Oviedo, ES
26-08-2018

Zeolite SSZ-70: new understanding of a successful catalytic material

Stef Smeets

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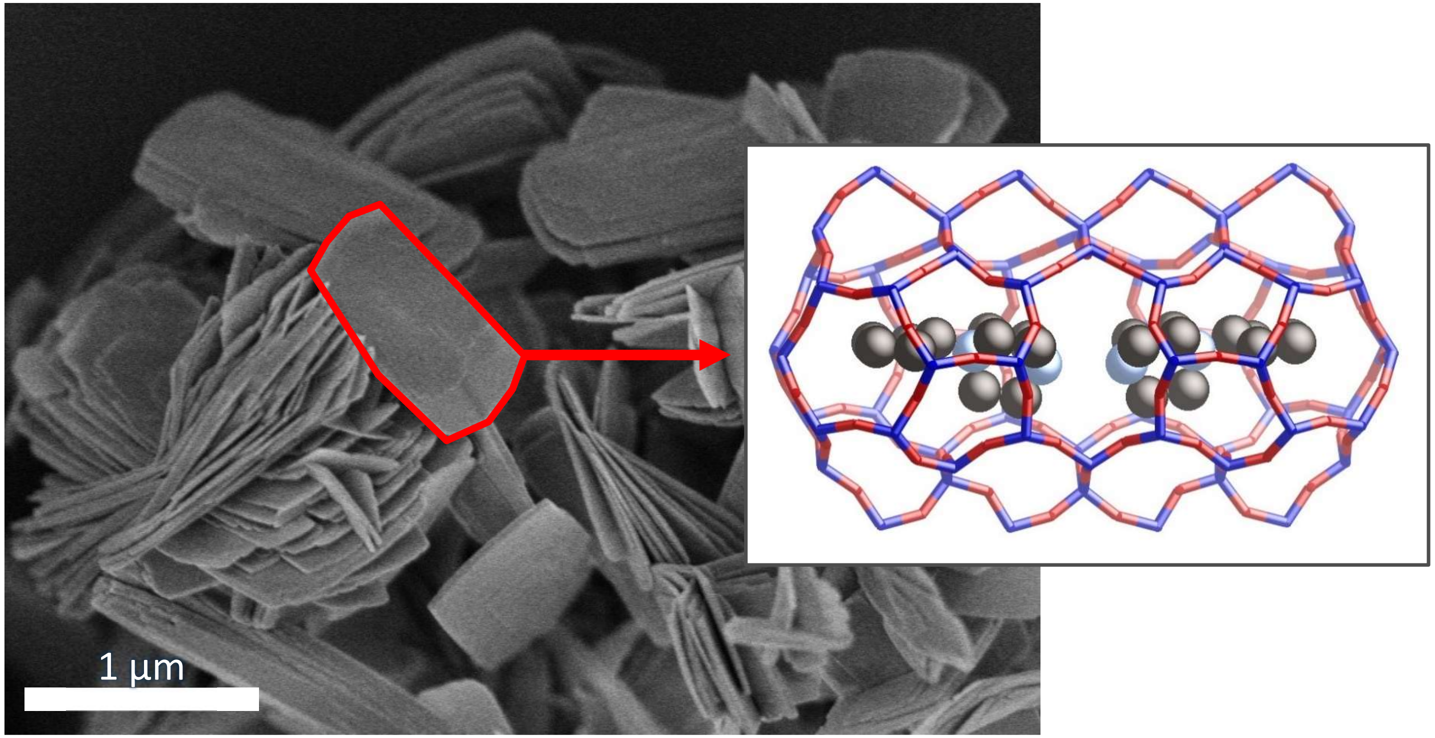
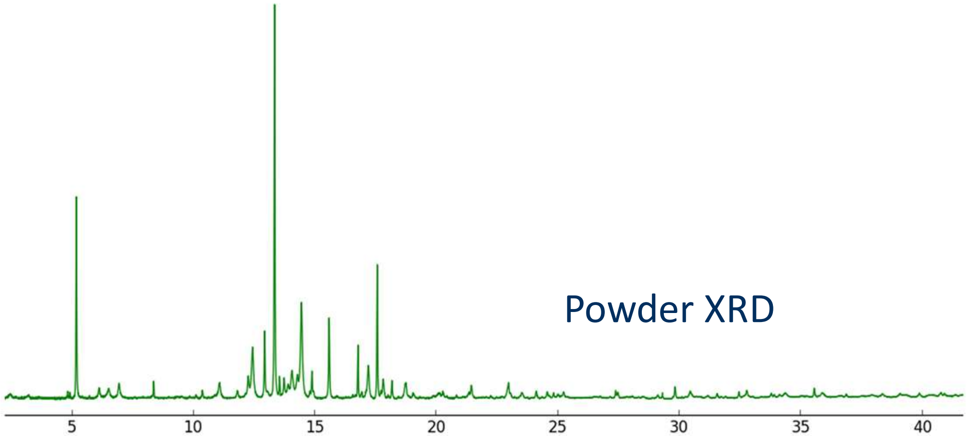
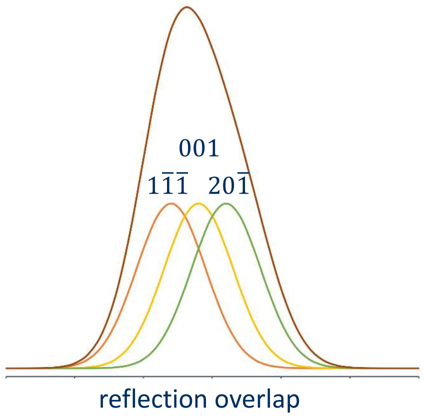
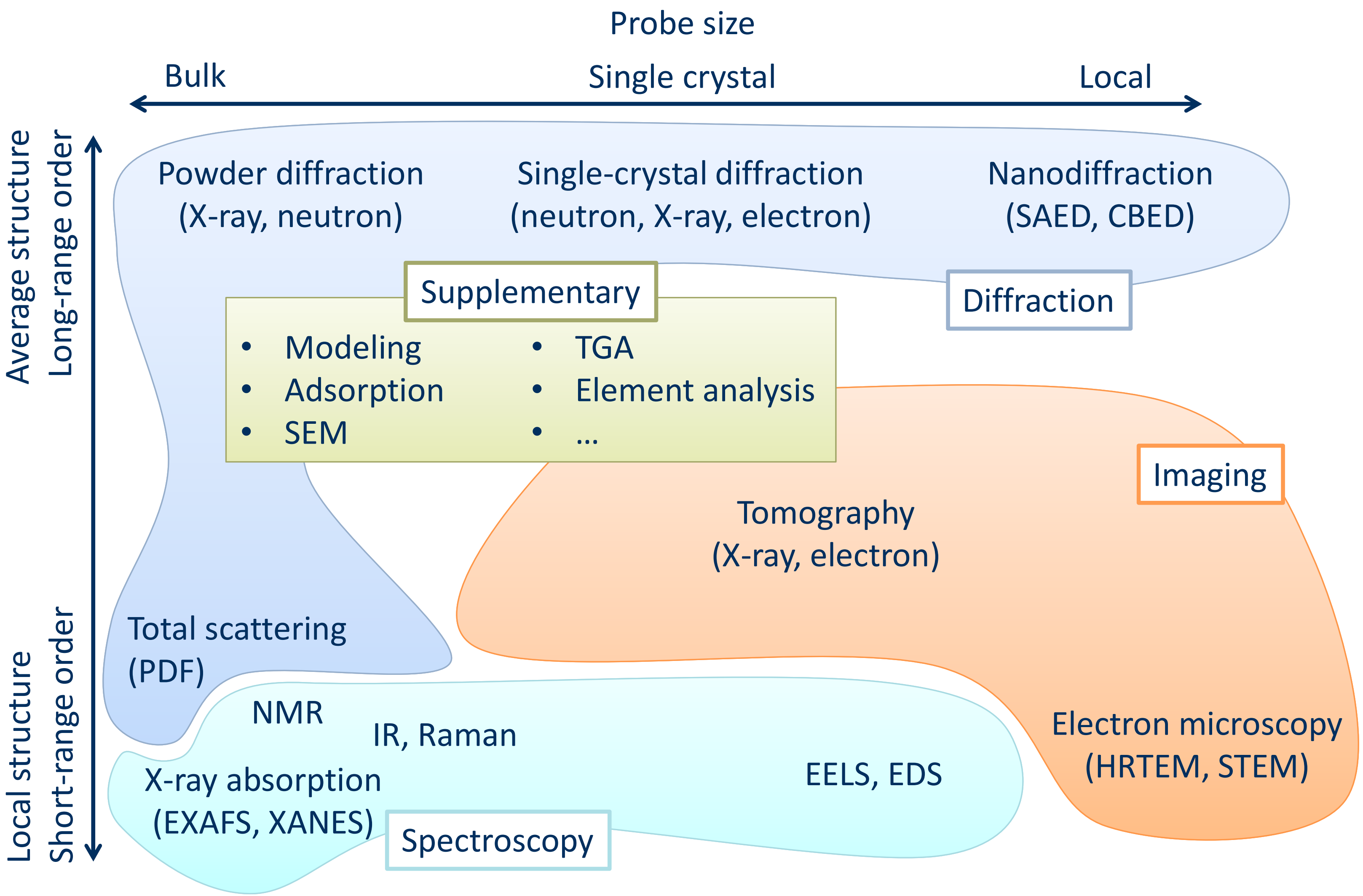

