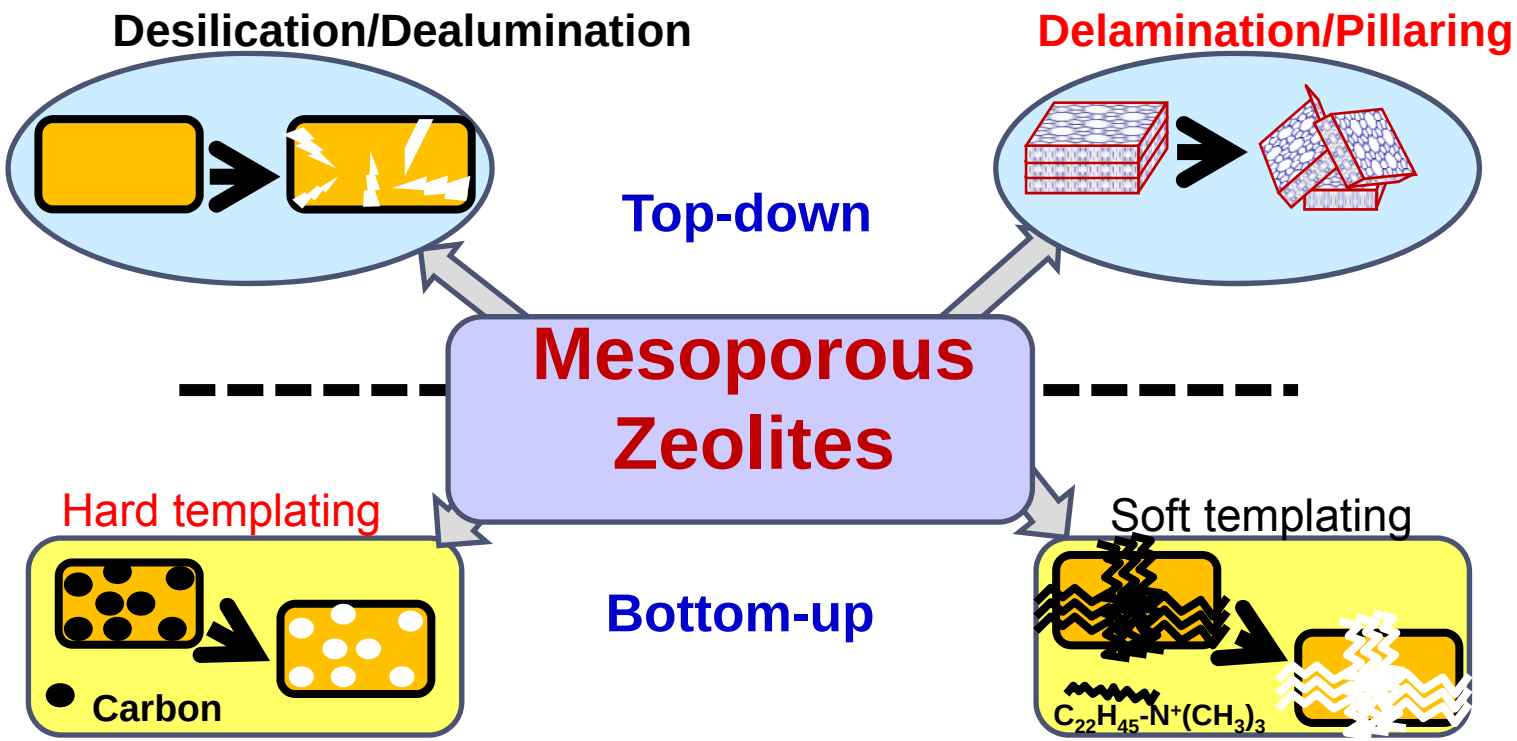
Two-Dimensional Zeolites

Michael Tsapatsis

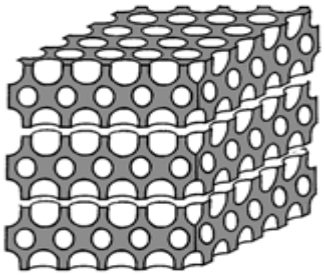
Controlling Micropore Diffusion Length and Pore Sizes Independently

Synthesis of hierarchical zeolites



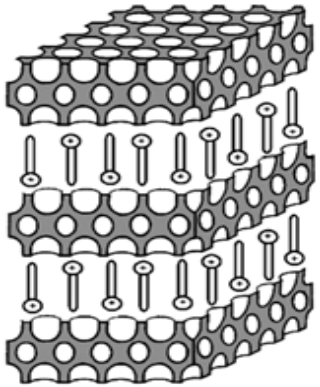
R. Chal., C. Gérardin, M. Bulut, S. van Donk, ChemCatChem, 2011, 3, 67.
K. Egeblad, C. H. Christensen, M. Kustova, C. H. Christensen, Chem. Mater. 2008, 20, 946.

Pillaring nanosheets to create hierarchical zeolites (first introduced by Mobil in 1990's for pillared MWW)



Swelling

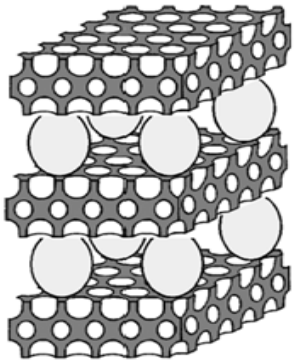
C_{16}TMAOH

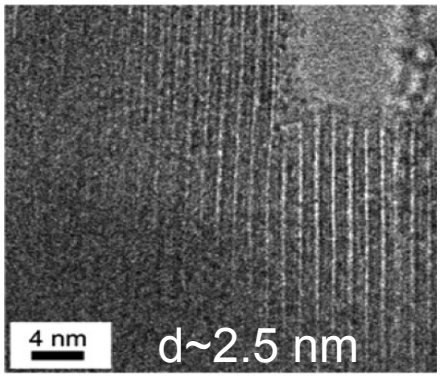


MCM-22 (P) (swelled)

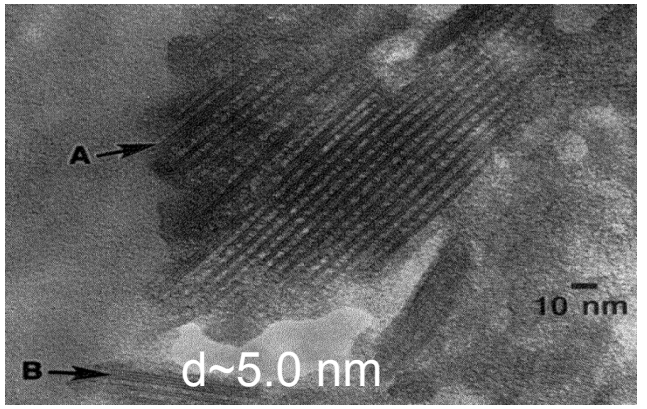
Pillaring and Calcination

TEOS





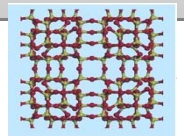
MCM-22 (P)



MCM-36

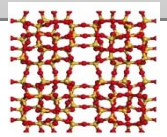
US Patent 5,292,698; W. J. Roth, C. T. Kresge, J. C. Vartuli, M. E. Leonowicz, A. S. Fung, S. B. McCullen, in *Stud. Surf. Sci. Catal., Vol. 94* (Eds.: H. K. Beyer, H. G. Karge, I. Kiricsi, J. B. Nagy), Elsevier, Amsterdam, **1995**, pp. 301-308.

