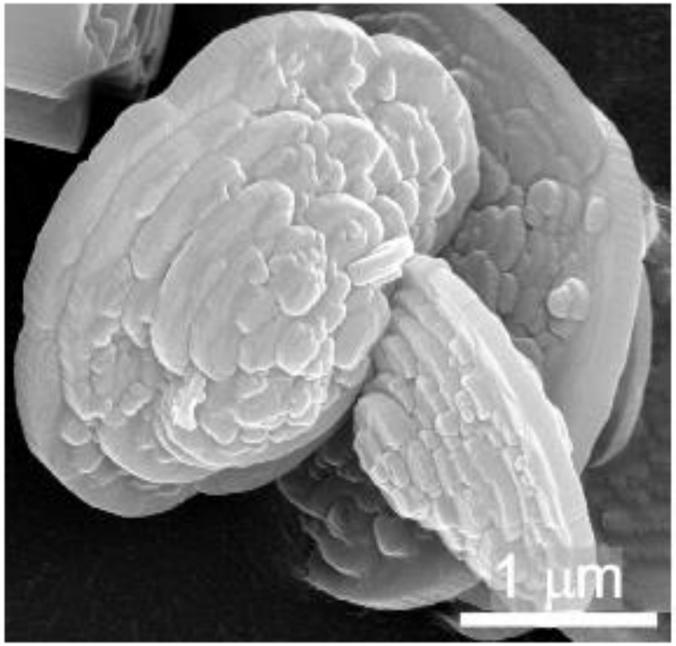
$T6_{1,2,6}$



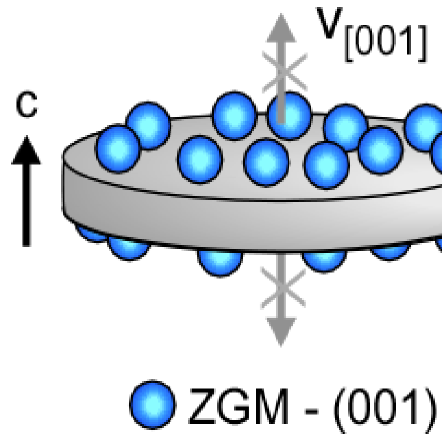
$T6_{1,2,3}$



Tunable crystal properties

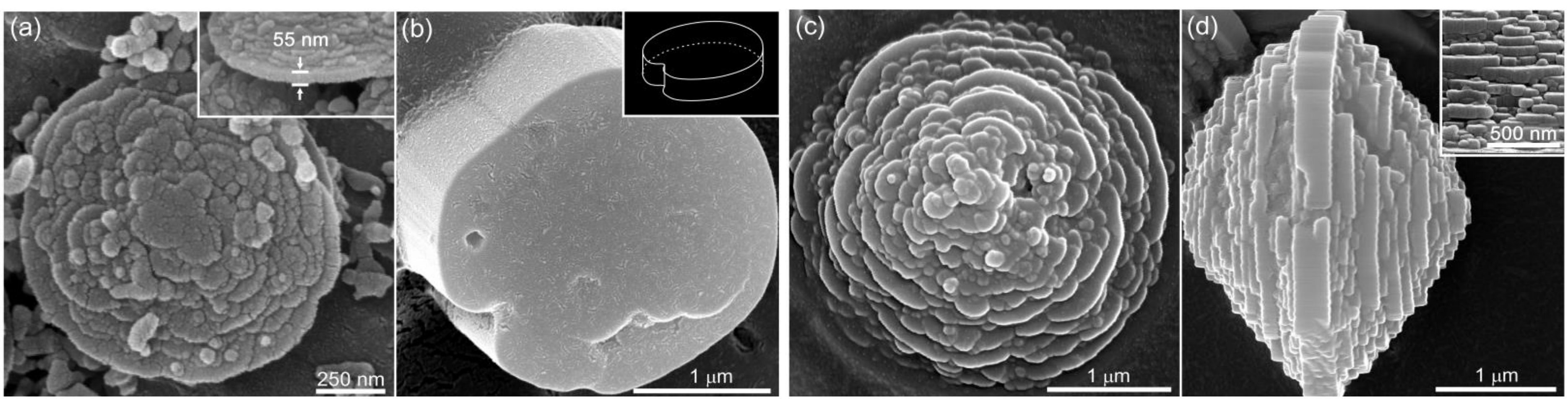


1,3-polyols are most effective



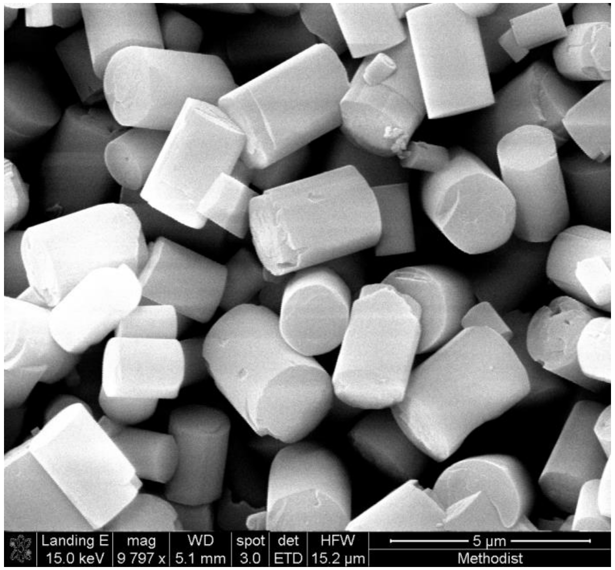
Modified Crystal Shape

Modified Surface Architecture

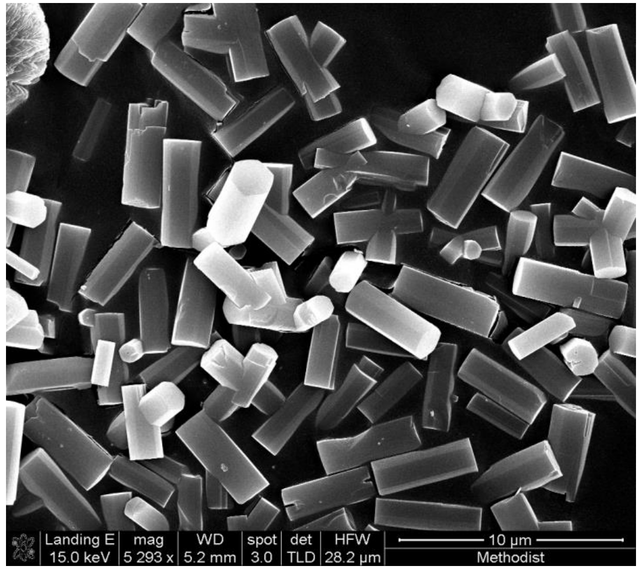


Versatile control of crystal morphology

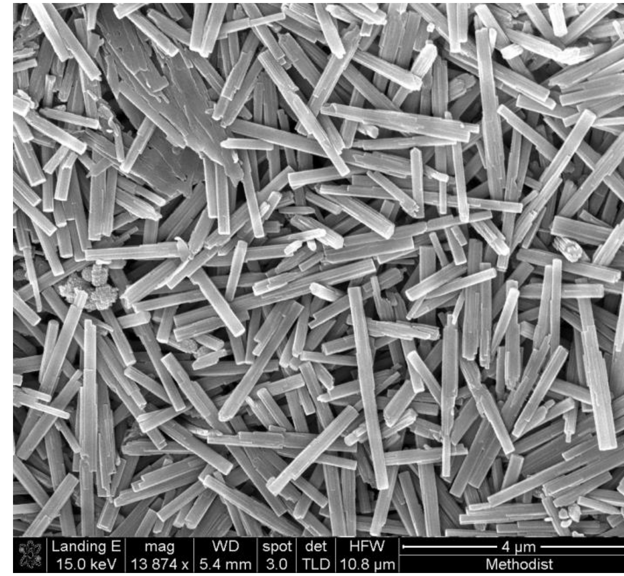
Control

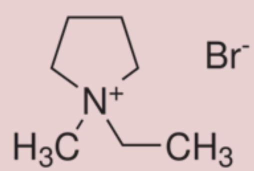
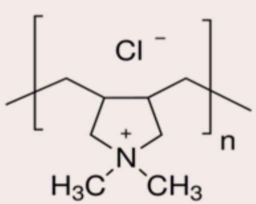


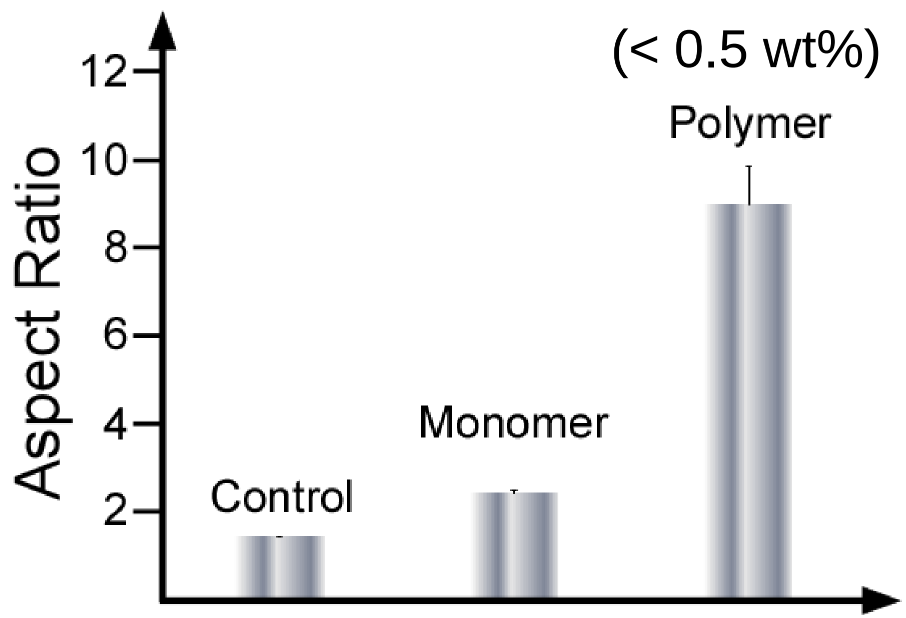
Monomer



Polymer

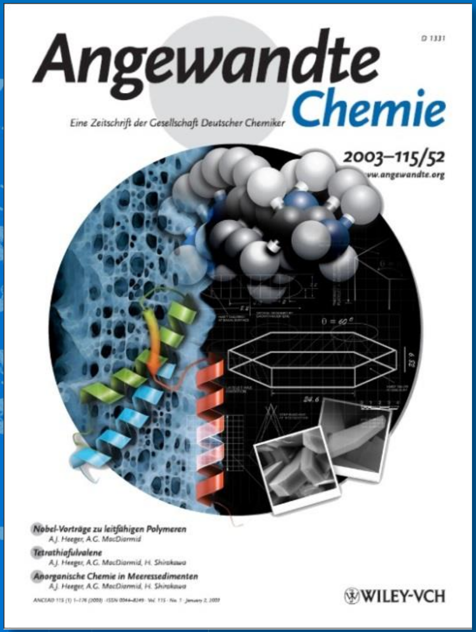


Name	Structure
1-ethyl-1-methylpyrrolidium bromide (EMPB)	
Poly(diallyldimethylammonium chloride) (PDDAC) (MW: 100K-200K)	