1 µm

?


Powder XRD
5
10
15
20
25
30
35
40

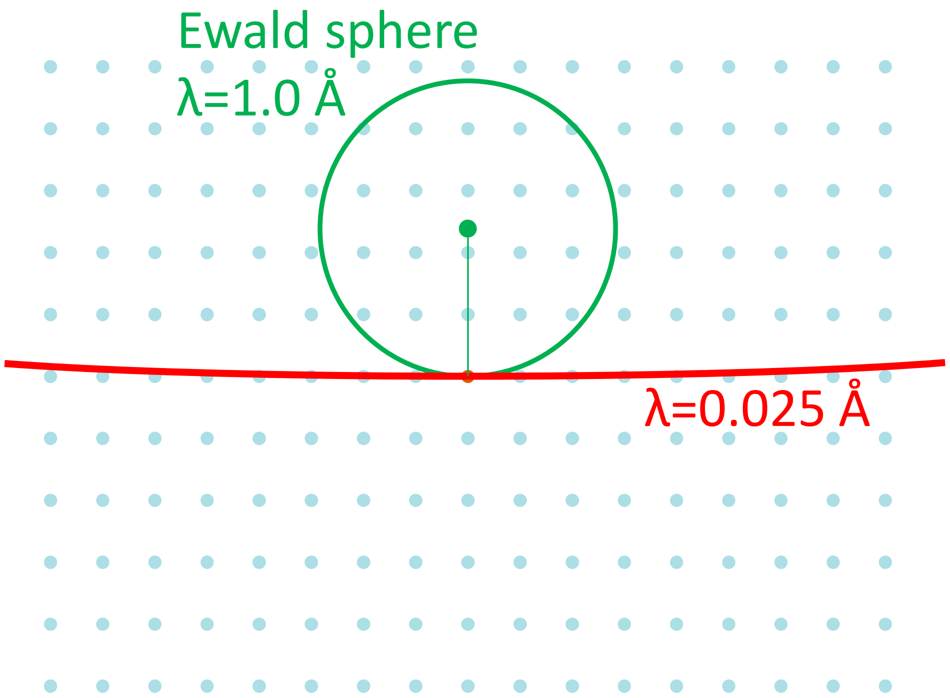

001
$1\bar{1}\bar{1}$
$20\bar{1}$
reflection overlap

Structure

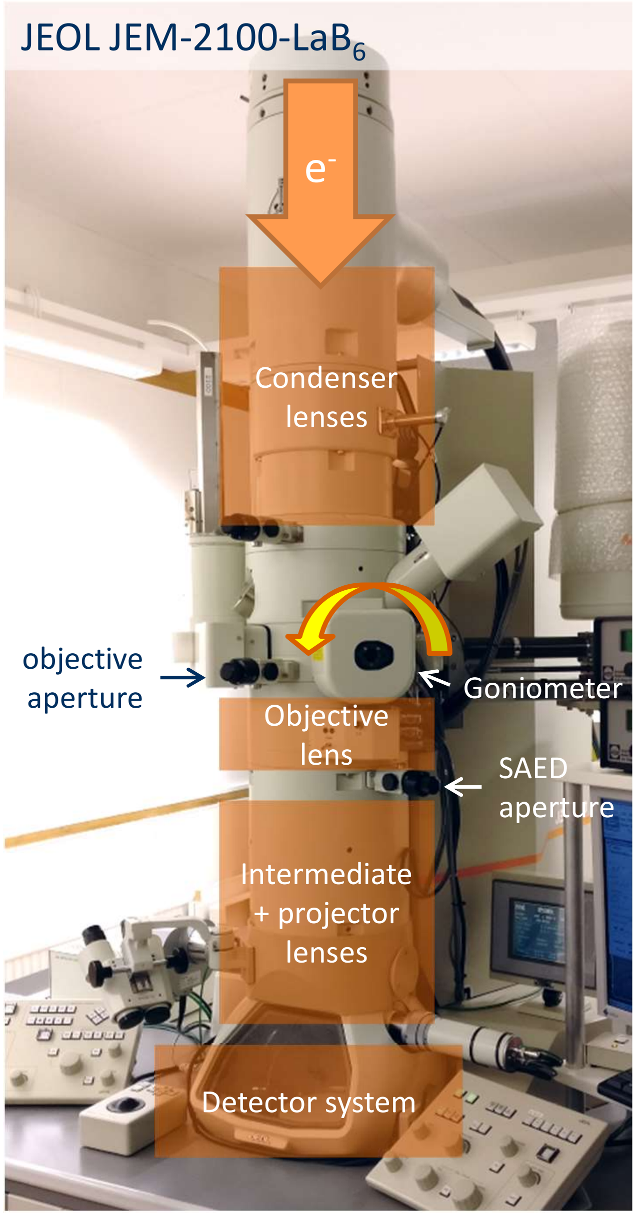


Probe size
Bulk
Single crystal
Local
Average structure
Long-range order
Local structure
Short-range order
Powder diffraction
(X-ray, neutron)
Single-crystal diffraction
(neutron, X-ray, electron)
Nanodiffraction
(SAED, CBED)
Diffraction
Supplementary
• Modeling
• Adsorption
• SEM
• TGA
• Element analysis
• …
Imaging
Tomography
(X-ray, electron)
Total scattering
(PDF)
NMR
IR, Raman
X-ray absorption
(EXAFS, XANES)
EELS, EDS
Electron microscopy
(HRTEM, STEM)
Spectroscopy