Intergrown Zeolites



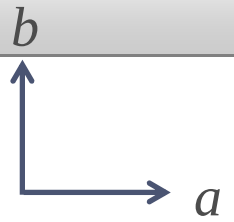
MEL

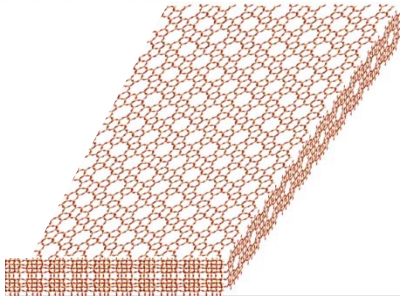
$I\bar{4}m2$

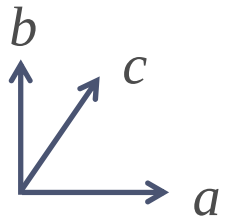


MFI

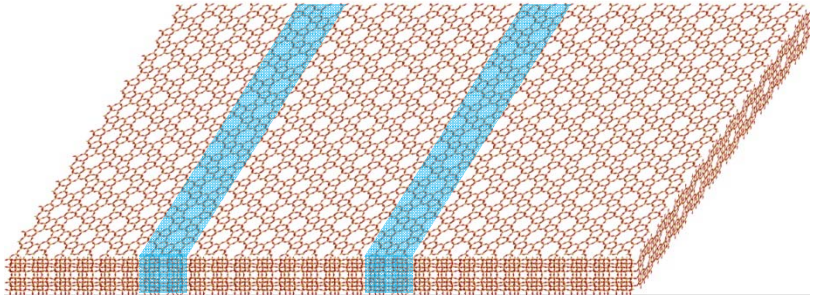
Pnma

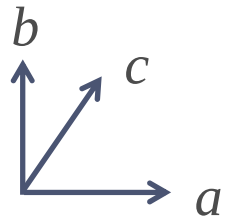




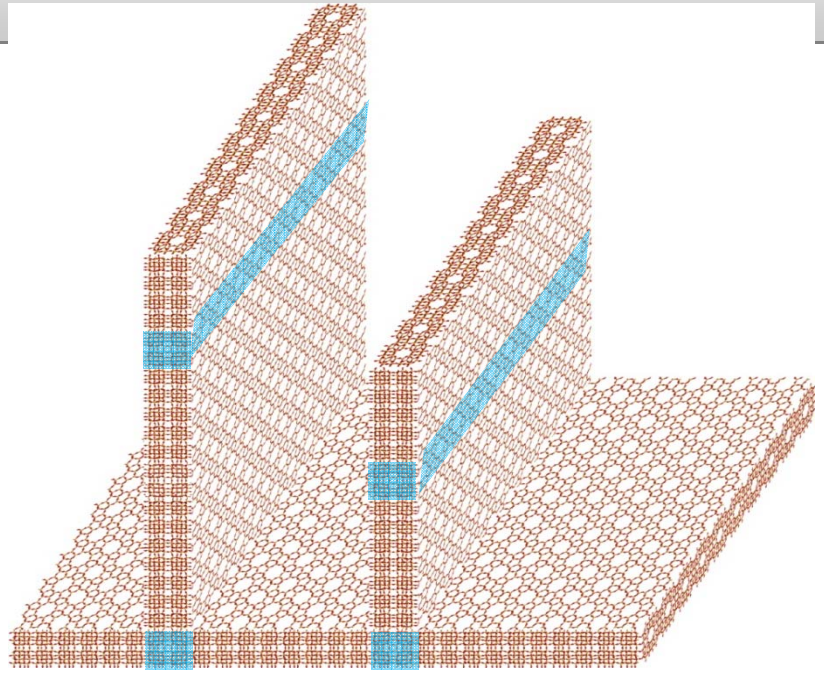


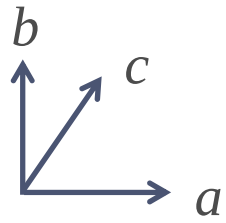
Zeolites



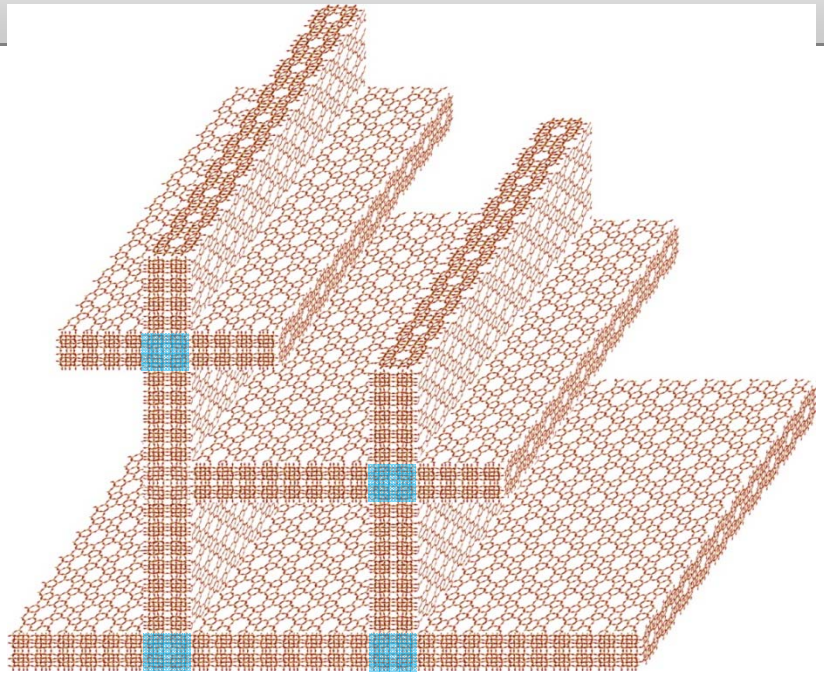


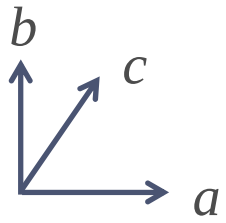
Zeolites



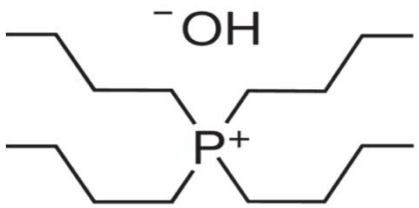


Zeolites

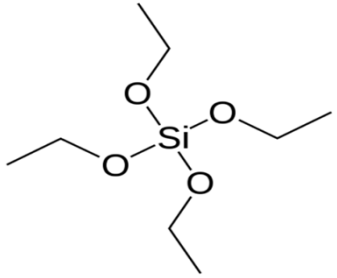




Hydrothermal synthesis



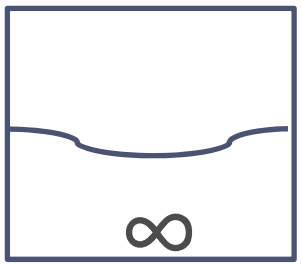
Tetrabutylphosphonium Hydroxide (TBPOH) (**SDA**)



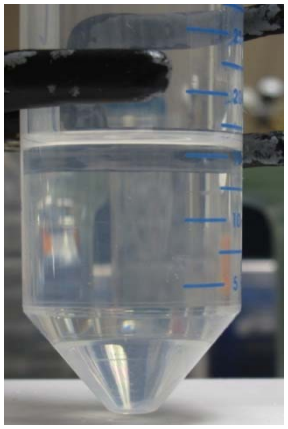
Tetraethyl orthosilicate (TEOS, **Si source**)

$$Si(OCH_2CH_3)_4+4H_2O->Si(OH)_4+4CH_3CH_2OH$$

TEOS
TBPOH
H_2O



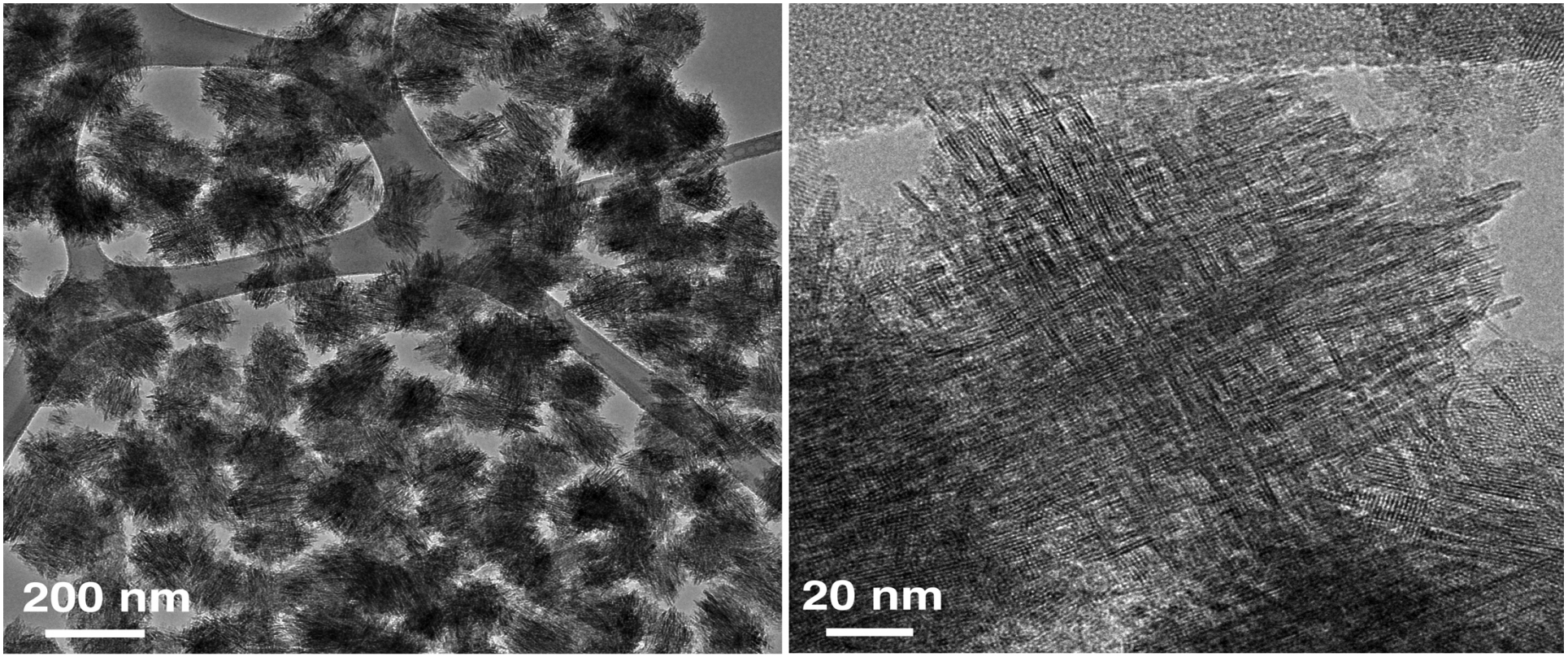
TEOS hydrolysis →



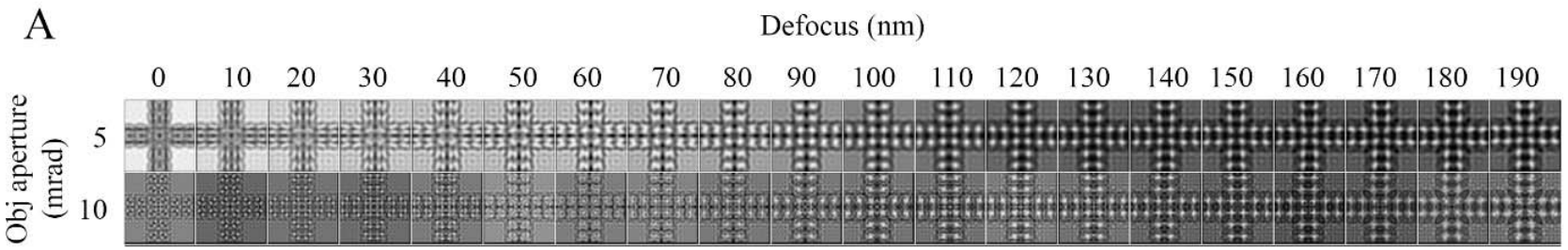
Hydrothermal Synthesis → **115°C**

Zeolite

Self-pillared zeolite nanosheets



Science 336, 1684-1687 (2012) Zhang X., Liu D., Xu D., Asahina S., Cychosz K., Varoon K., Al Wahedi Y., Bhan A., Al Hashimi S., Terasaki O., Thommes M. and Tsapatsis M. *Direct Synthesis of Self-Pillared Zeolite Nanosheets by Repetitive Branching.*