Blueprint for rational design

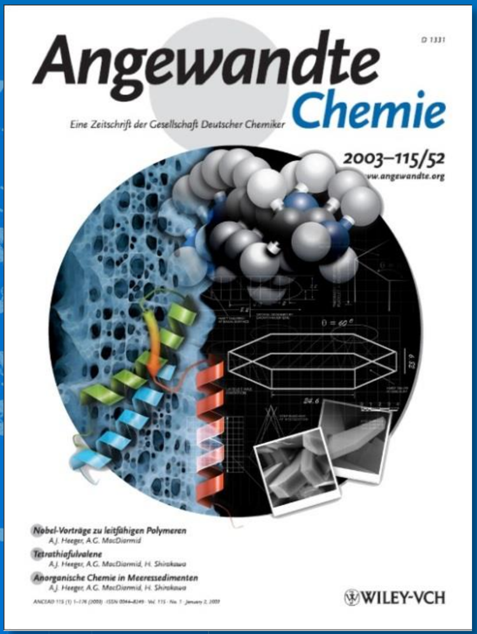
- Commercially viable approach
  - Inexpensive organics
  - Recoverable (recycling)
  - Facile application

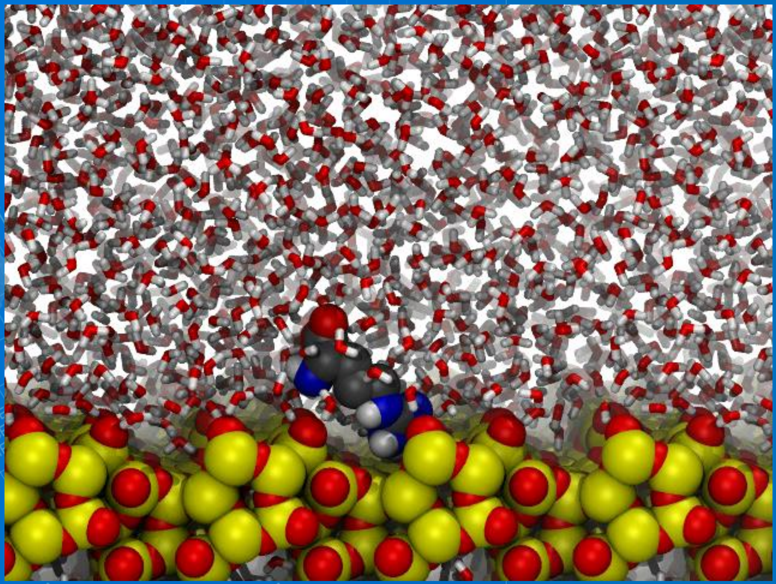


Lupulescu and Rimer, *Angew. Chem. Int. Ed.* 2012

Blueprint for rational design

- Commercially viable approach
  - Inexpensive organics
  - Recoverable (recycling)
  - Facile application
- Versatile approach
  - Validated for MFI & LTL
  - Heuristic guidelines
  - Molecular-level studies



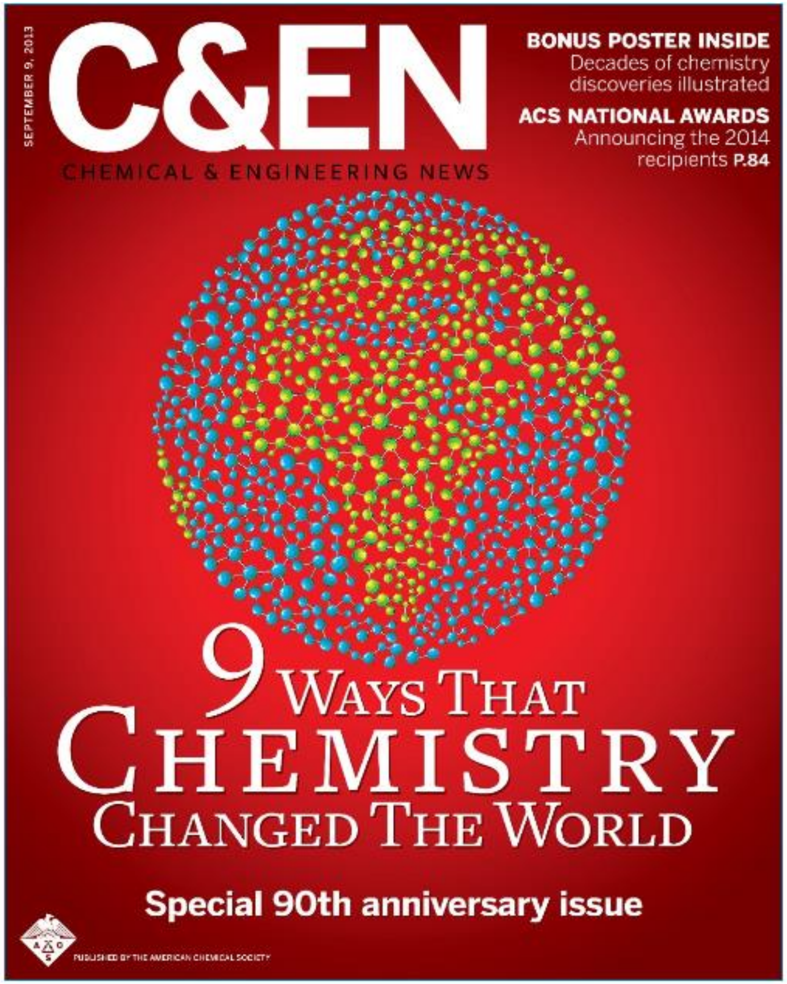


M. Doxastakis (Univ. Houston)

Zeolite synthesis: optimization challenges

"Catalysis has changed its status from that of an art to a science in the past 10 years"

– 1953, Paul H. Emmett (Mellon Institute)



C&E News, Sept. 9 2013

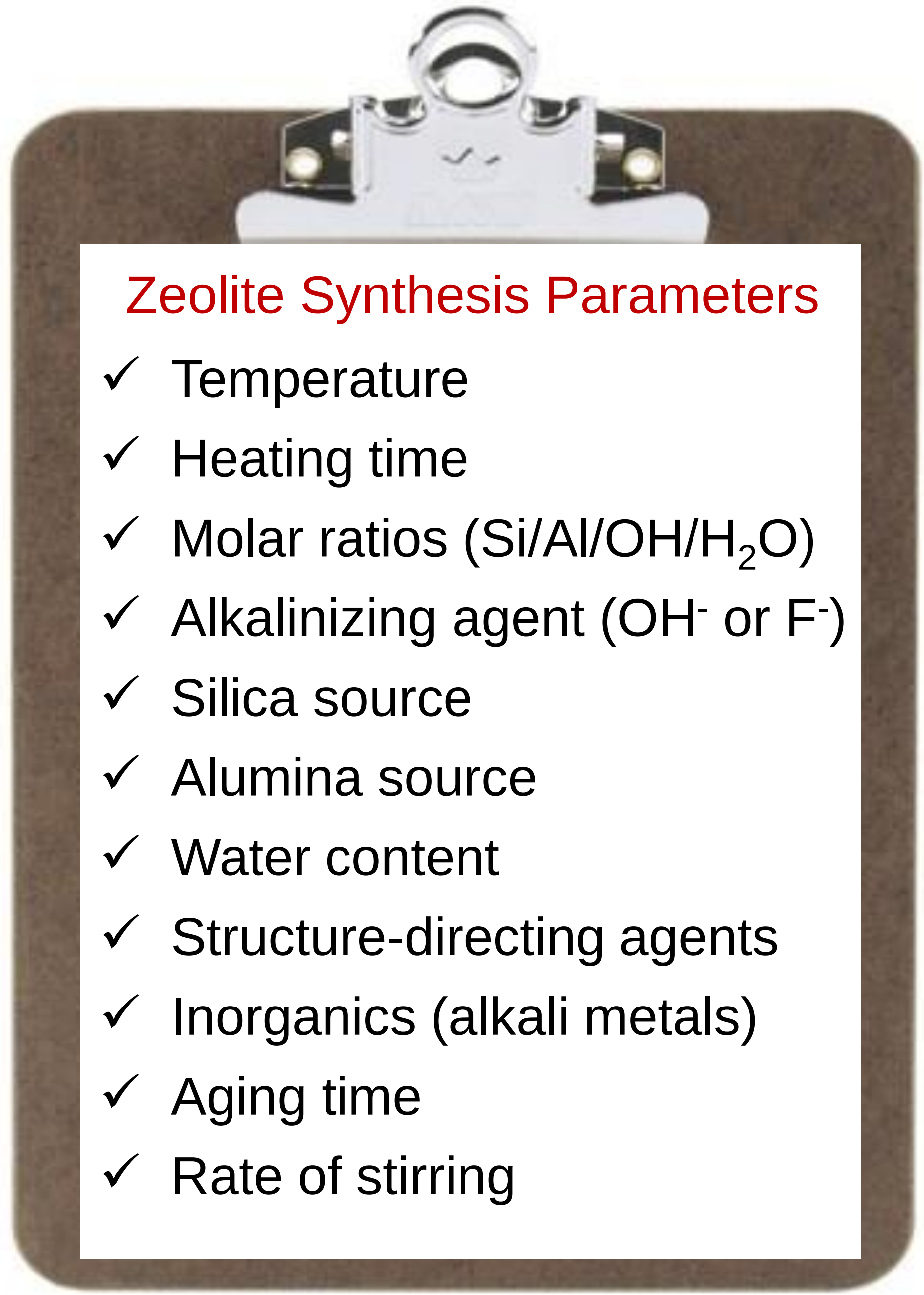
Zeolite synthesis: optimization challenges