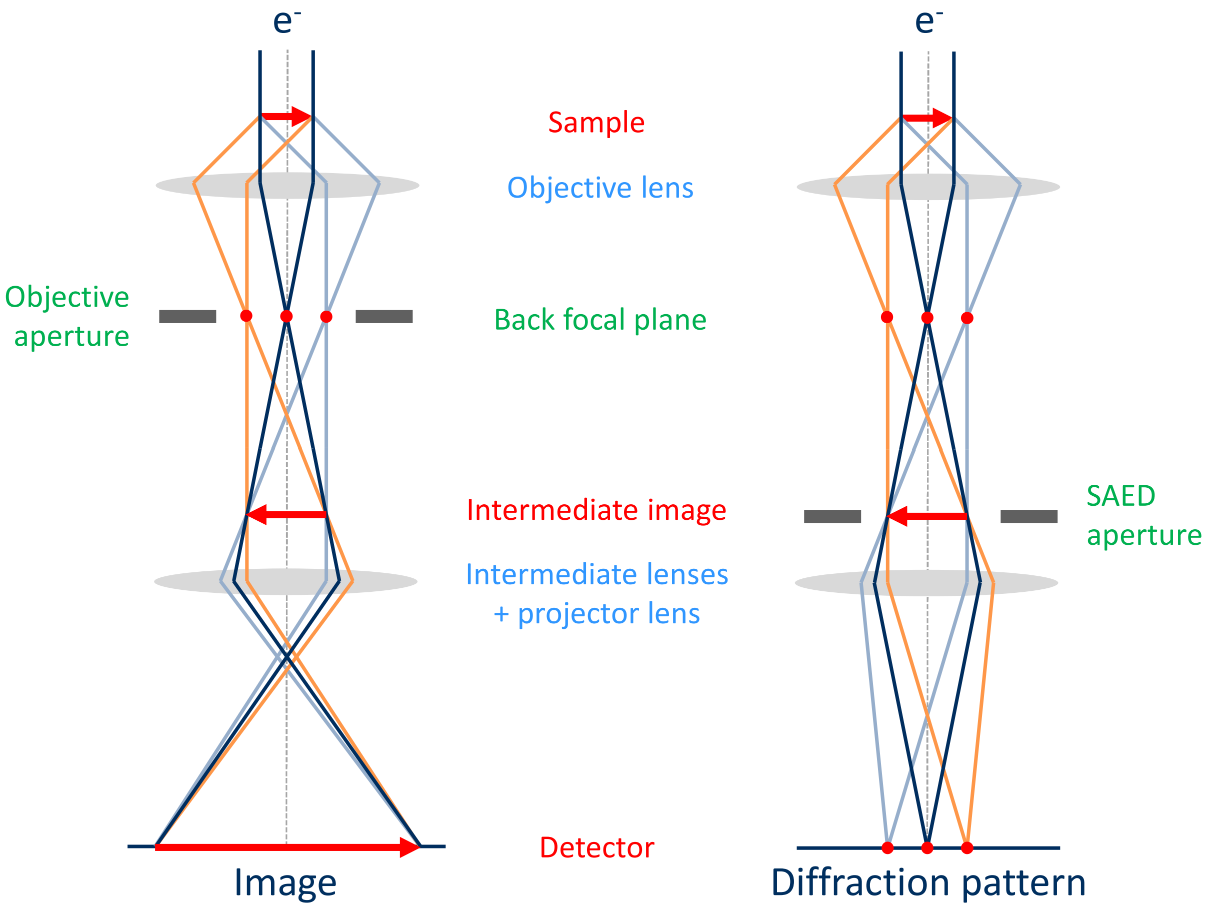
Electrons as a radiation source



- Accelerating voltage: 100 to 300 keV
- Wavelength: 0.0251 Å @ 200 keV
- Probe electrostatic potential
- Strong interaction (10^6 stronger than X-rays)
- Require small samples (< 1 µm)
- High vacuum (<10^{-3} mbar)

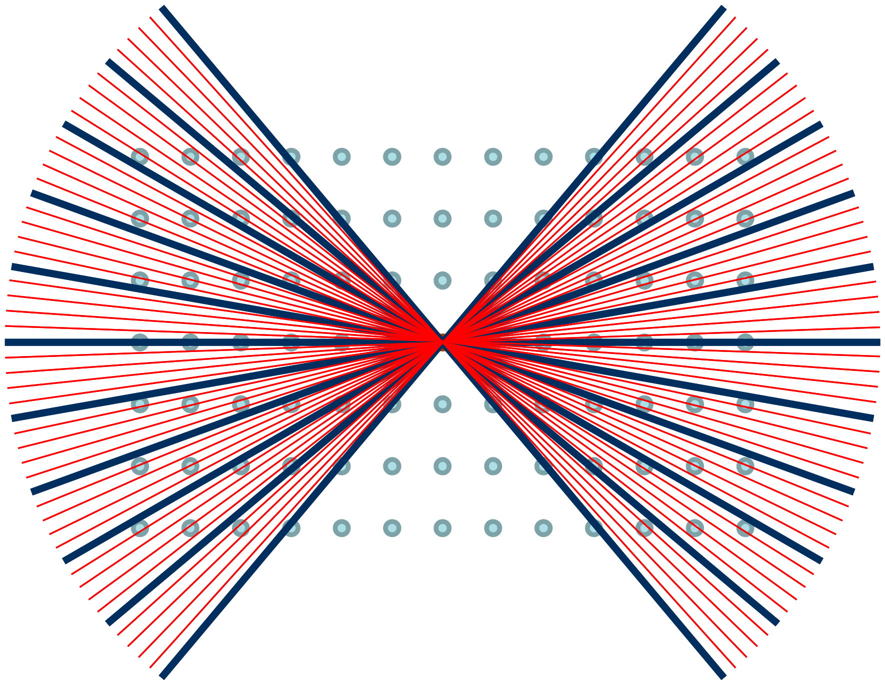


Electron ‘diffractometer’



RED: Fine slicing using beam tilt

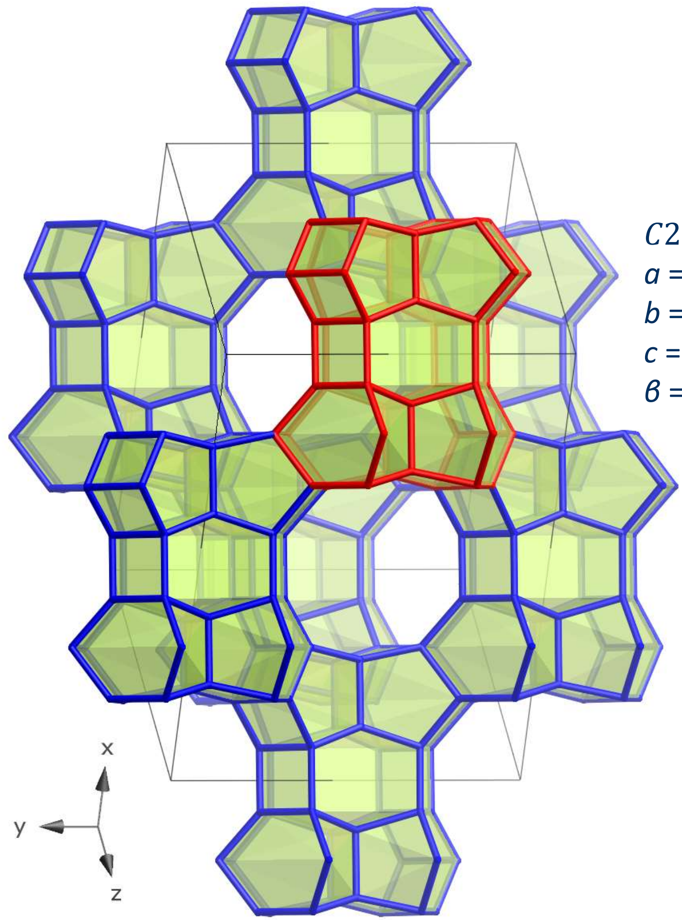
Zhang *et al.*, Z. Krist. (2010), 225:94
Wan *et al.*, J. Appl. Cryst. (2013), 46:1863