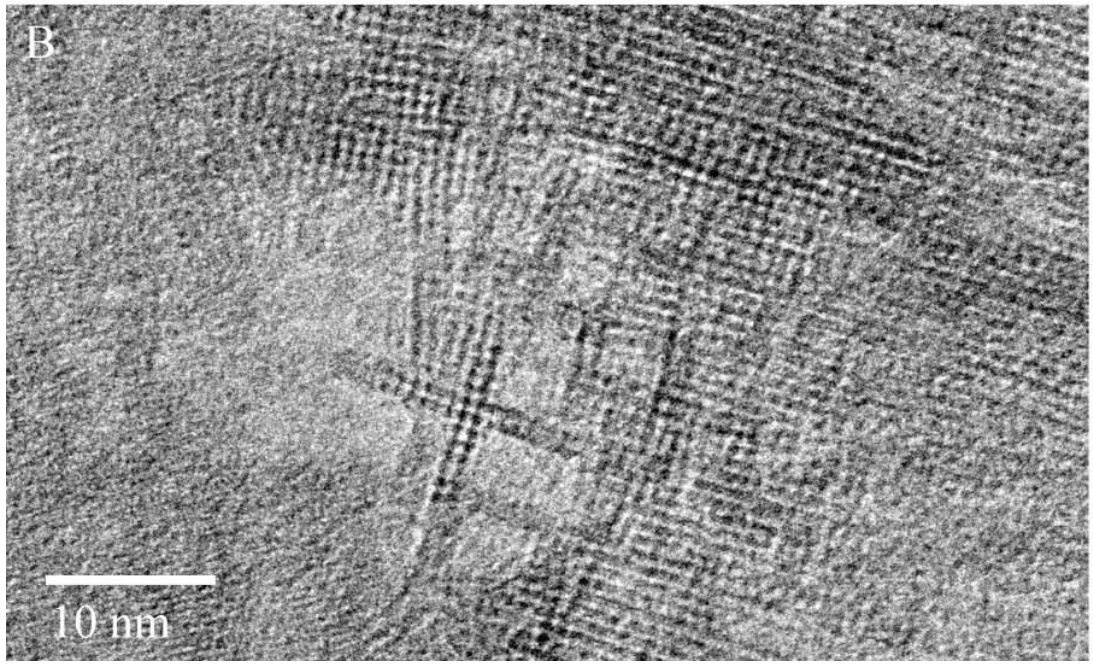
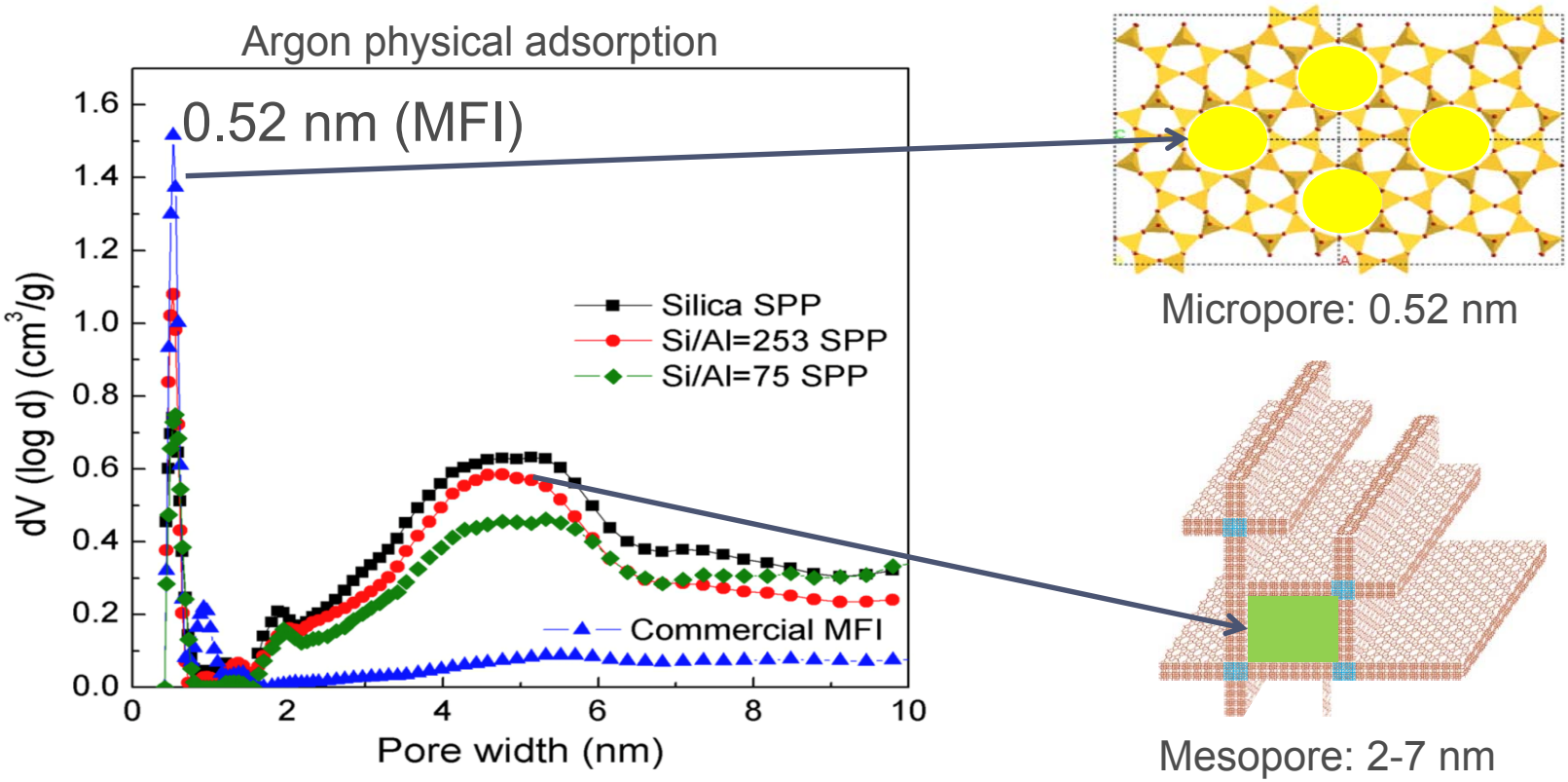


Table I

Multislice simulation parameters

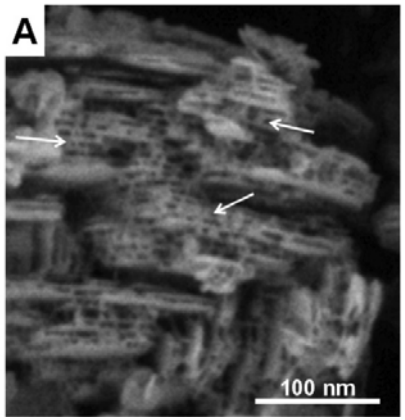
Quantity	Value
Beam energy	200 kV
Temperature	300 K
Spherical aberration (Cs3)	1.2 mm
Objective aperture cutoff	5 mrad
Defocus range (1-20)	0 – 190 nm
Defocus step	10 nm

Pore size distribution



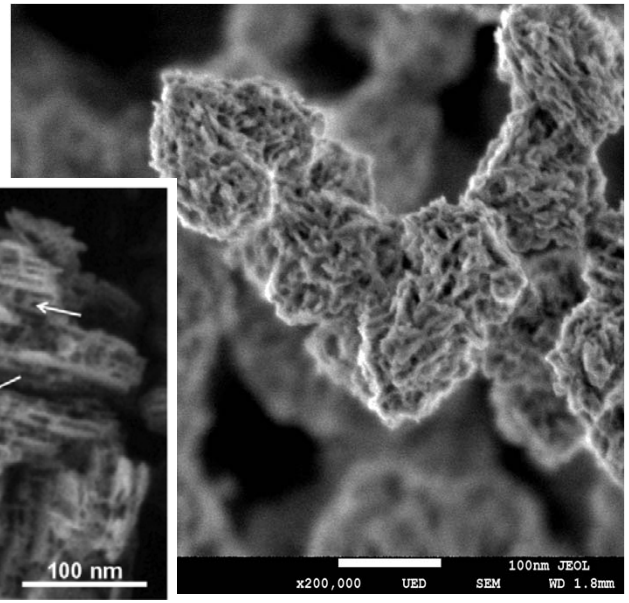
M. Thommes, in *Stud. Surf. Sci. Catal., Vol. 168* (Eds.: J. Cejka, H. van Bekkum, A. Corma, F. Schüth), Elsevier, **2007**, pp. 495-525.
P. I. Ravikovitch, A. V. Neimark, *Colloids Surf., A* **2001**, *187*, 11-21.
Argon adsorption analysis done by Dr. Katie Cychosz and Dr. Matthias Thommes (Quantachrome)

Hierarchical porosity improves deactivation behavior Example: Self-etherification of HMF