Tailor material properties

1. Crystal size / shape
2. Shape selectivity
3. Composition (Si/Al ratio)
4. Polymorphism

Optimization challenges:

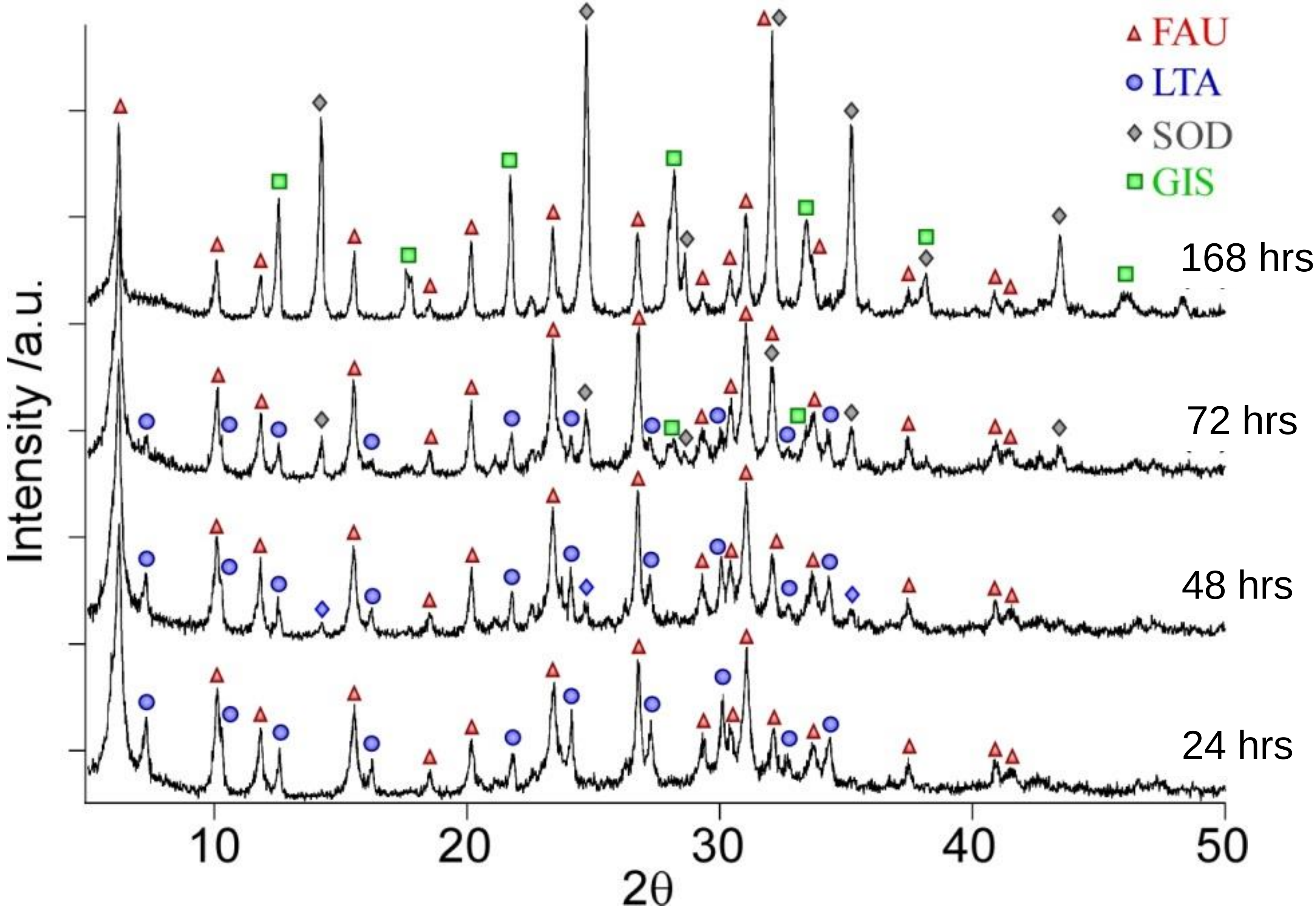
- ❑ Avoid empirical approaches
- ❑ Fundamental understanding of growth mechanisms



Zeolite Synthesis Parameters

- ✓ Temperature
- ✓ Heating time
- ✓ Molar ratios (Si/Al/OH/H_2O)
- ✓ Alkalinizing agent (OH^- or F^-)
- ✓ Silica source
- ✓ Alumina source
- ✓ Water content
- ✓ Structure-directing agents
- ✓ Inorganics (alkali metals)
- ✓ Aging time
- ✓ Rate of stirring

Example: OSDA-free synthesis

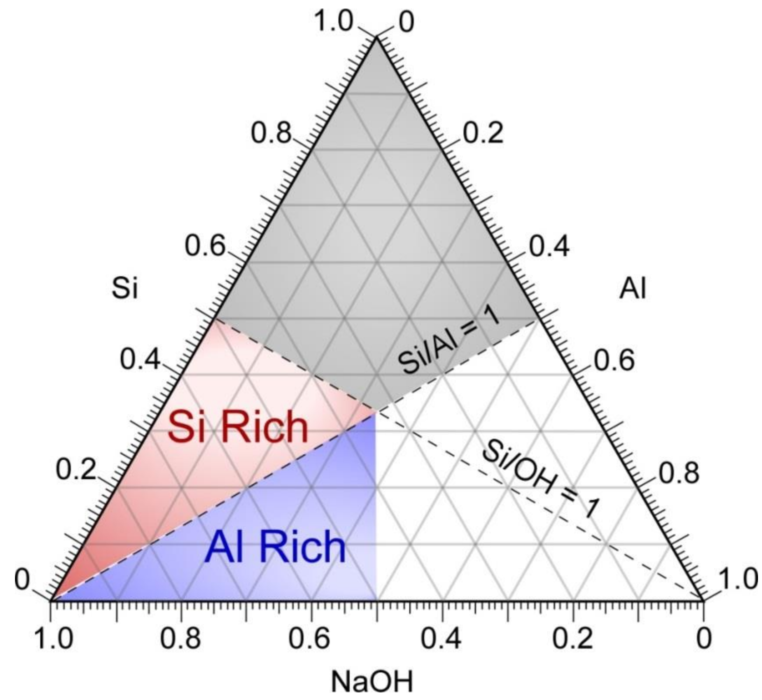


Maldonado et al., *J. Am. Chem. Soc.* 2013

New platform: Kinetic phase diagrams

Fixed parameters:

- ❑ Water content, NaOH:H_2O
- ❑ Temperature
- ❑ Heating time
- ❑ Extraframework cation (Na^+)

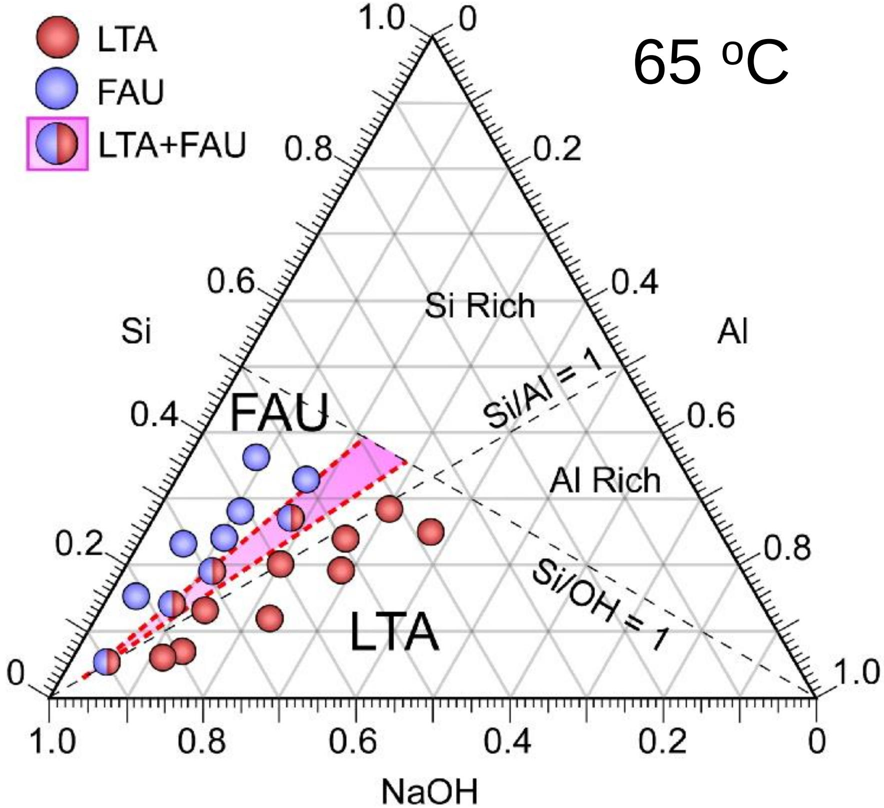


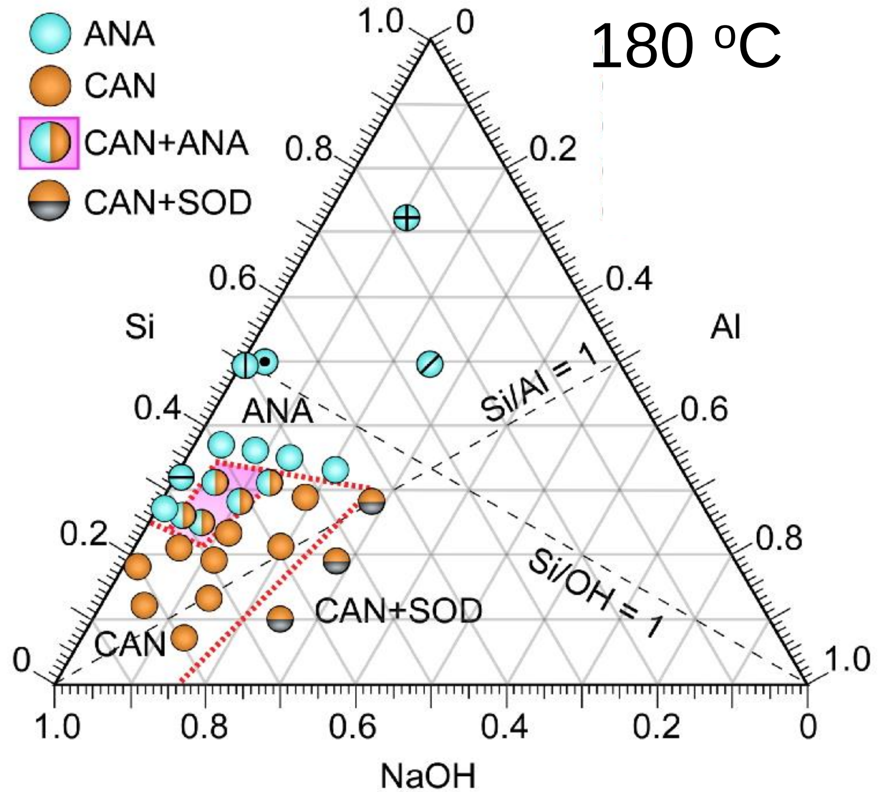
Benefits of this approach:

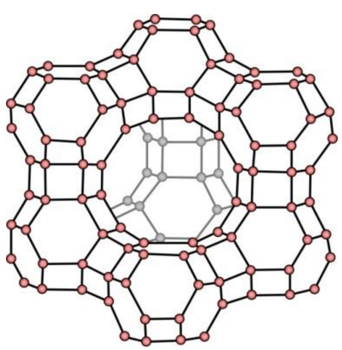
- ❑ Improved purity
- ❑ Optimized composition (e.g. high Si)
- ❑ Mechanistic insights
- ❑ Synergism with ZGMs (size, morphology)

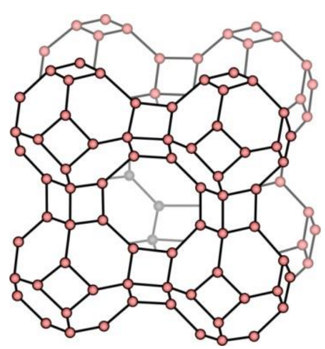
Maldonado et al., *J. Am. Chem. Soc.* 2013

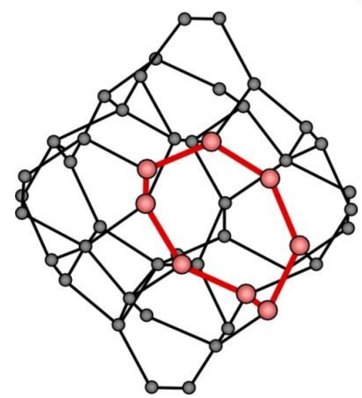
Kinetic phase diagrams

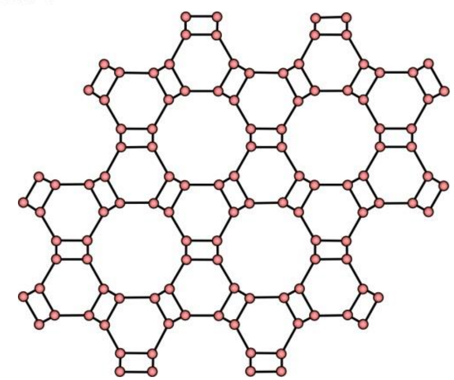





FAU (zeolite X, Y)

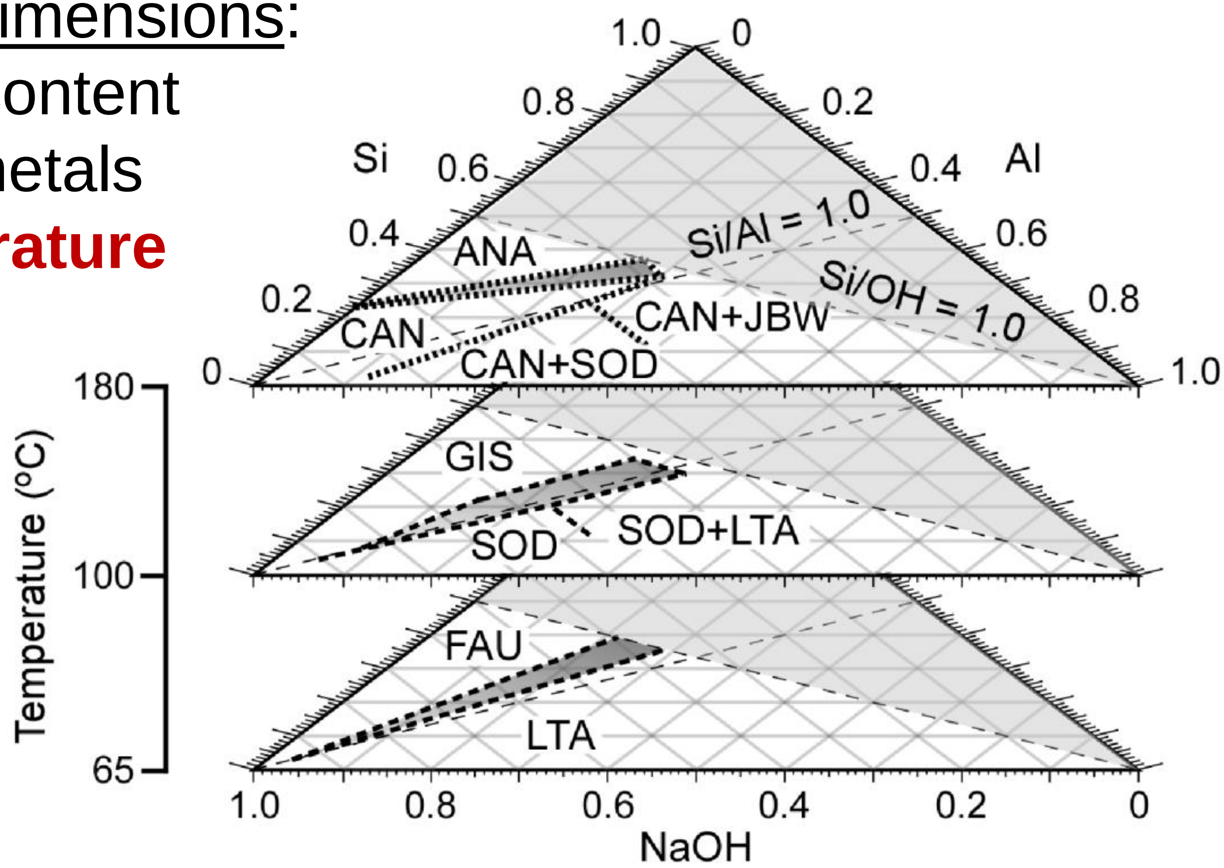

LTA (zeolite A)


ANA


CAN

Multiple Dimensions:

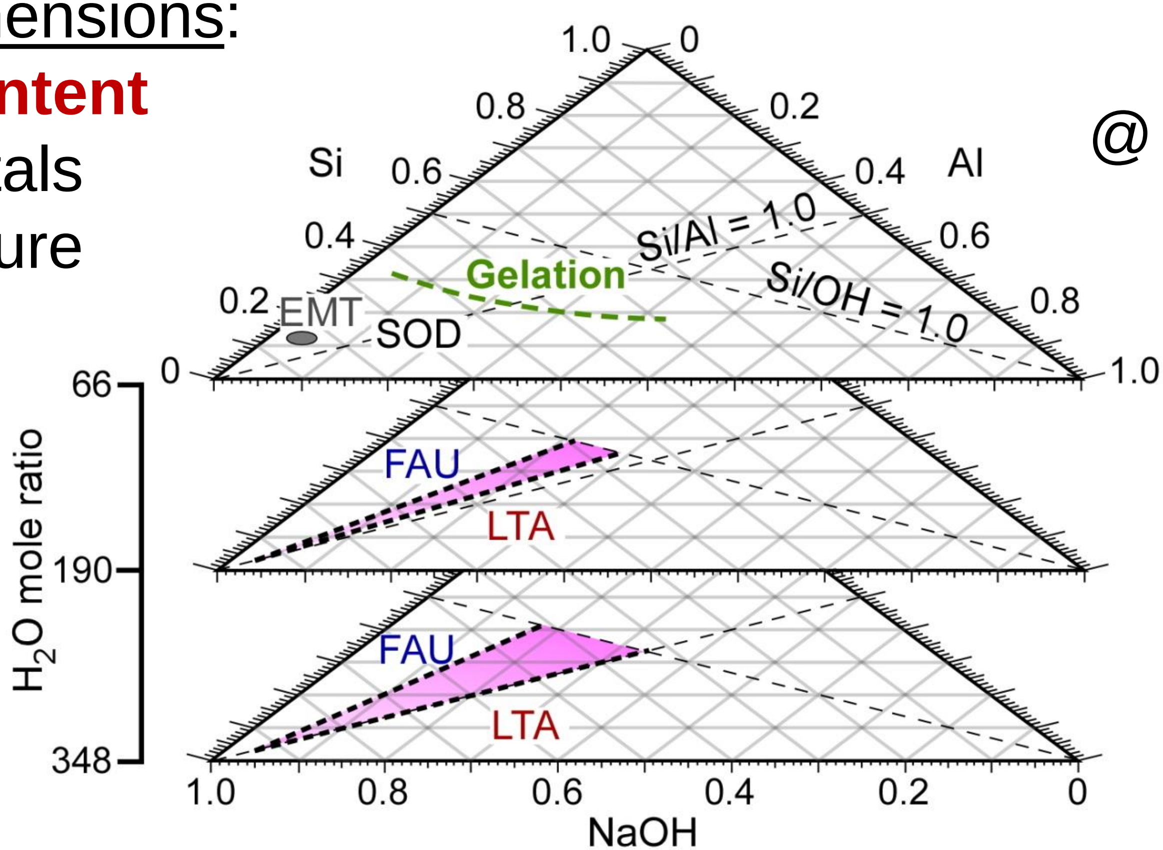
- Water content
- Alkali metals
- **Temperature**
- Time