Tilt range ±50° (0.2° /step)
0.2 s exposure

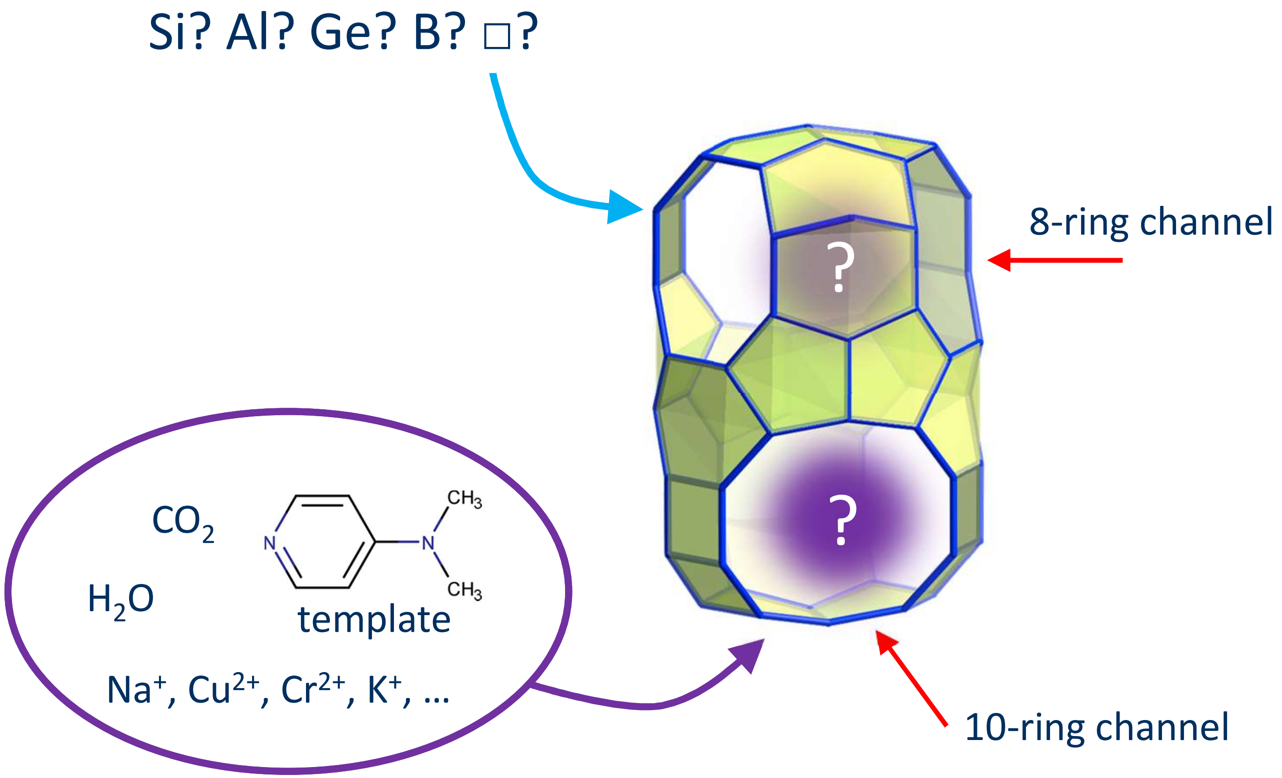
Zeolite SSZ-87

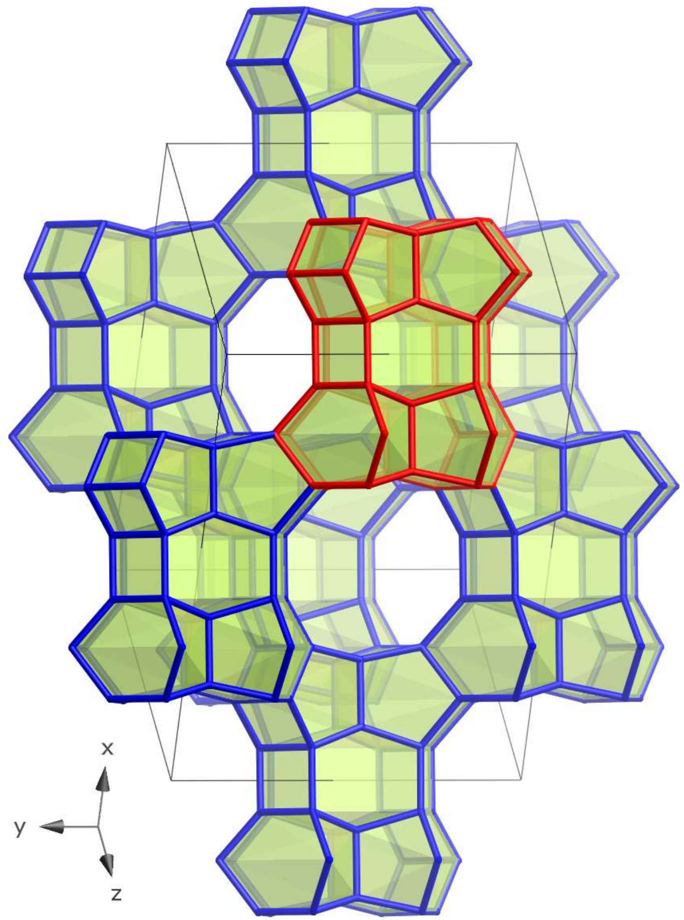
Framework structure solved using FOCUS



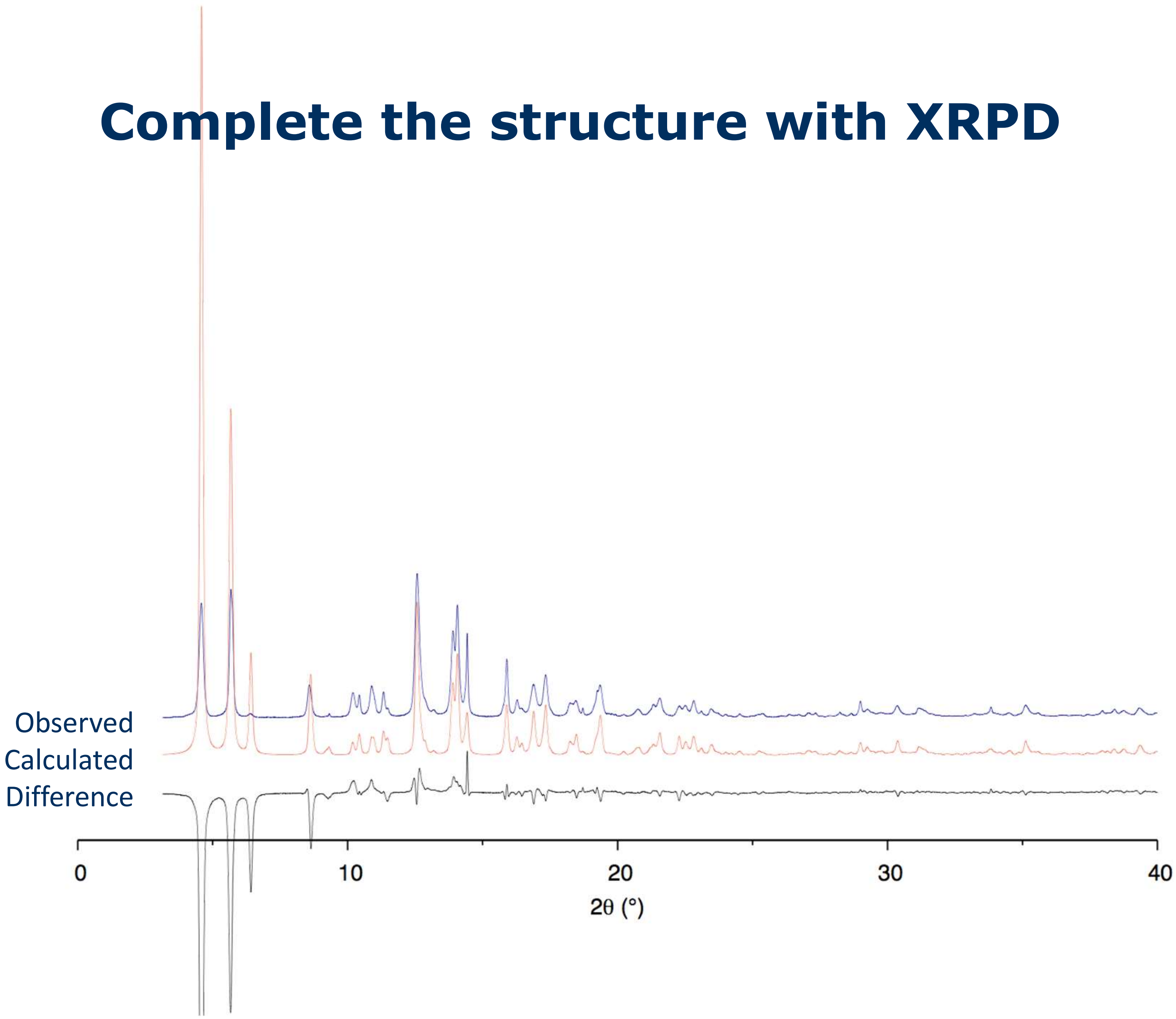
Smeets *et al.*, *J. Am. Chem. Soc.* (2015), 137:2015