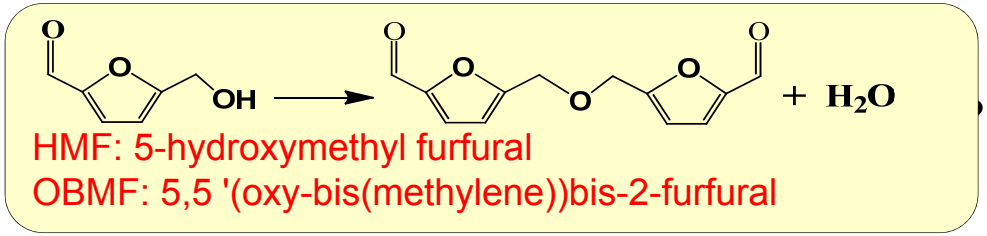


Pillared MFI

Ryoo, Terasaki and co-workers J. Am. Chem. Soc. ***2010****, 132, 4169.*

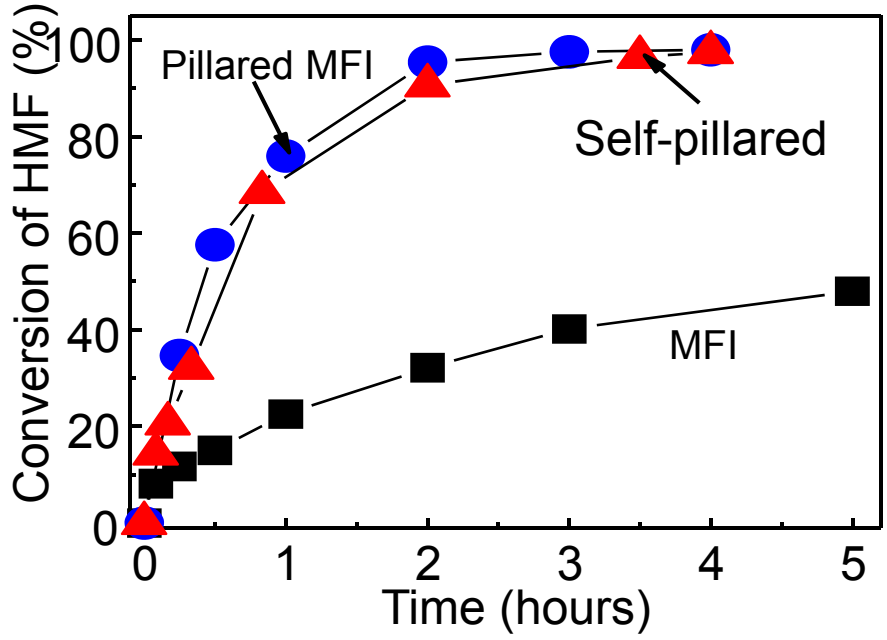


Self-pillared

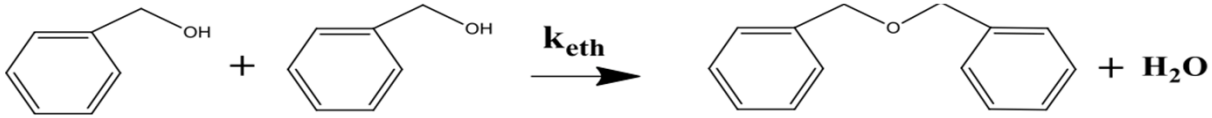


HMF: 5-hydroxymethyl furfural

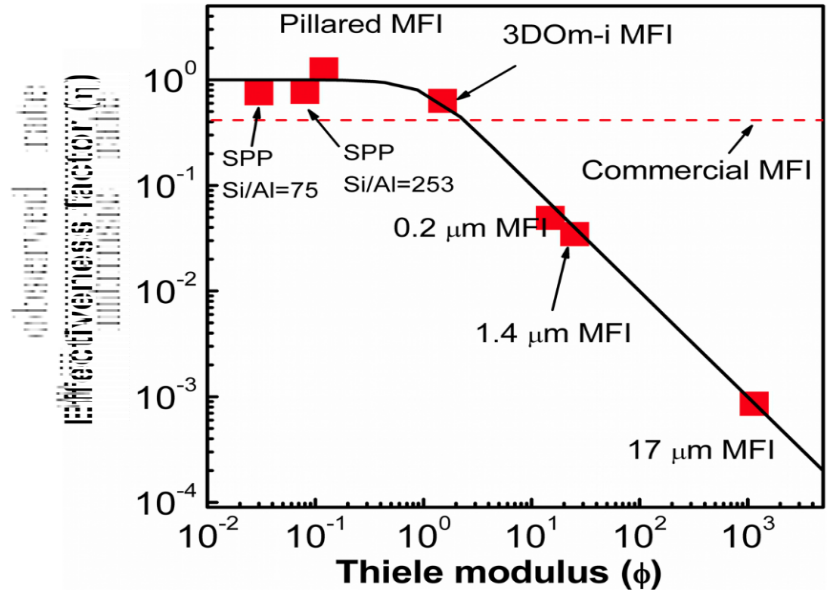
OBMF: 5,5 '(oxy-bis(methylene))bis-2-furfural