Maldonado et al., *J. Am. Chem. Soc.* 2013

Oleksiak and Rimer, *Rev. Chem. Eng.* In Press

Multiple Dimensions:
- **Water content**
- Alkali metals
- Temperature
- Time



@ 65 ^oC

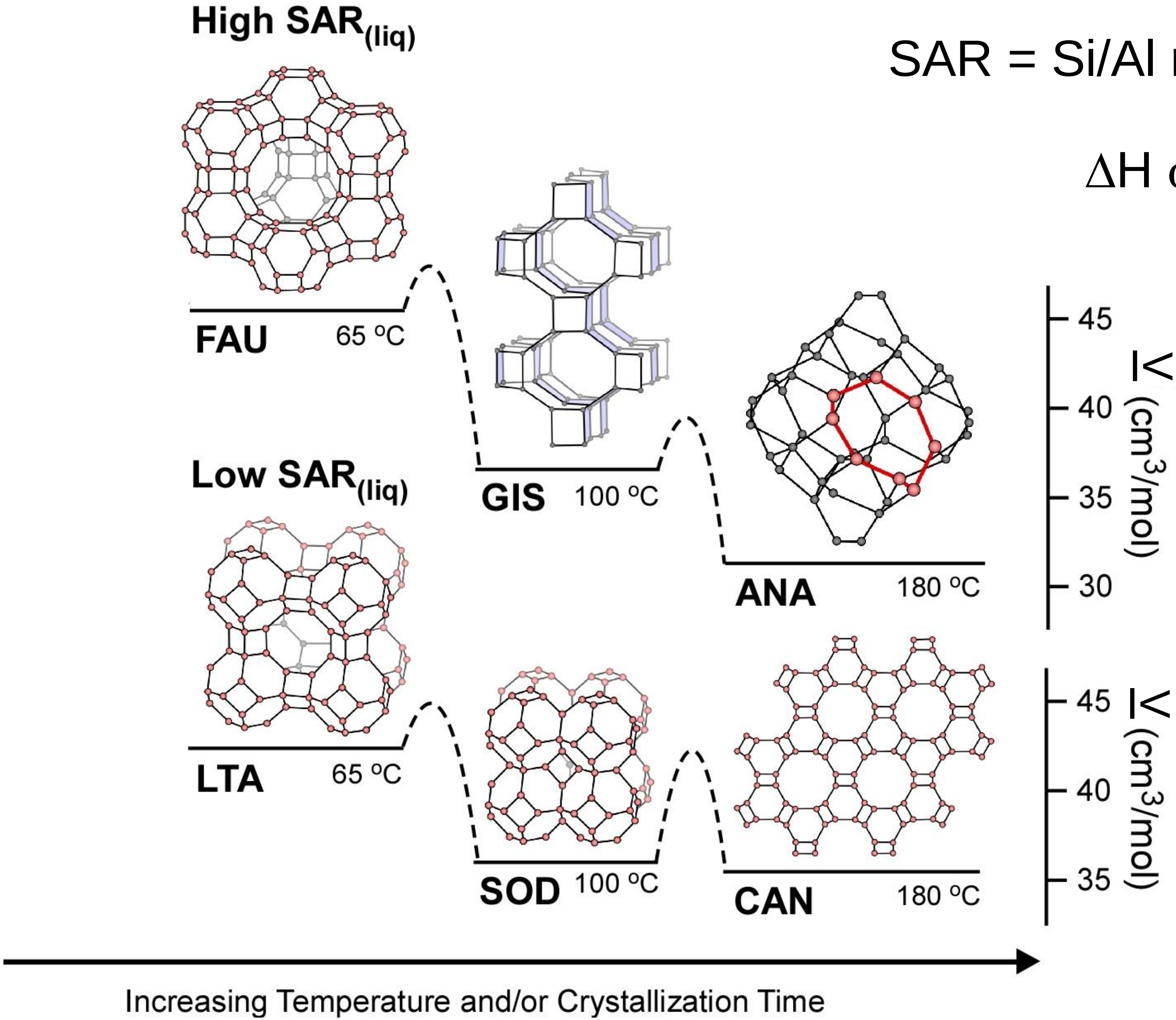
New platforms for rational design:

- ❑ Tuning composition (hydrothermal stability, acidity)
- ❑ Reducing impurities (polymorphism)
- ❑ Discovery of new crystal structures

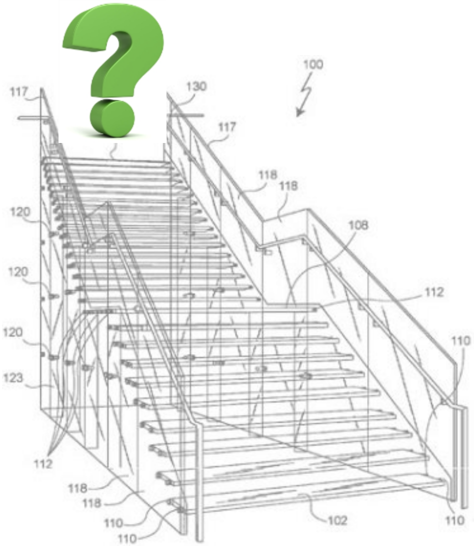
Phase transformations: Ostwald step rule

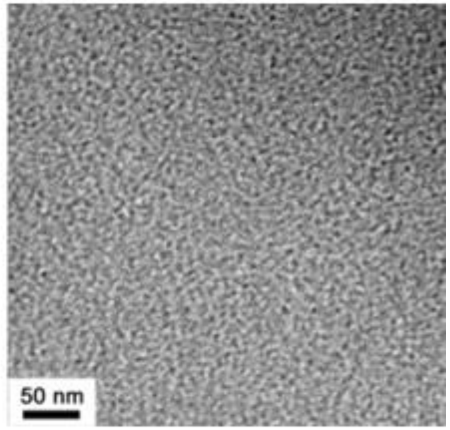
SAR = Si/Al ratio

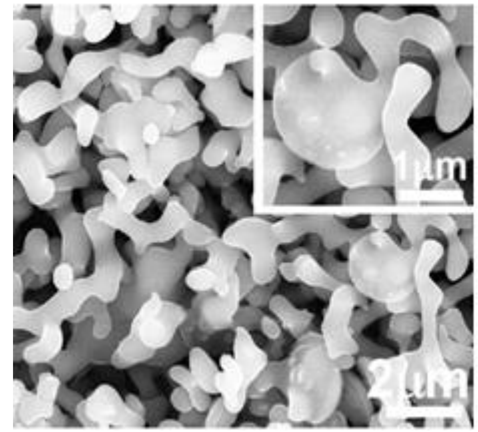
$\Delta H \propto \underline{V}$

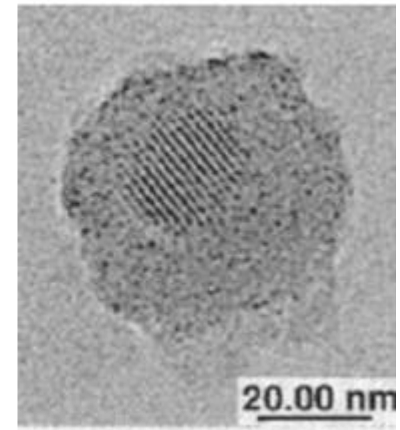


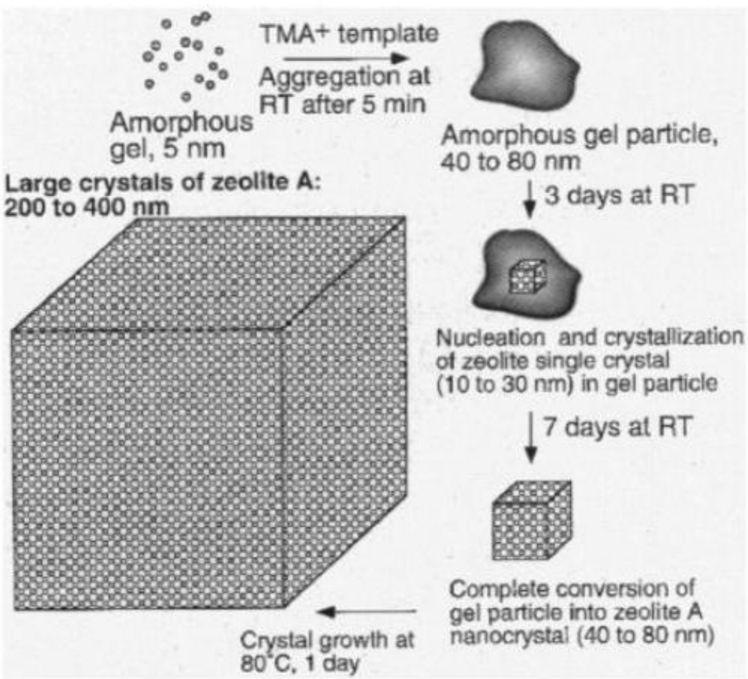
Crystal nucleation



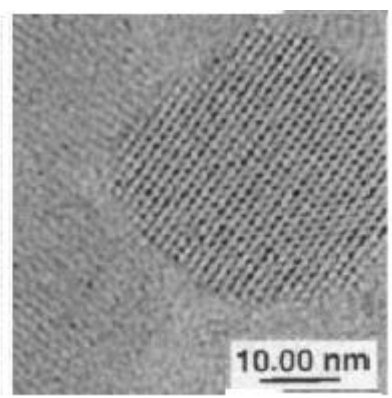


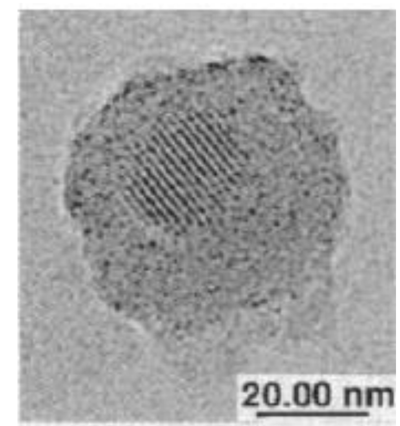






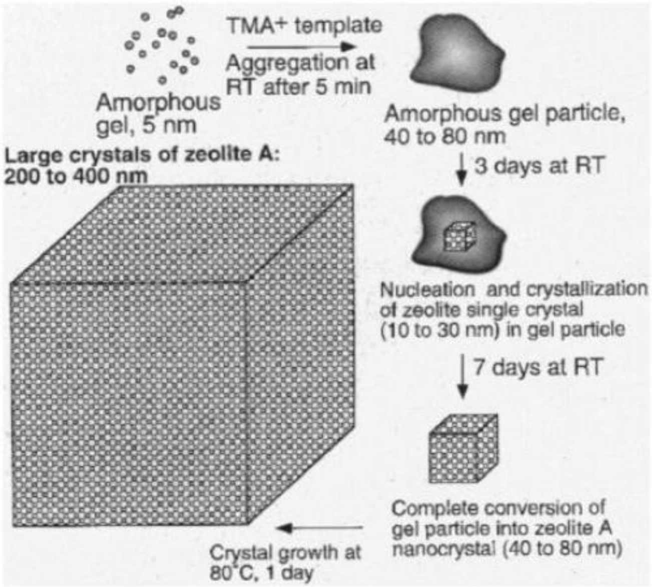
Sol gel synthesis ?