Framework structure from RED

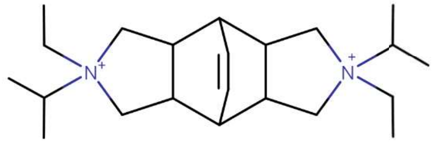


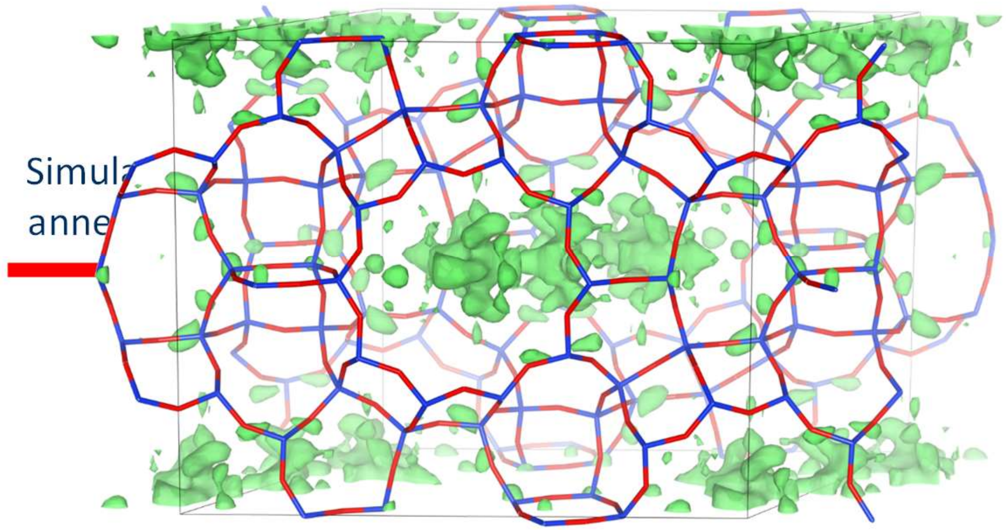


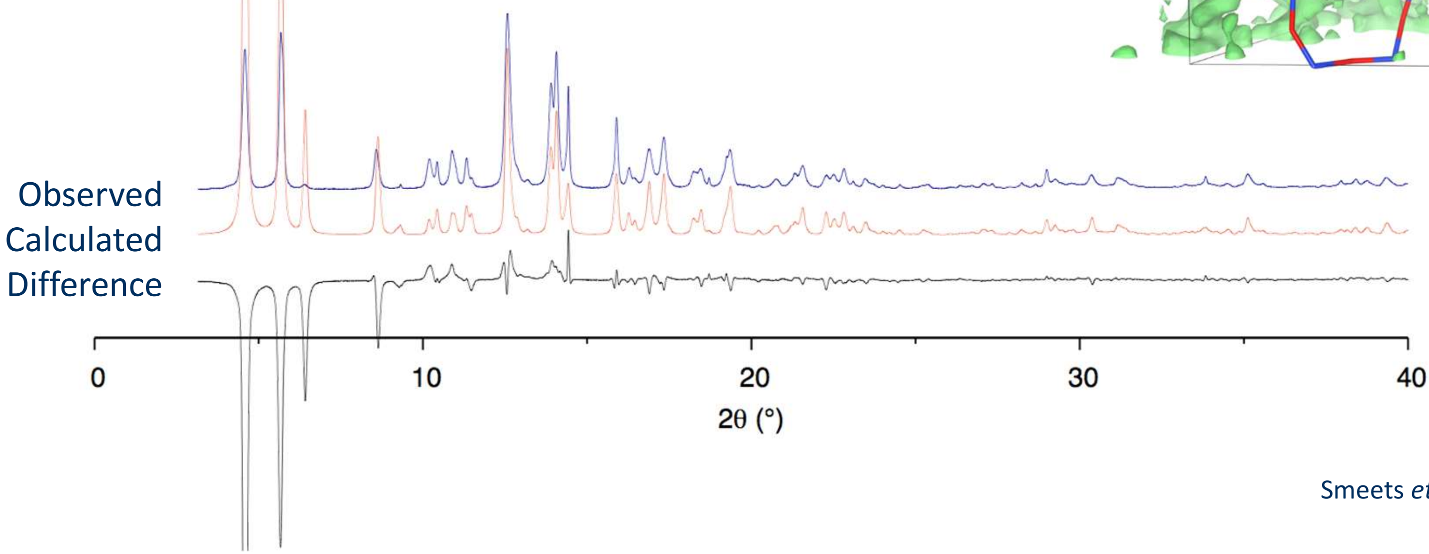
Complete the structure with XRPD



Complete the structure with XRPD

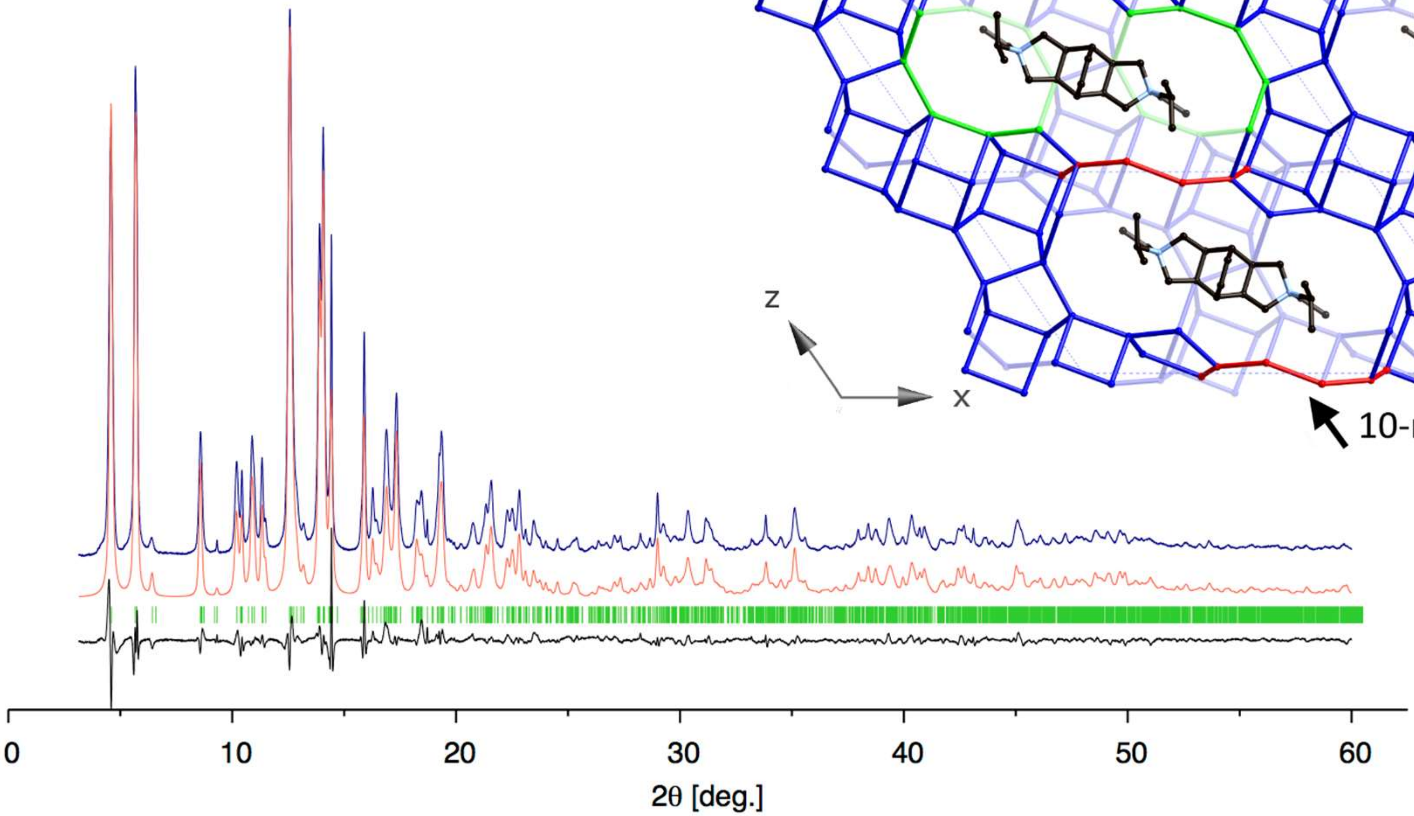


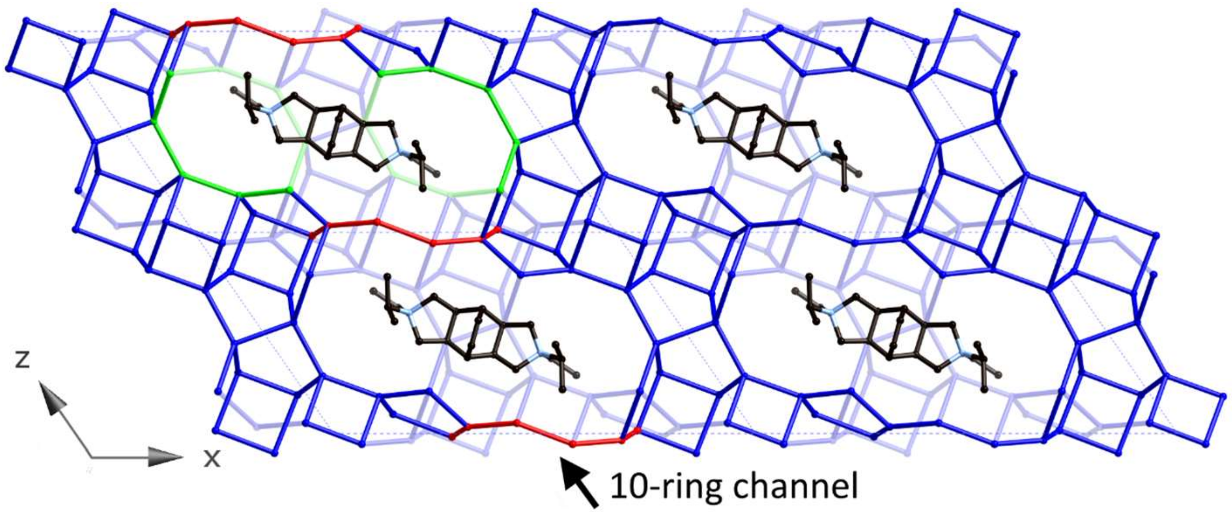




Smeets *et al.*, *J. Am. Chem. Soc.* (2015), 137:2015