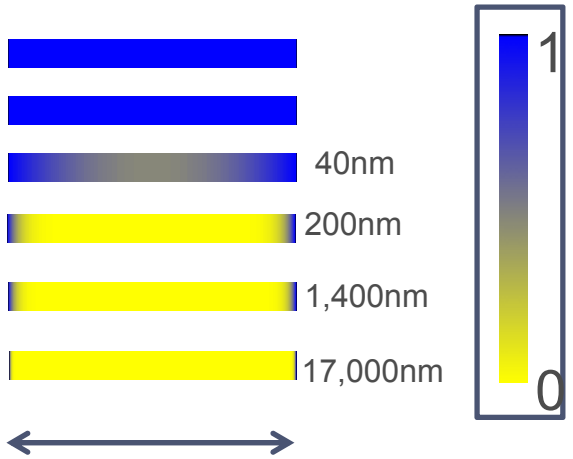


Reaction-diffusion



Self-etherification reaction of benzyl alcohol



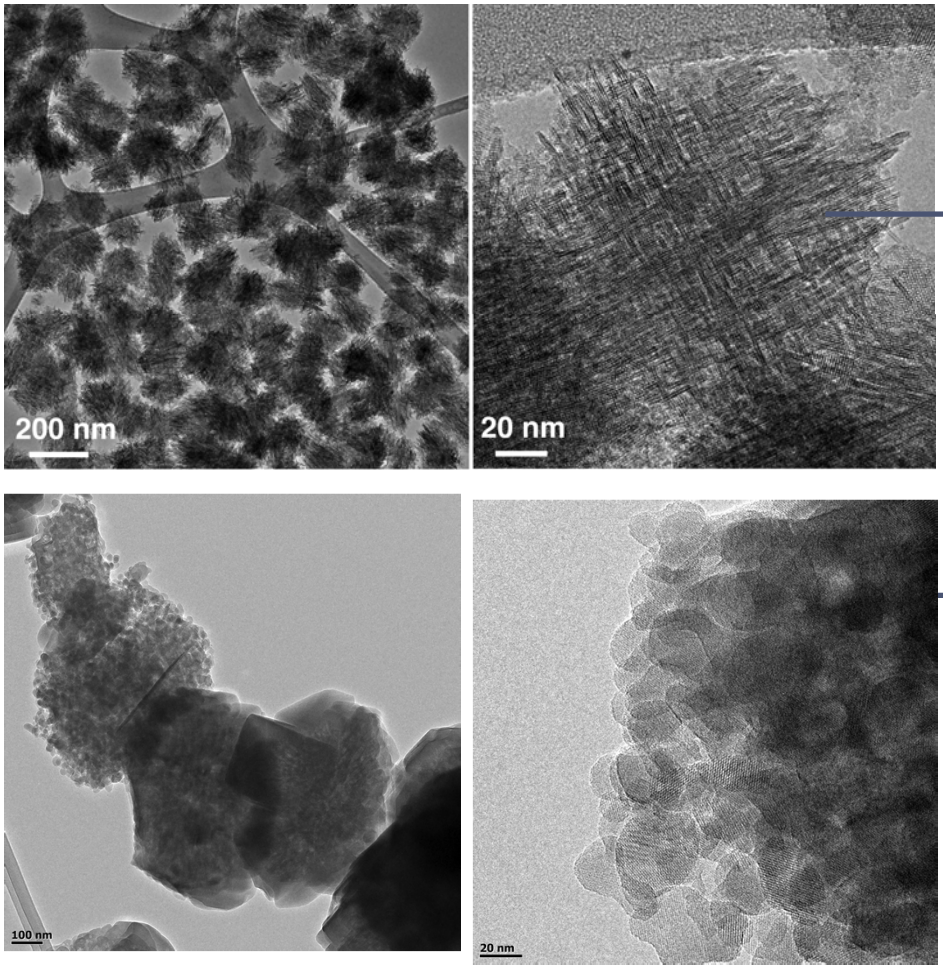


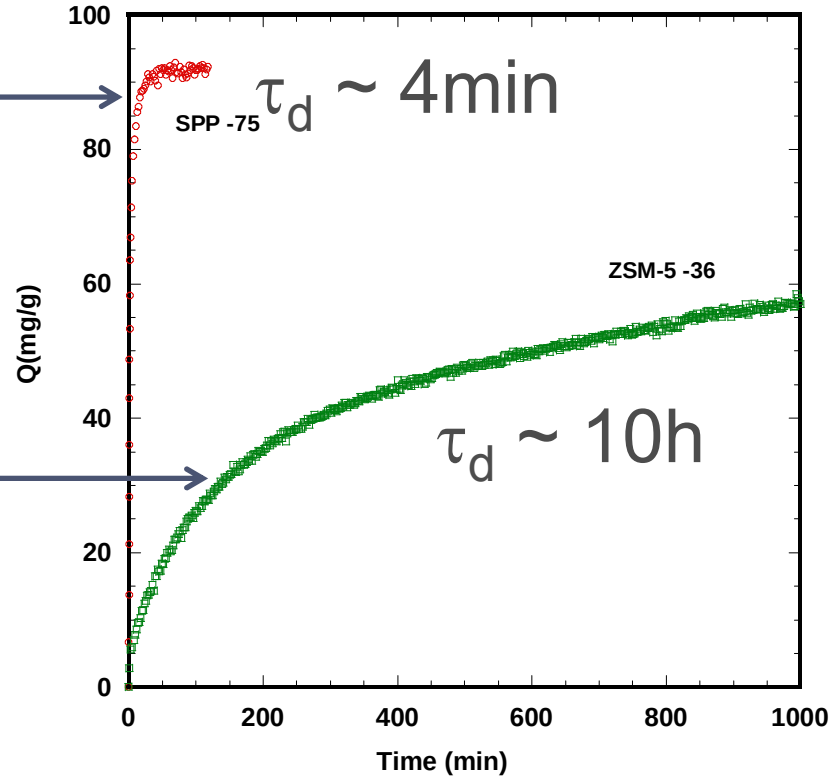
Dimensionless crystal size

Classical diffusion-reaction model: zeolitic behavior

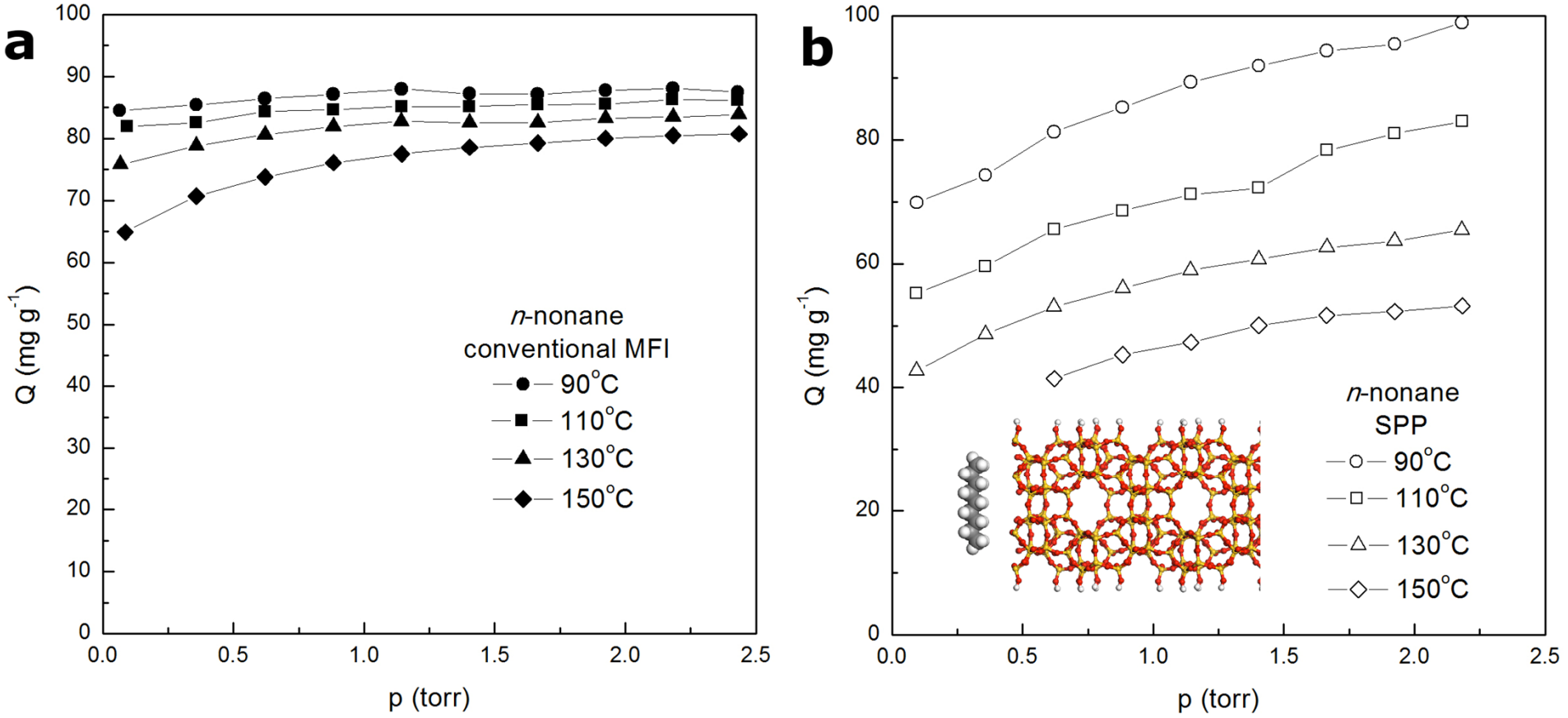
M. E. Davis, R. J. Davis, in *Fundamentals of chemical reaction engineering*. (McGraw-Hill Higher Education, New York, NY, 2003), chap. 6.
R. Aris, in *Elementary Chemical Reactor Analysis*. (Dover, 1989), chap. 6.

2,2 DMB 30°C


200 nm
20 nm
100 nm
20 nm

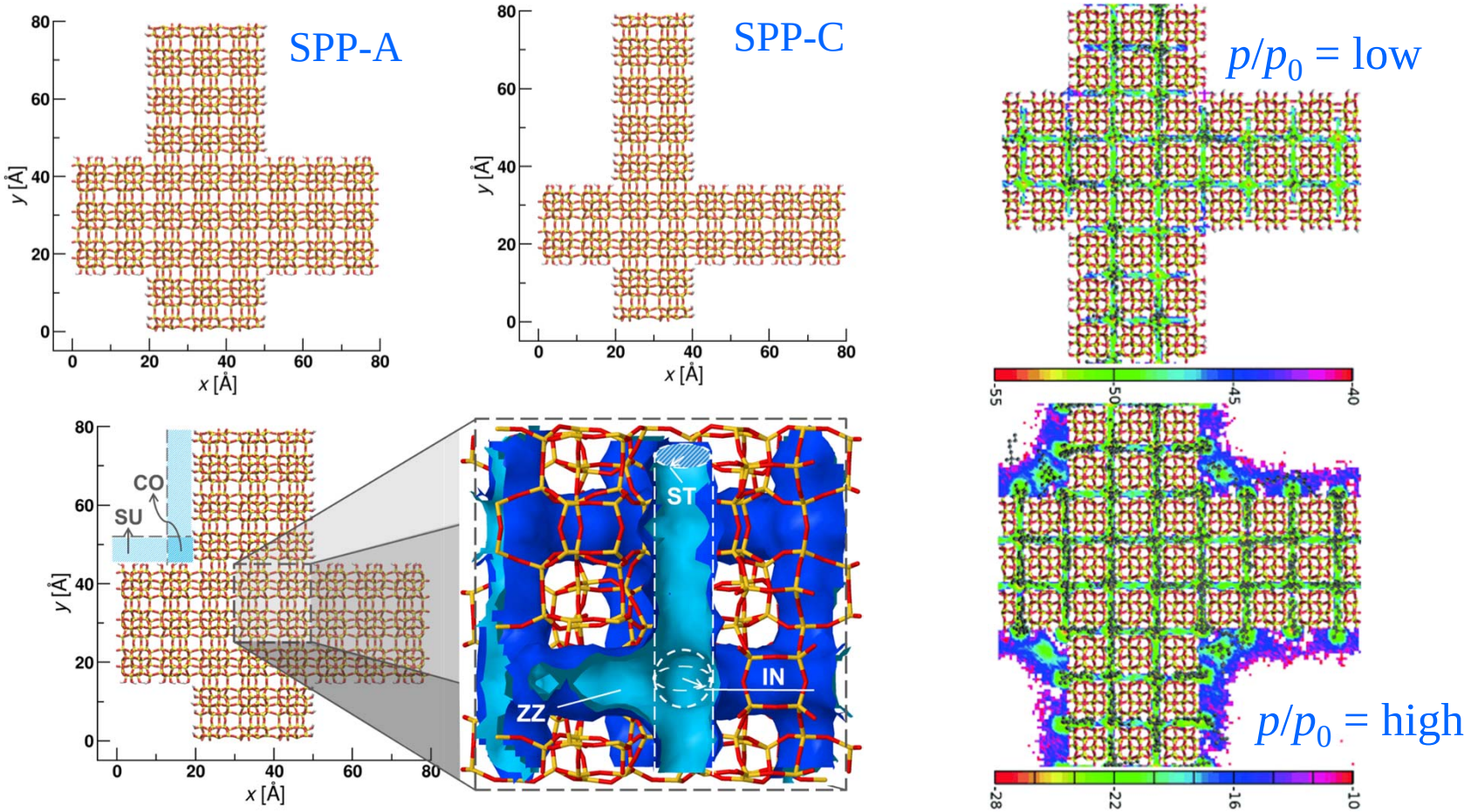

100
80
60
40
20
0
Q(mg/g)
0
200
400
600
800
1000
Time (min)
SPP -75
τd ~ 4min
ZSM-5 -36
τd ~ 10h

n-nonane

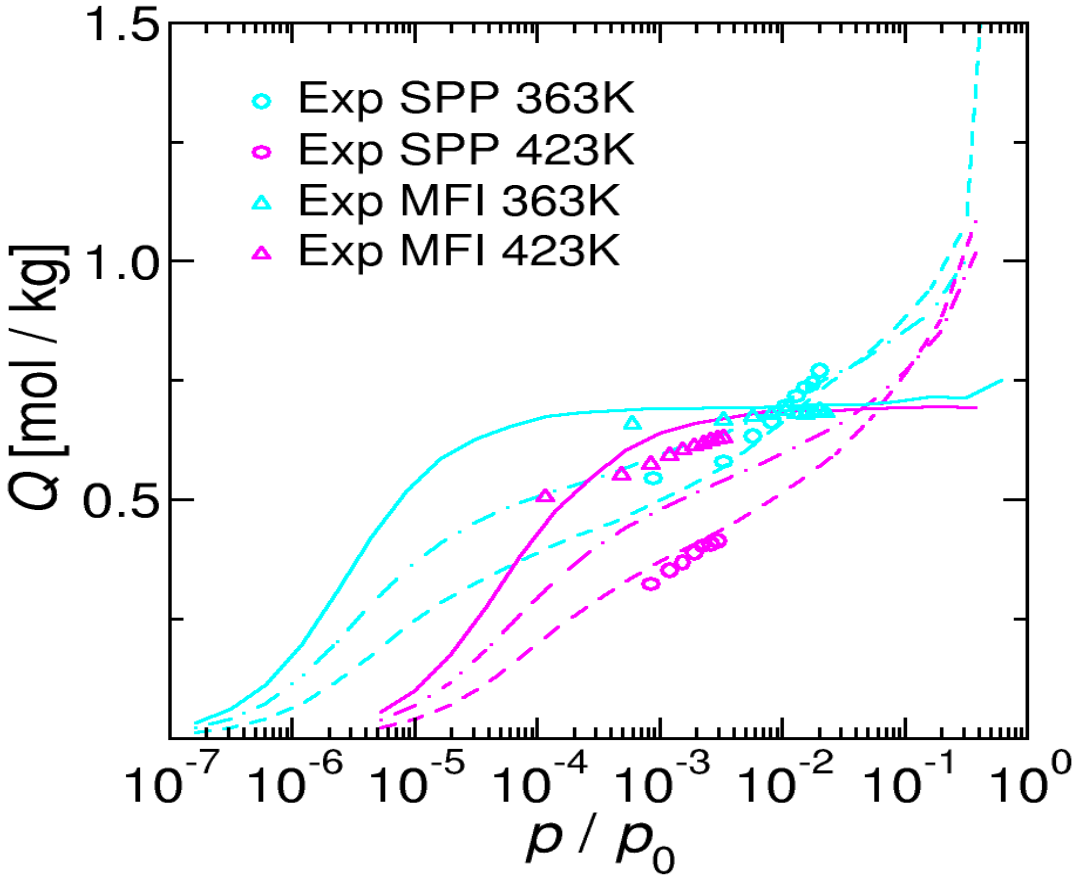


Advanced Functional Materials 24(2), 201-208 (2014)