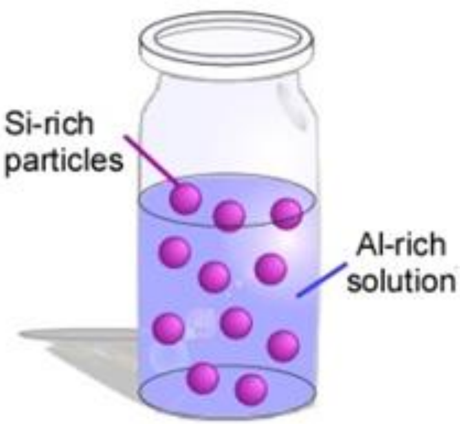


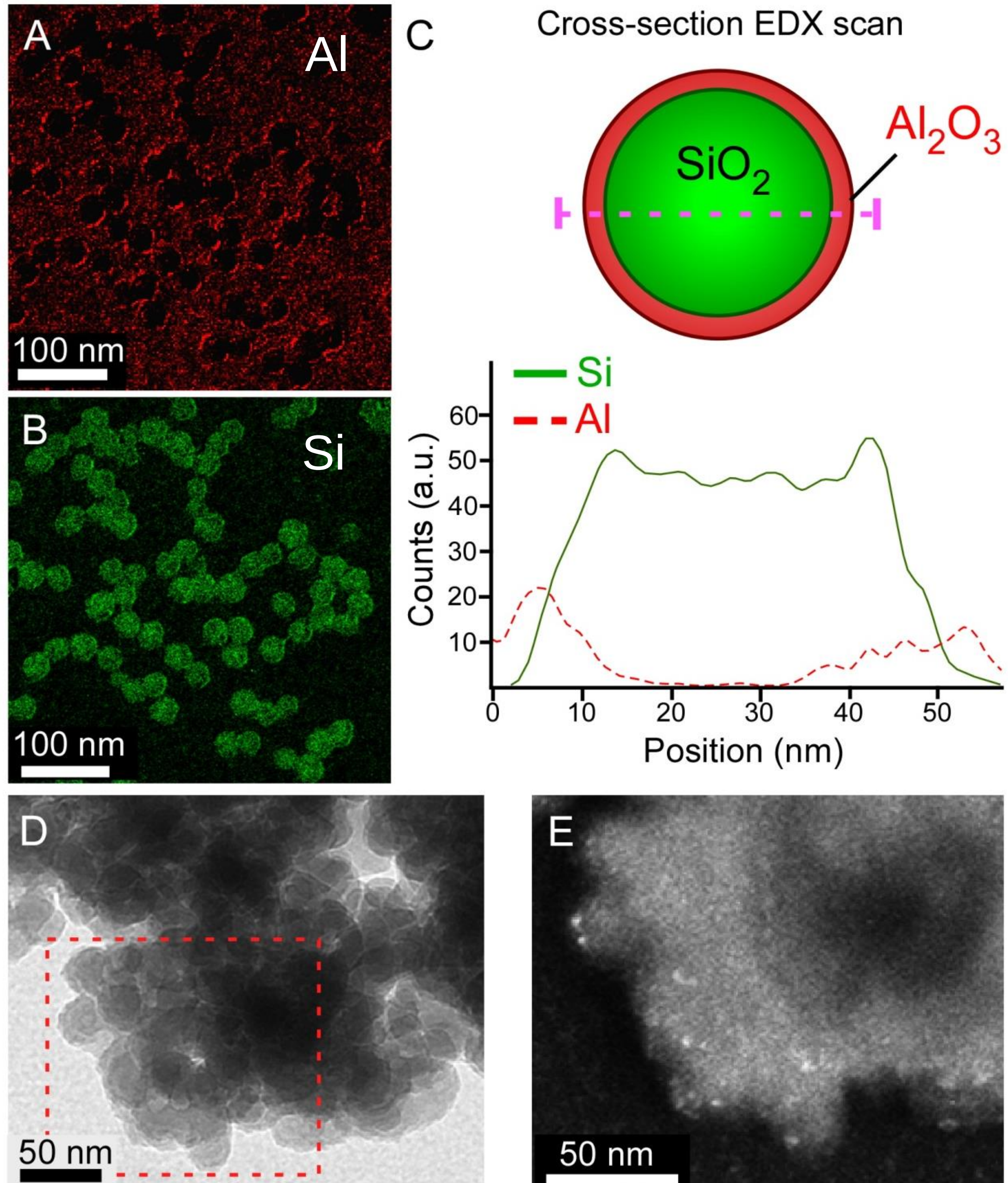
Bein, Mintova, and Valtchev, *Science* 1999

Mechanism of nucleation



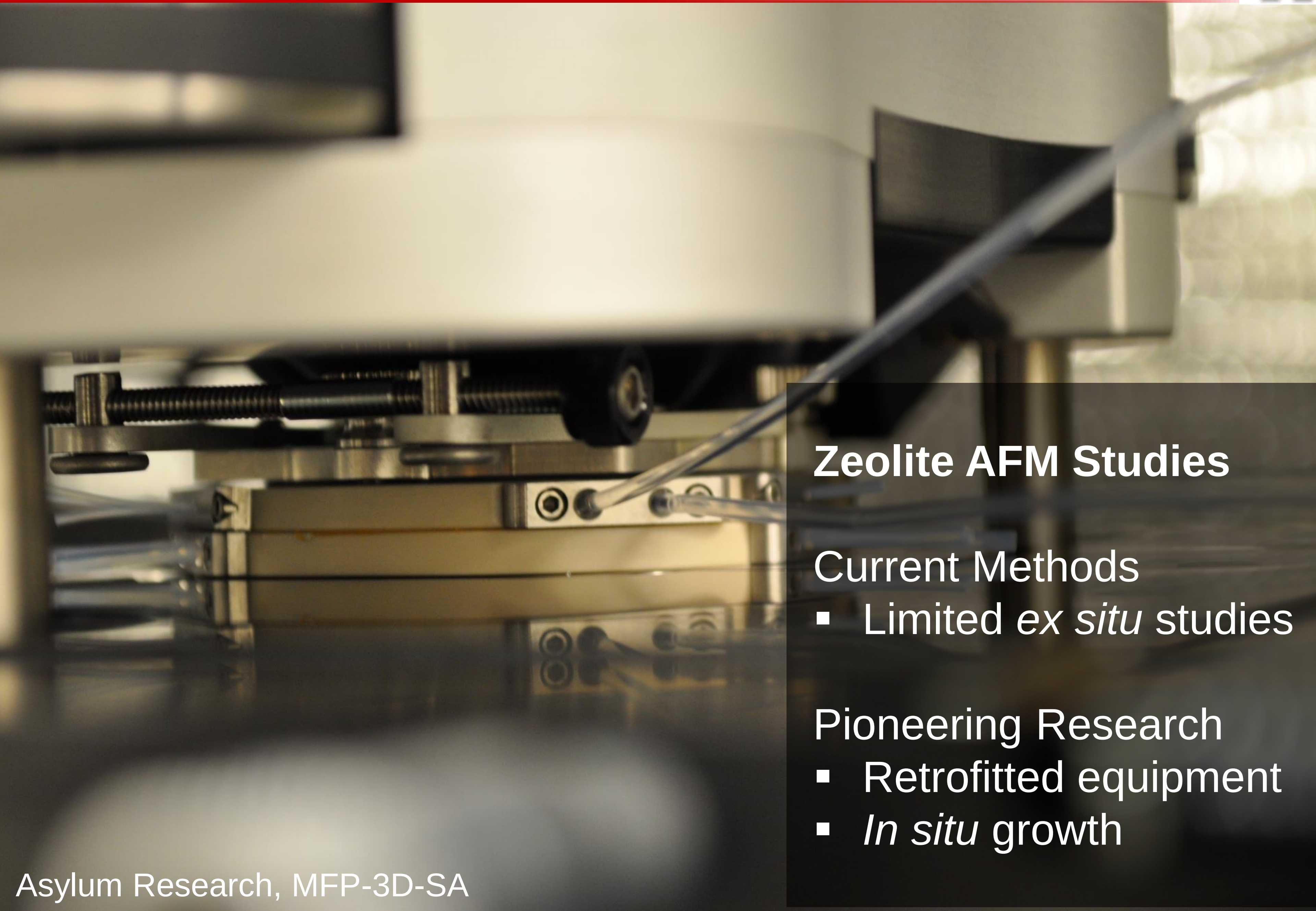
Bein et al., *Science* 1999





- ❑ Amorphous silica (25 nm)
- ❑ Alumina shell

Zeolite surface science



Zeolite AFM Studies

Current Methods

- Limited *ex situ* studies

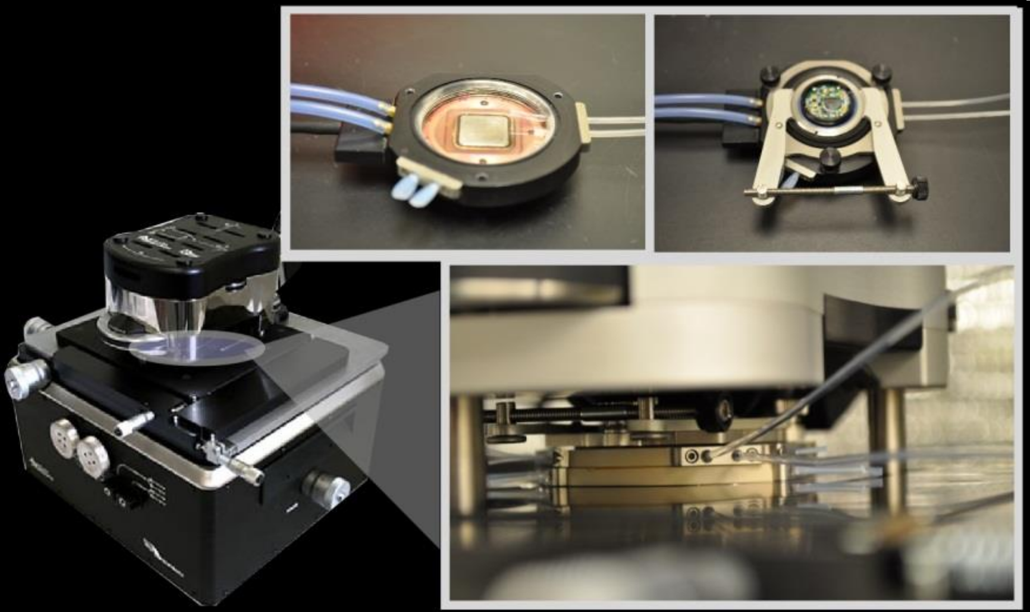
Pioneering Research

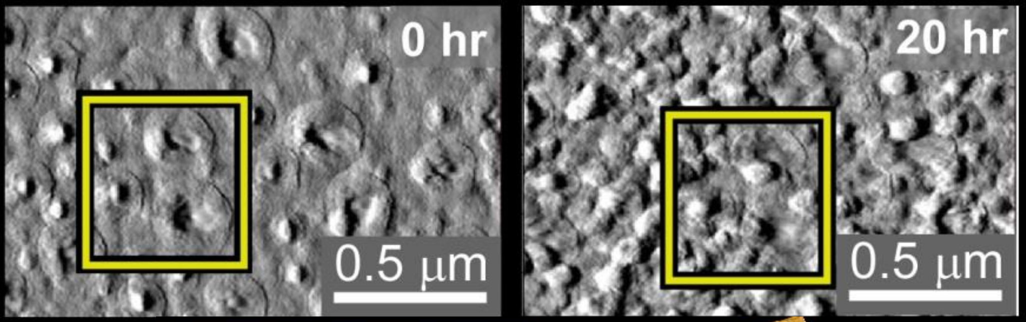
- Retrofitted equipment
- *In situ* growth