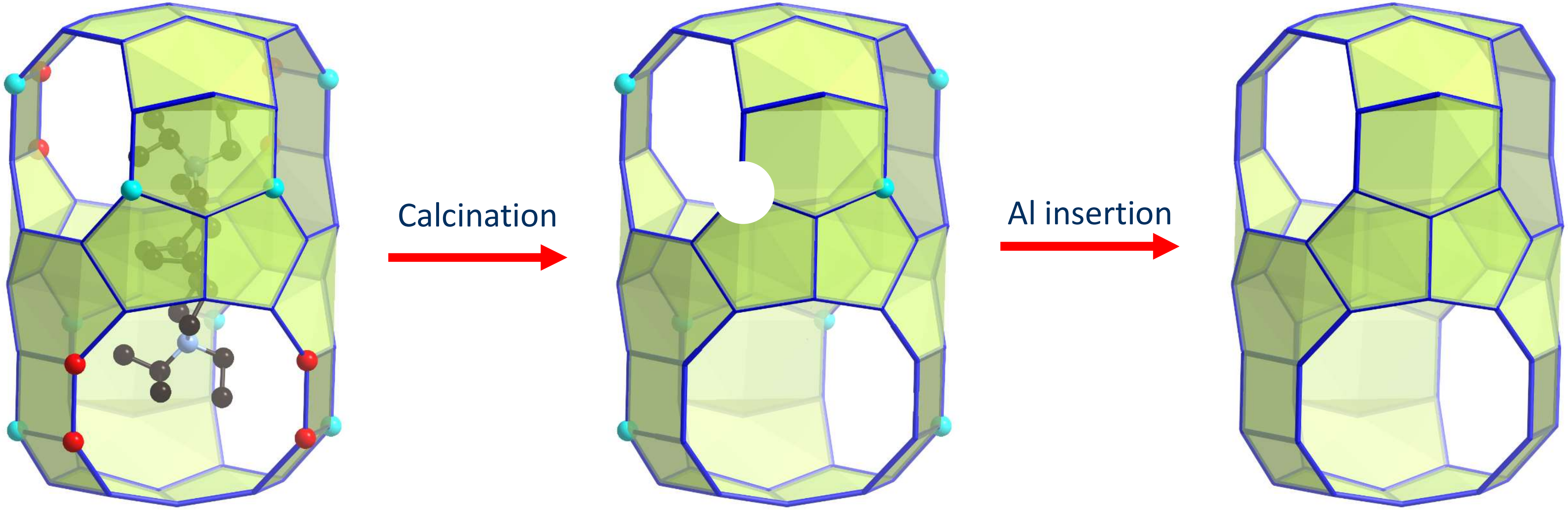
Complete the structure with XRPD





Smeets *et al.*, *J. Am. Chem. Soc.* (2015), 137:2015

Locate heteroatoms from XRPD



As-synthesized

- 0.8 Si, 0.2 B
- 0.7 Si, 0.3 B

Calcined

- 1.0 Si
- 0.5 Si, 0.3 B, 0.2 □

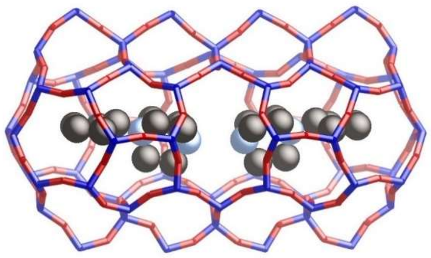
(+ ^{29}Si MAS-NMR)