Understanding the Unusual Adsorption Behaviour in Hierarchical Zeolite Nanosheets



Bai et al. ChemPhysChem15, 2225-2229 (2014)



Filled Lines: MFI

Dash-dotted lines: SPP-A

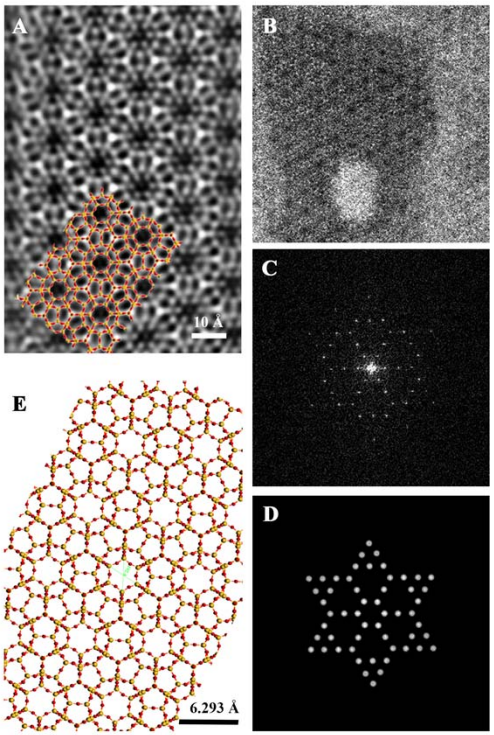
Dashed lines: SPP-C

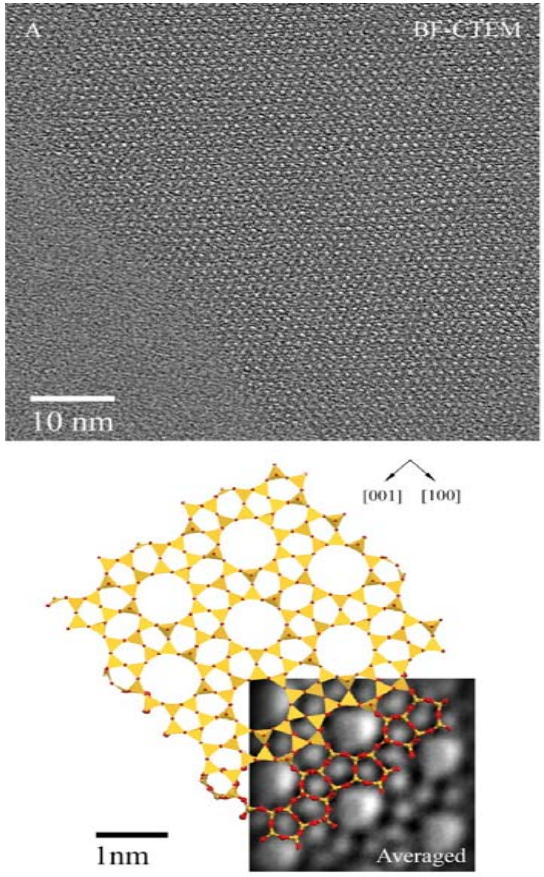
An approach for synthesis of hierarchical zeolites based on rotational intergrowths was demonstrated for single-unit-cell thick layers of MFI.

External and internal catalytic activity was quantitatively analyzed by classical reaction diffusion modeling.

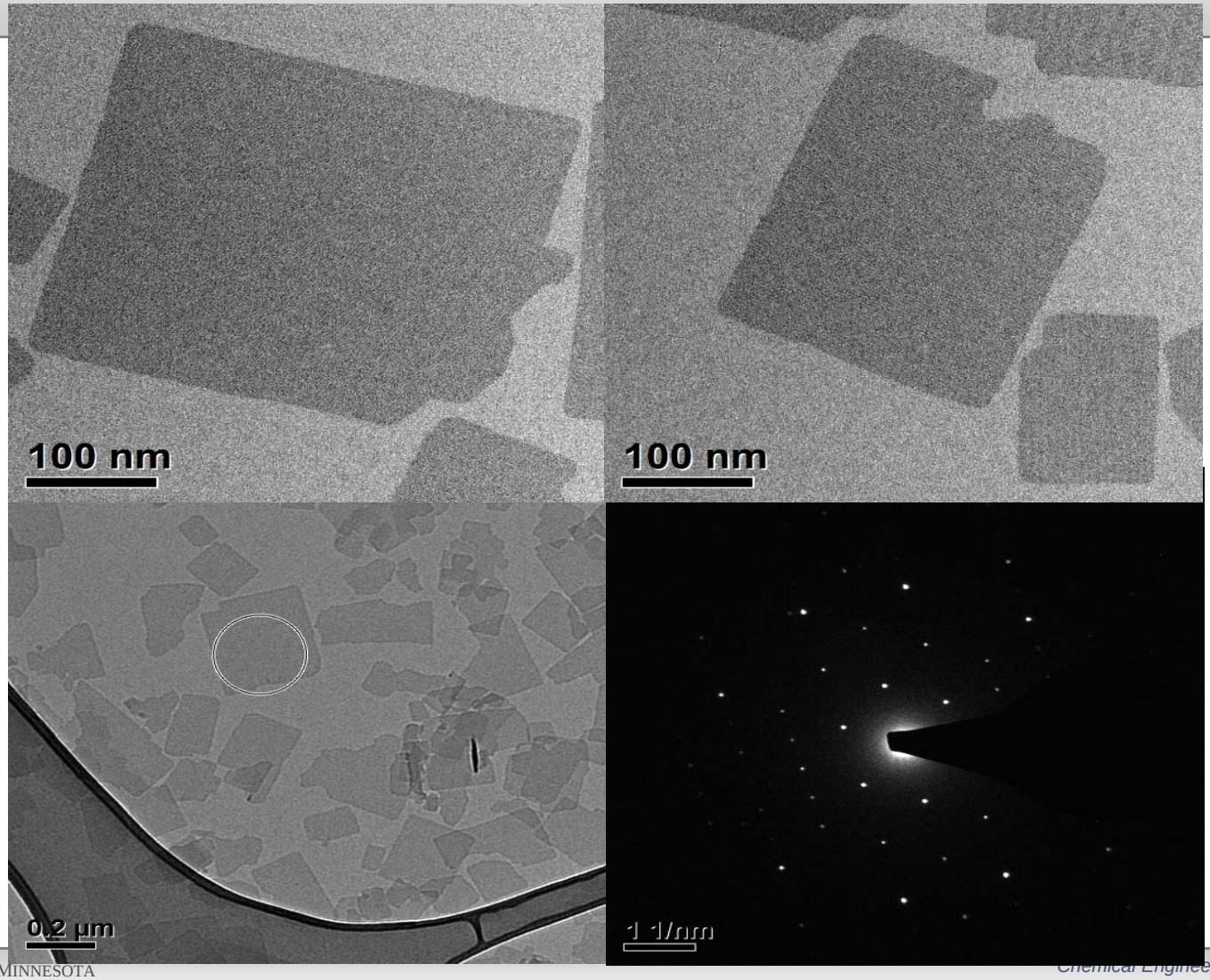
Adsorption properties of single-unit-cell zeolites can be different from those of micro- and nanocrystals.