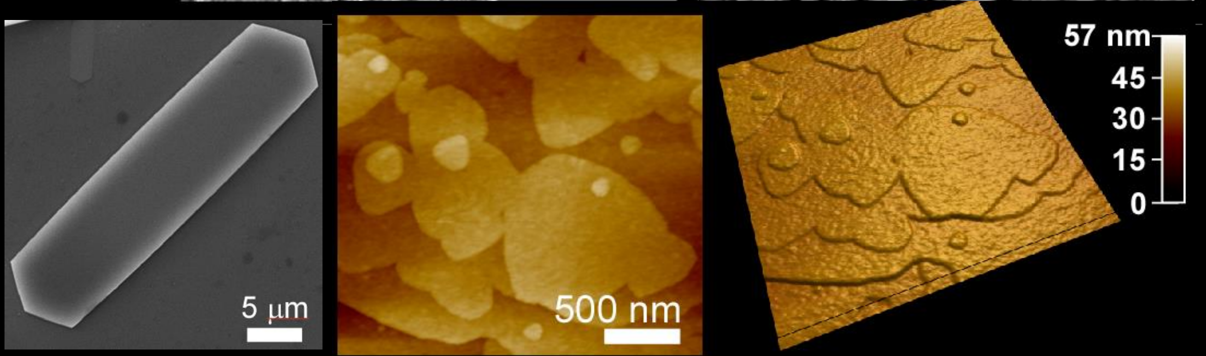
Asylum Research, MFP-3D-SA

Challenges of *in situ* AFM

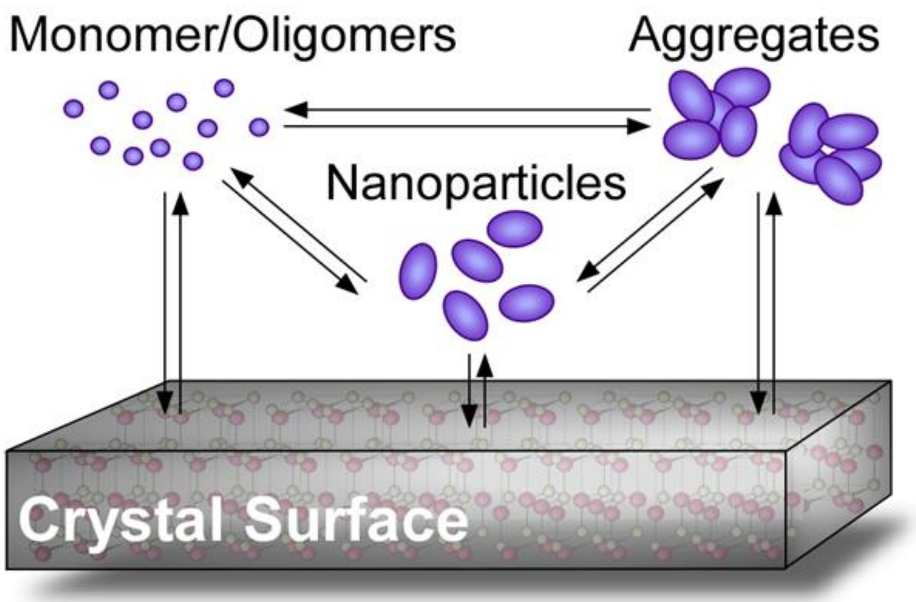
- ❑ Realistic growth conditions
  - High temperature, pH
  - Clear solution
- ❑ Liquid sample cell
  - Leakage
  - Bubbles
- ❑ Image stabilization
  - Drift correlation
  - Feedback control
- ❑ Crystal substrate
  - Large crystals
  - Smooth surface

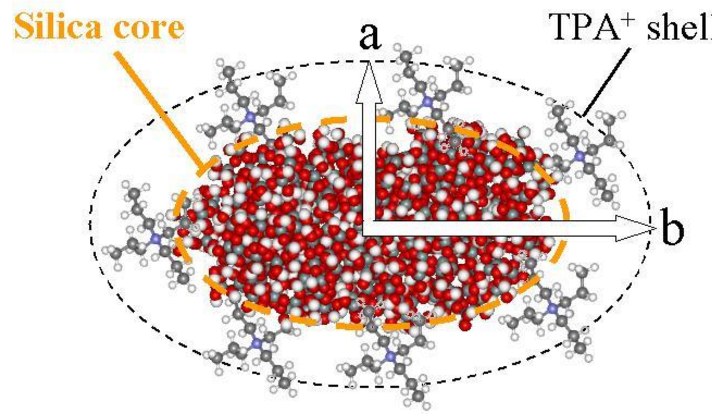






The 25-year question: What is the growth mechanism of silicalite-1?





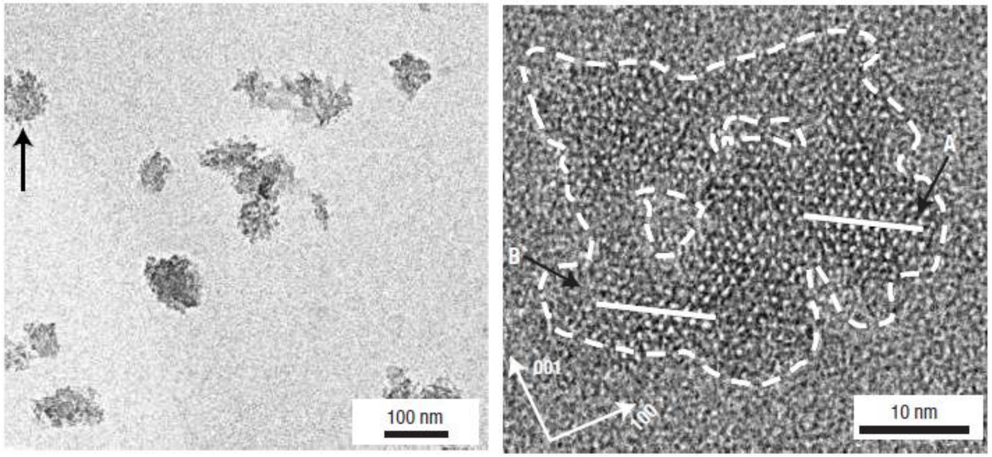
Rimer et al., *Chem. Mater.* 2006
Rimer et al., *J. Phys. Chem. B* 2005
Rimer et al., *Langmuir* 2005

Nanoparticle Addition

- van Santen, Martens, Tsapatsis, Vlachos, …..