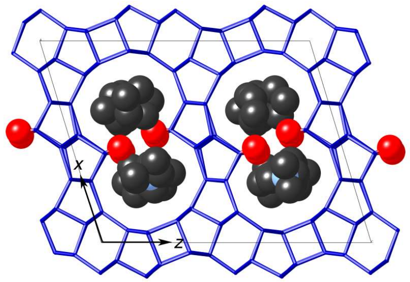
Aluminated

- 1.0 Al/Si
- 1.0 Al/Si

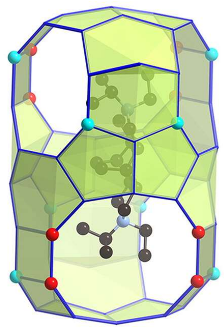
Smeets *et al.*, *J. Am. Chem. Soc.* (2015), 137:2015

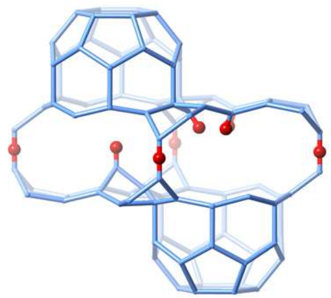
Structure determination using X-rays and electrons

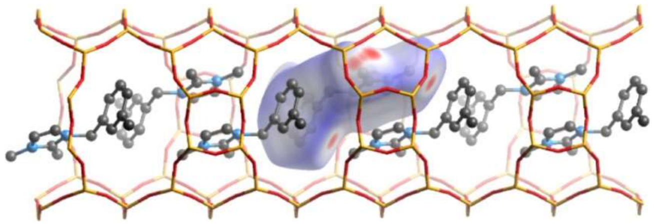

SSZ-45; S. Smeets *et al.*, *Chem. Mater.*, 2014

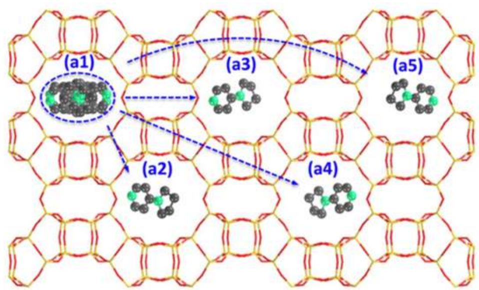


SSZ-61; S. Smeets *et al.*, *Angew. Chem.*, 2014

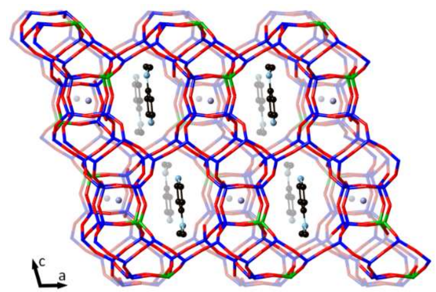

SSZ-87; S. Smeets *et al.*, *J. Am. Chem. Soc.*, 2015


SSZ-70; S. Smeets *et al.*, *J. Am. Chem. Soc.*, 2017


CIT-13; J.H. Kang *et al.*, *Chem. Mater.*, 2017



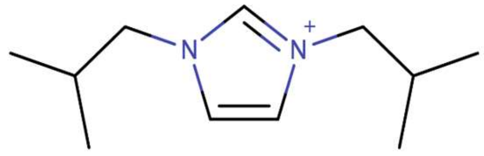
SCM-14; Y. Luo *et al.*, *Chem.-Eur. J.*, 2017



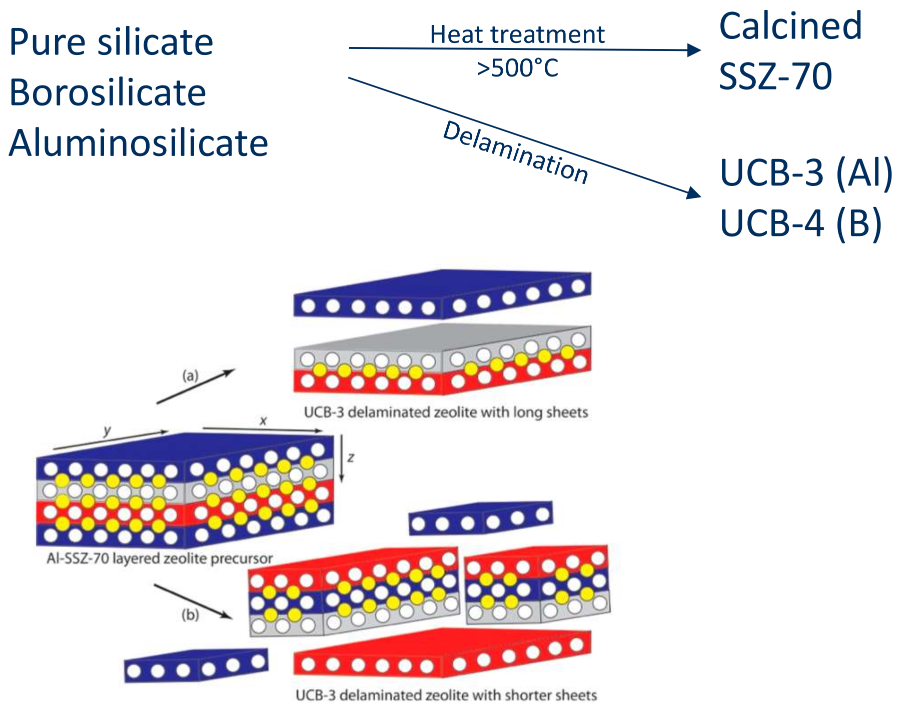
IM-18; M.O. Cichocka *et al.*, *Cryst. Growth Des.*, 2018