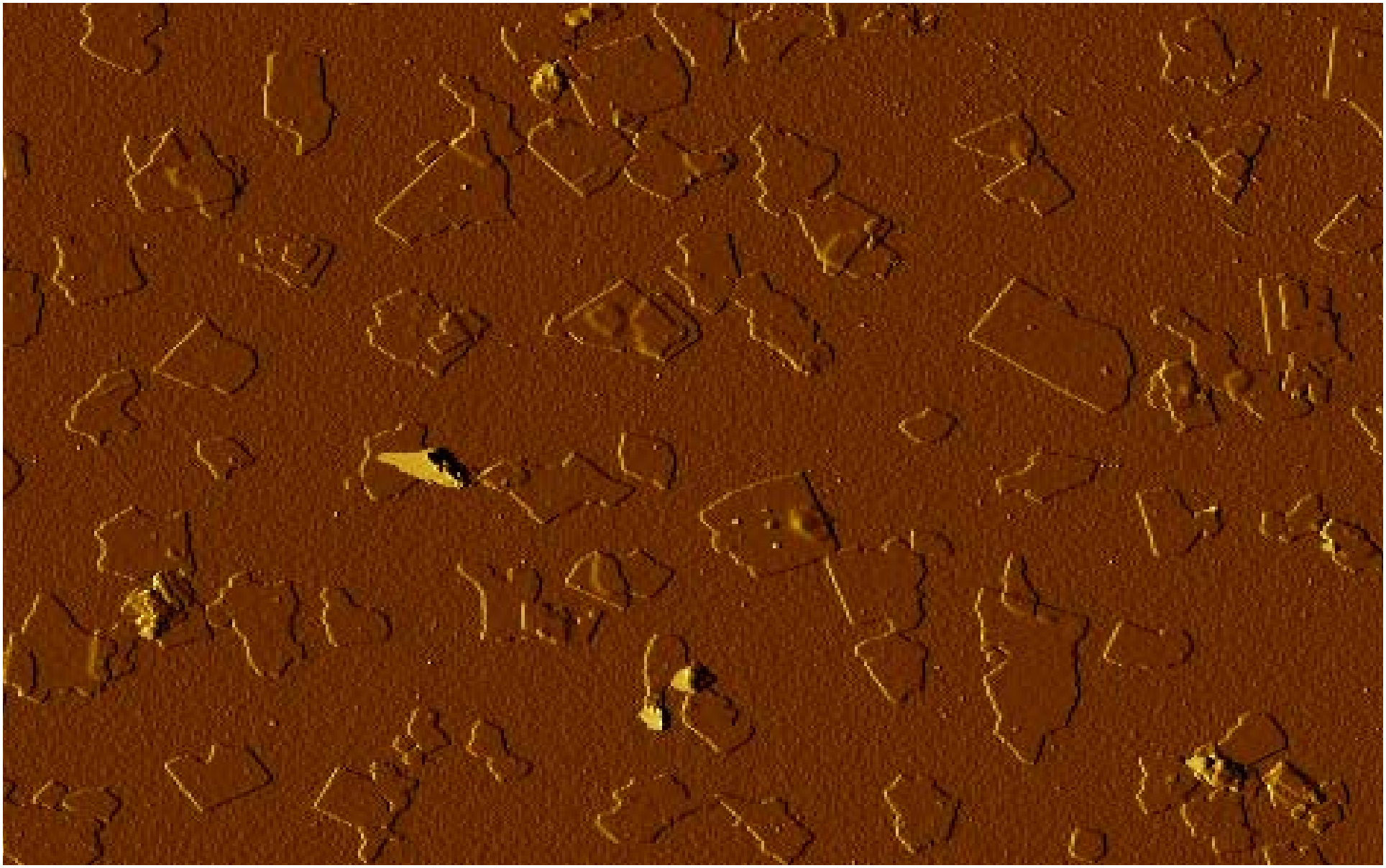
Zeolite nanosheets: MWW and MFI

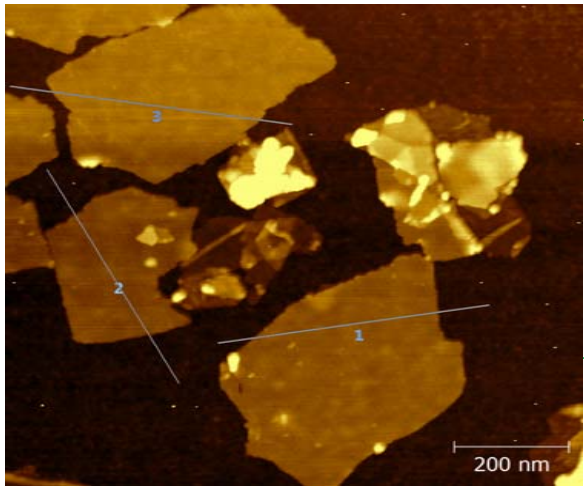


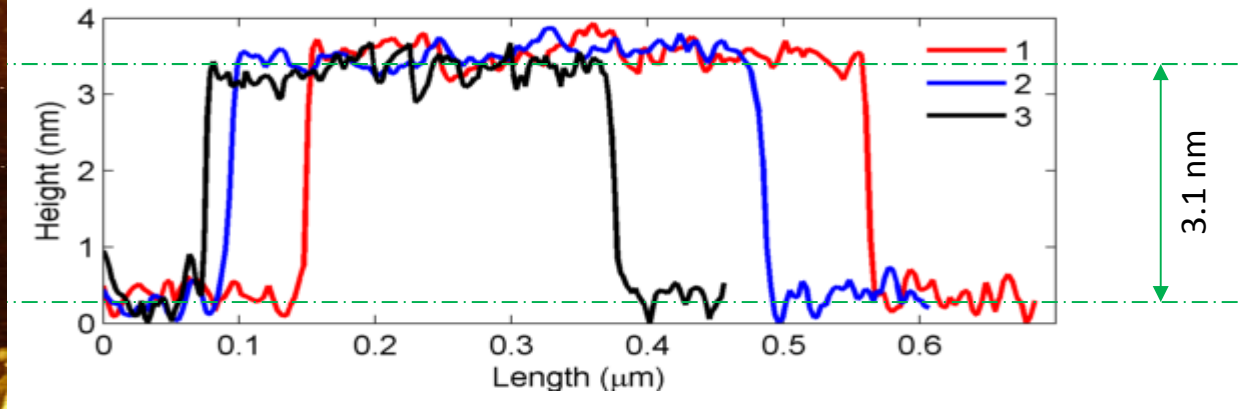


Exfoliation of layered MFI by melt compounding with polystyrene

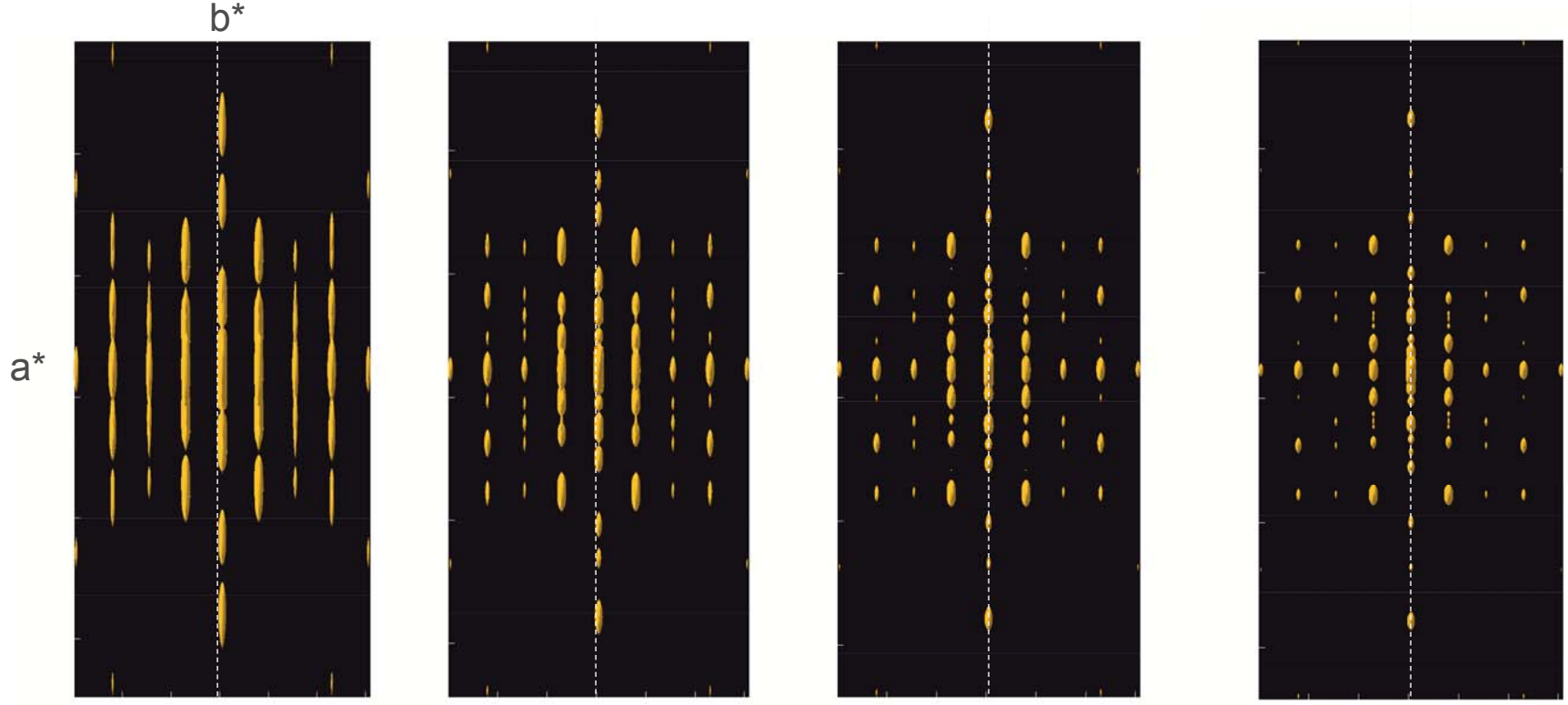




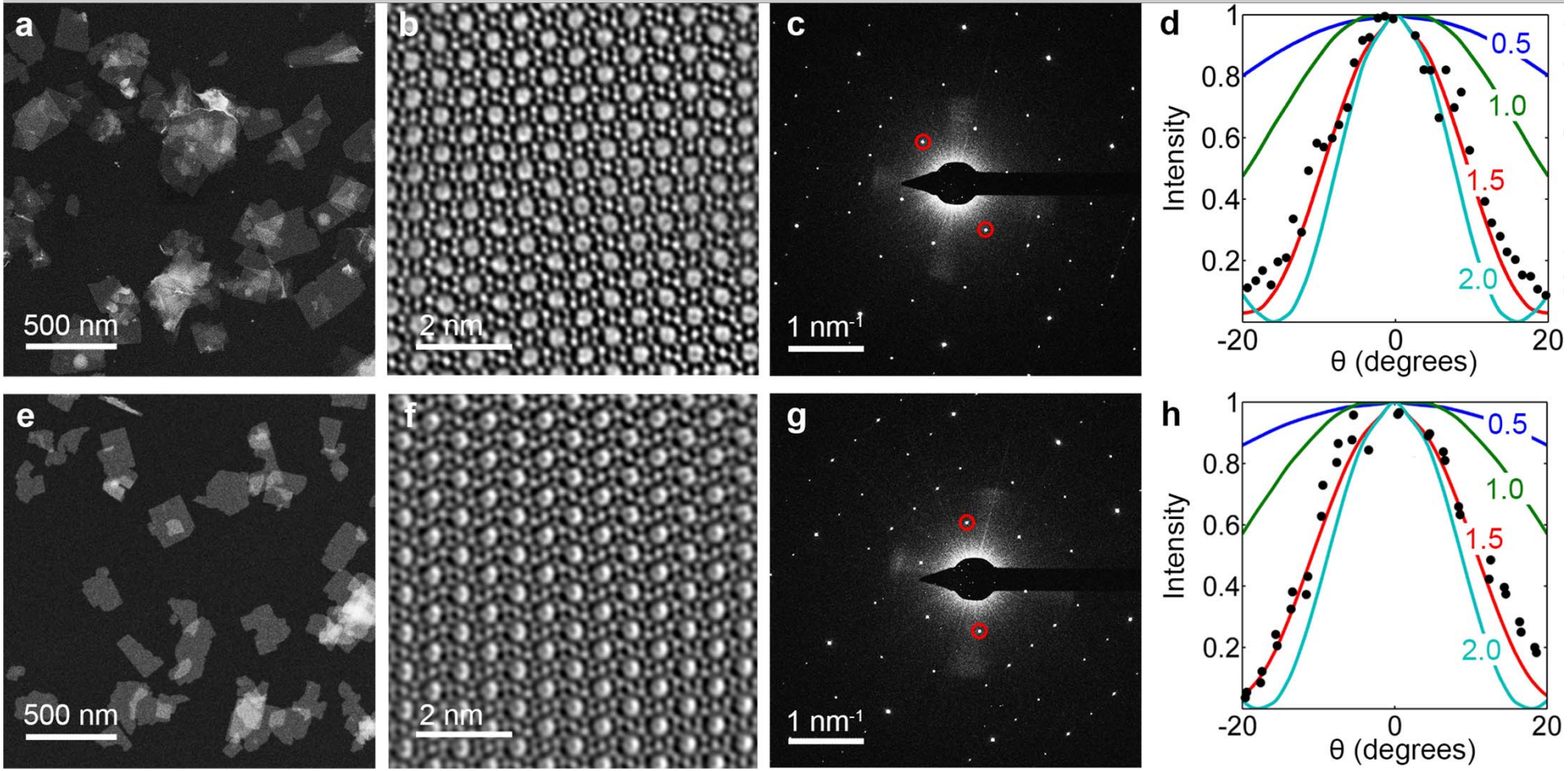

3
2
1
200 nm


Height (nm)
Length (μm)
0
1
2
3
4
0
0.1
0.2
0.3
0.4
0.5
0.6
1
2
3
3.1 nm

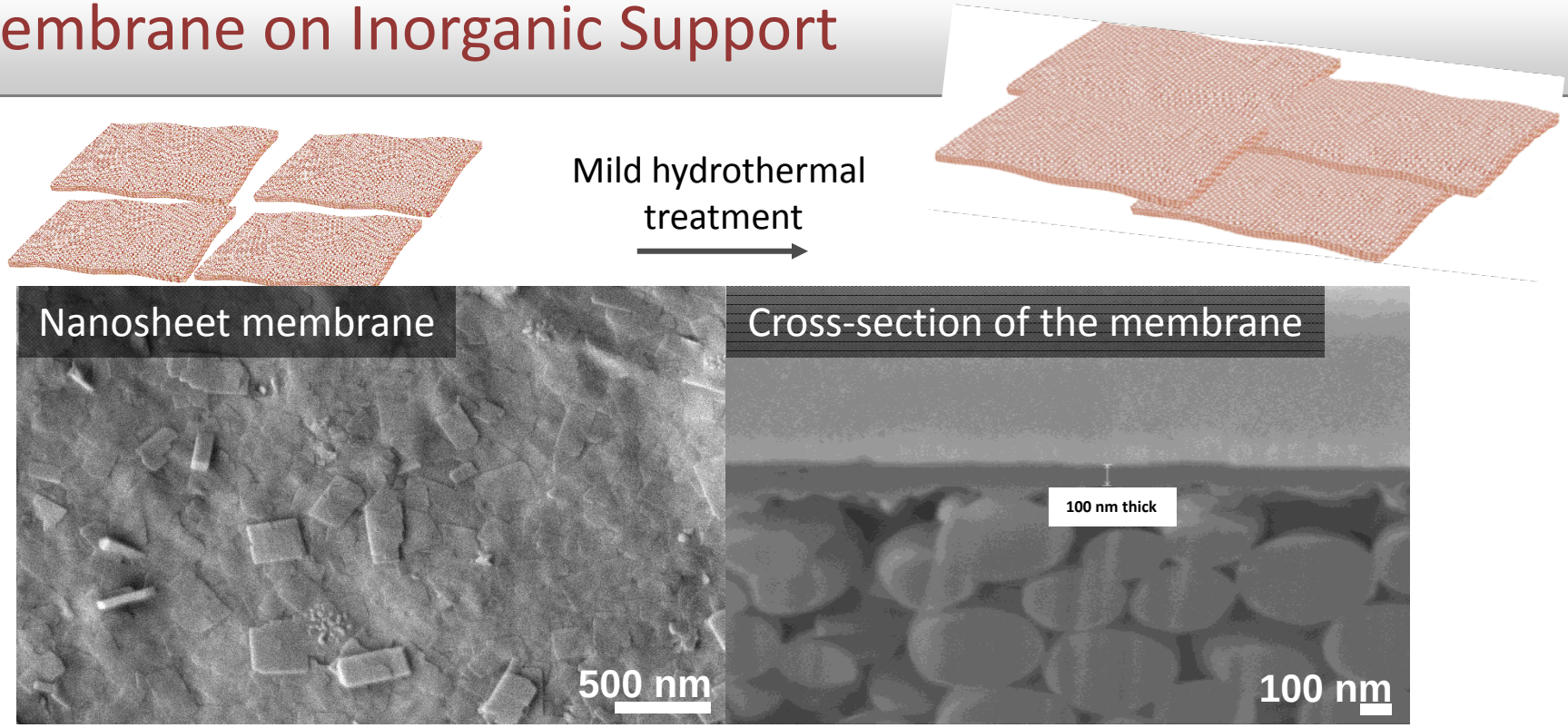
Reciprocal lattice models (**re**ciprocal **l**attice **rods**)



Comparison before and after de-templation by acid wash



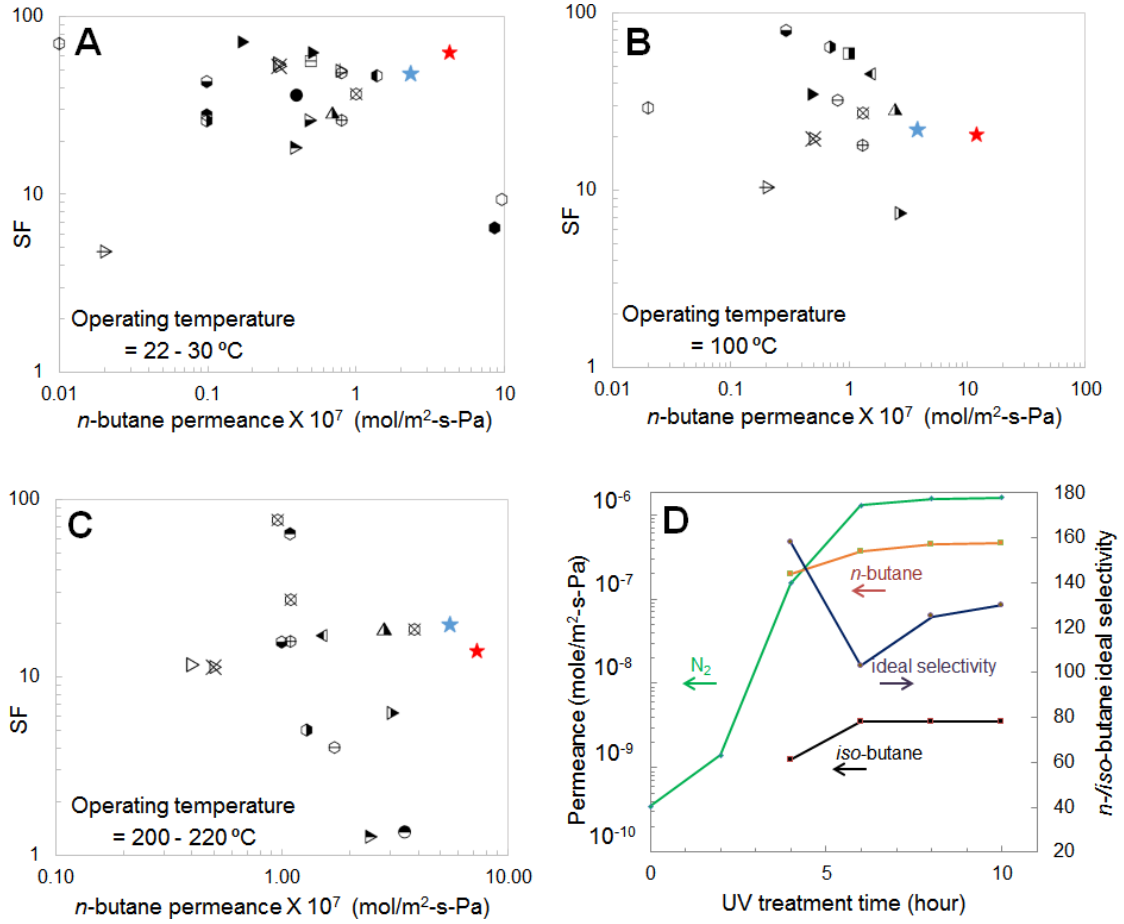
Membrane on Inorganic Support



AIChE Journal 59(9), 3459-3467 (2013) Agrawal K.V., Topuz B., Navarro M., Nguenkam K., Elyassi B., Francis L. Tsapatsis M. *Solution–Processable Exfoliated Zeolite Nanosheets Purified by Density Gradient Centrifugation*- Invited contribution in *Founders Tribute to Professor Neal R. Amundson* DOI: 10.1002/aic.14099