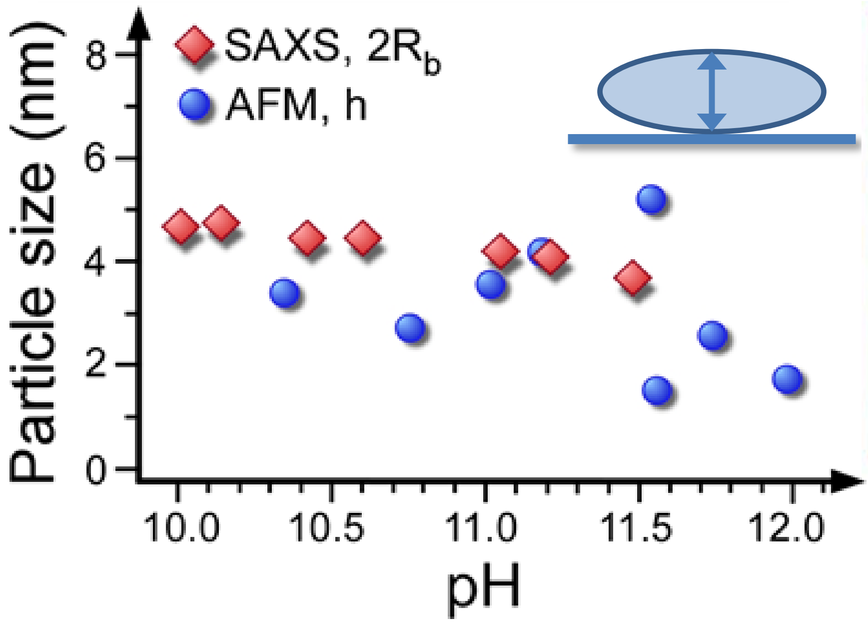
Monomer/Oligomer Addition

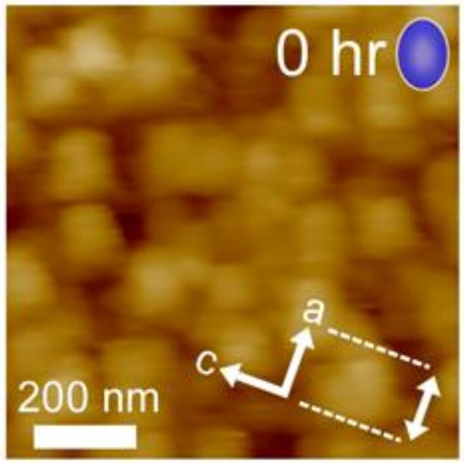
- Schoeman and Davis

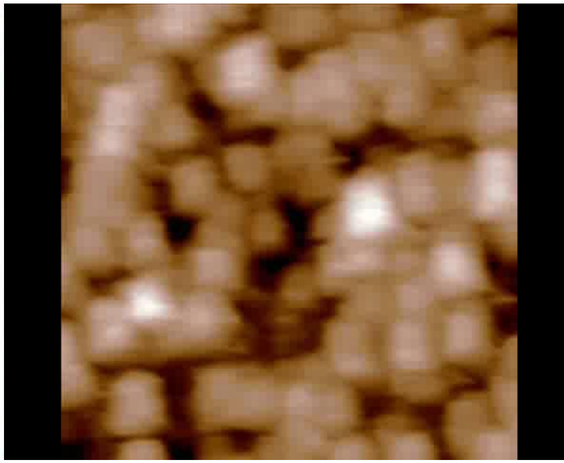


Davis et al., *Nat. Mater.* 2006

Real time imaging of surface growth







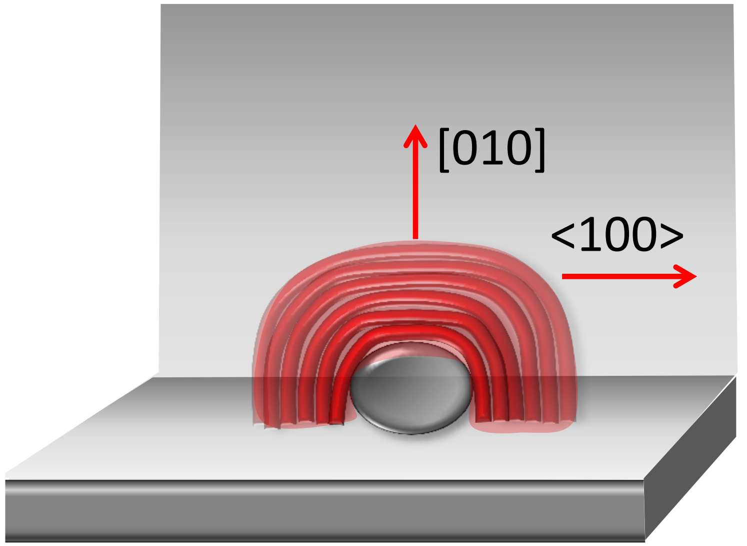
Dynamics of surface growth

I. Nanoparticle attachment

II. Reconstruction

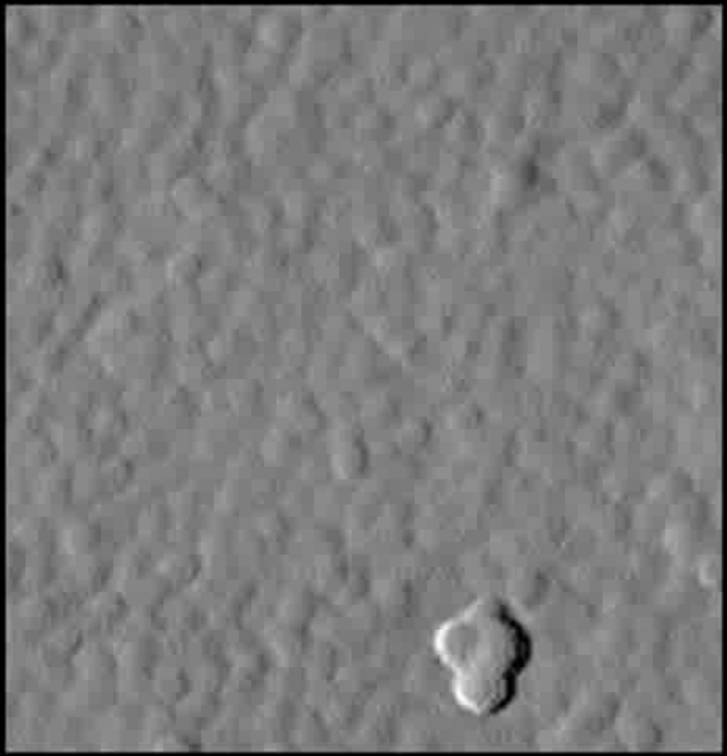
- Dissolution (Ostwald ripening)
- Solid-state restructuring

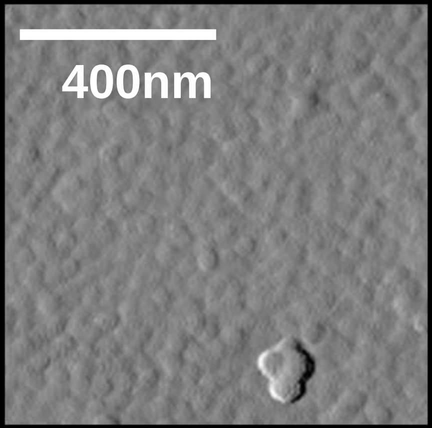
III. Molecule addition



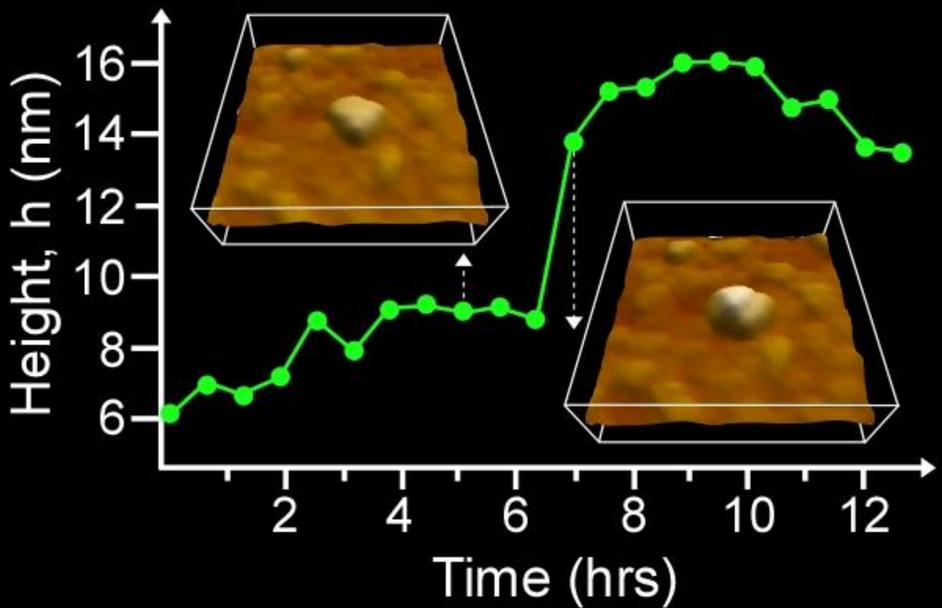
Lupulescu and Rimer, *Submitted*

Dynamics of 3D island growth





Reference (0 hrs)



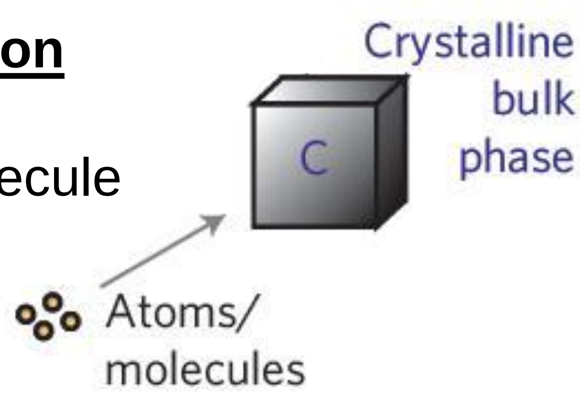
Growth Conditions:

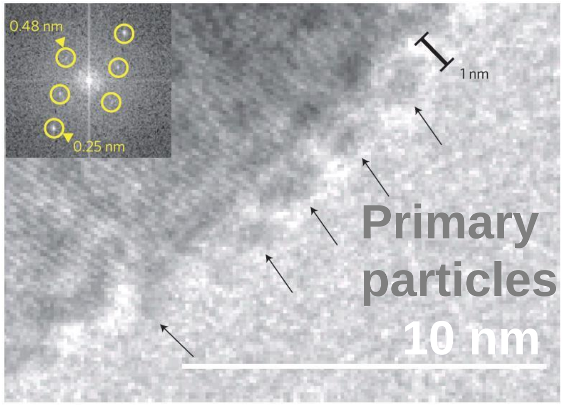
- ❑ Time: 10 hrs
- ❑ Temperature: 80 ºC
- ❑ Synthesis solution

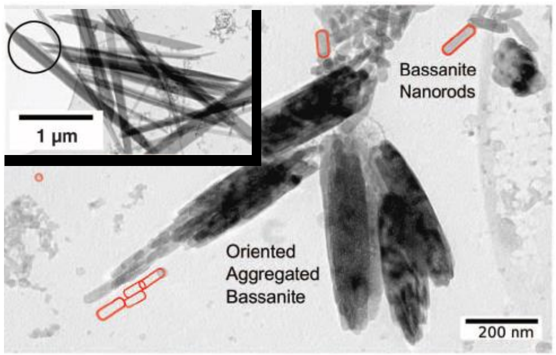
Non-classical crystallization

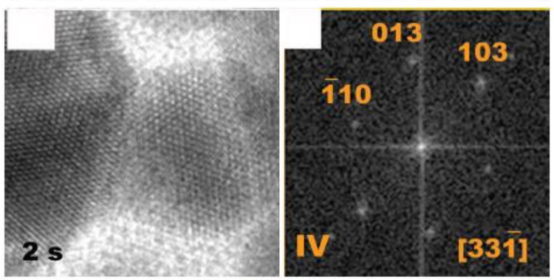
Classical Crystallization

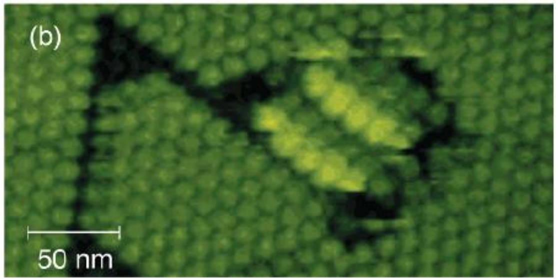
Building unit: atom/molecule











Magnetite, Fe_3O_4

Gypsum, $CaSO_4$-$2H_2O$ — Van Driessche et al., *Science* 2012

Iron Oxyhydroxide, Fe_2O_3-$9H_2O$ — Li et al., *Science* 2012

Proteins, Apoferritin — Yau and Vekilov, *JACS* 2001

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Left to Right: (Back) Megan, Sahar, Alex, Matt, Jeff, Manjesh, Wei, Rui, Zheng **(Front)** Katy, Jihae, Arian, Ricardo, Marlo

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