Science 334, 72-75 (2011) Varoon K., Zhang X., Elyassi B., Brewer D., Gettel M., Kumar S., Lee J.A., Maheshwari S., Mittal A., Sung C.-Y., Cococcioni M., Francis L.F., McCormick A.V. Mkhoyan A., Tsapatsis M. *Dispersible Exfoliated Zeolite Nanosheets and Their Application as a Selective Membrane.* DOI: 10.1126/science.1208891

Butane Isomer Permeation



1.5-unit cell (1-D) zeolite MFI nanosheets
(approximately 3 nm x 200 nm x 200 nm)
can be prepared as suspensions in various solvents.

They can be transferred on porous and non-porous supports and on the air water interface.

TEM, ED, in-plane XRD consistent with expected structure.
Crystallographic perfection and surface structure still unexplored.

Functional (high performance) MFI membranes demonstrated.
Fast, low cost, scalable, processing possible.

Need for thin film/small quantity adsorption measurements.

Advanced Functional Materials 24(2), 201-208 (2014) Xu D., Swindlehurst G.R., Wu H., Olson D.H., Zhang X., Tsapatsis M. *On the Synthesis and Adsorption Properties of Single-Unit-Cell Hierarchical Zeolites Made by Rotational Intergrowths*- Invited contribution for *Special Issue on Porous Materials* DOI: 10.1002/adfm.201301975

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