MS14-P01

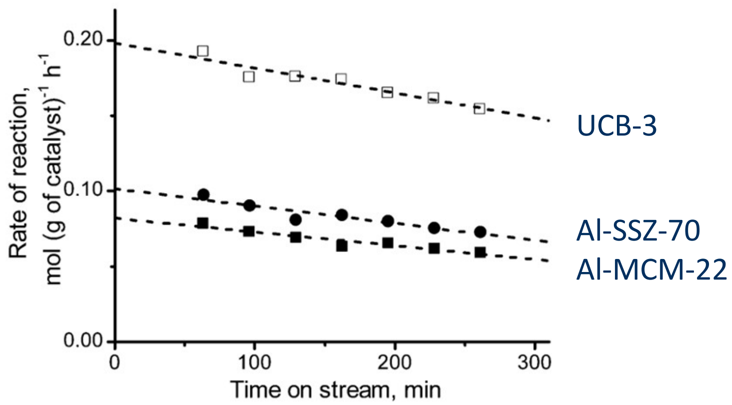
Zeolite SSZ-70



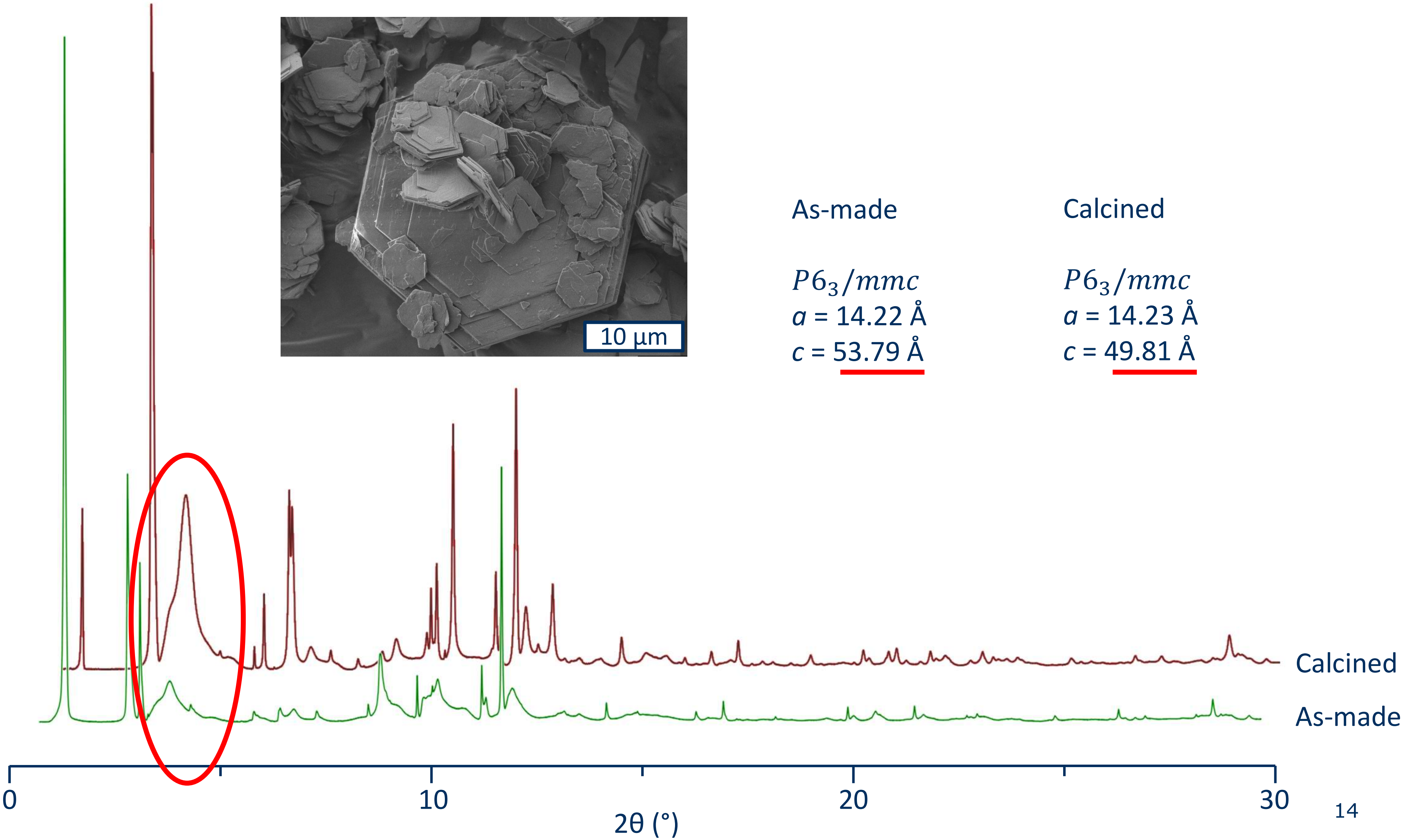
Stacey Zones and Alan Burton, US Patent 7,108,843 B2 (2006)
Molecular sieve SSZ-70 composition of matter and synthesis thereof



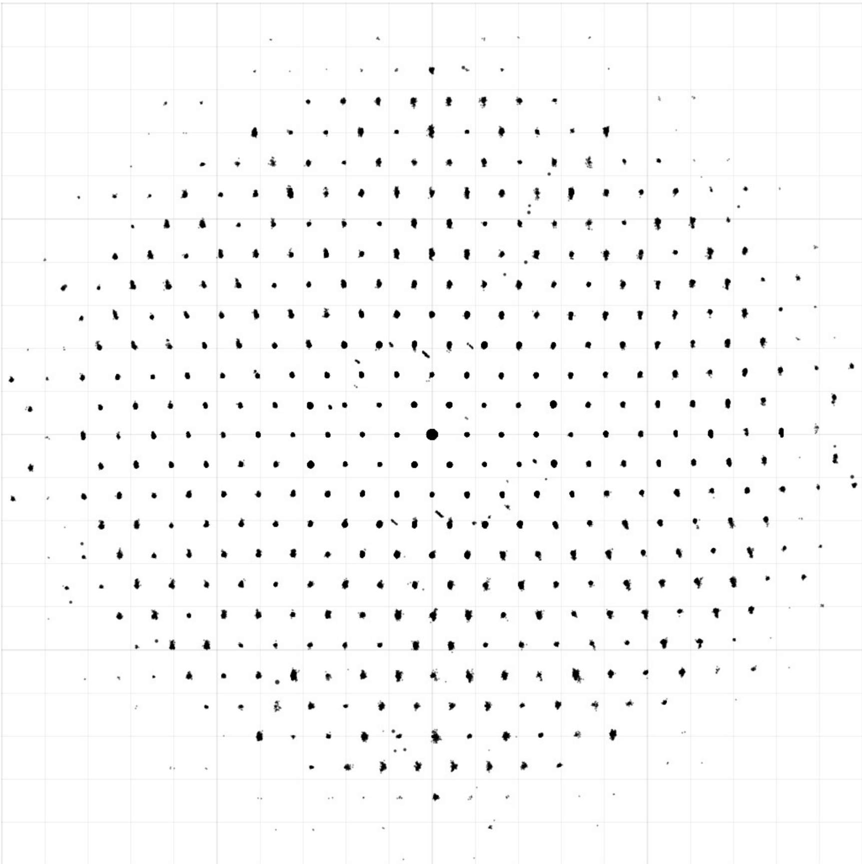
Catalysis: aromatic alkylation



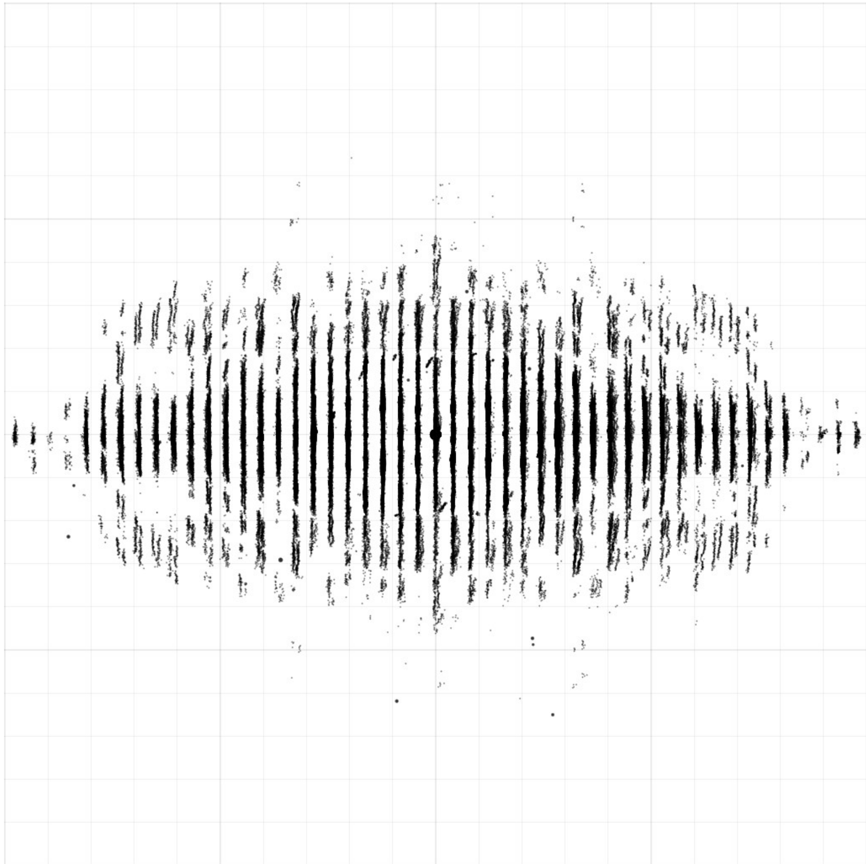
Runnebaum *et al.*, **2014**, *ACS Catal.*, 4, 2364


10 μm
As-made
$P6_3/mmc$
a = 14.22 Å
c = 53.79 Å
Calcined
$P6_3/mmc$
a = 14.23 Å
c = 49.81 Å
Calcined
As-made
0
10
20
30
2θ (°)

Rotation Electron diffraction (as-made)

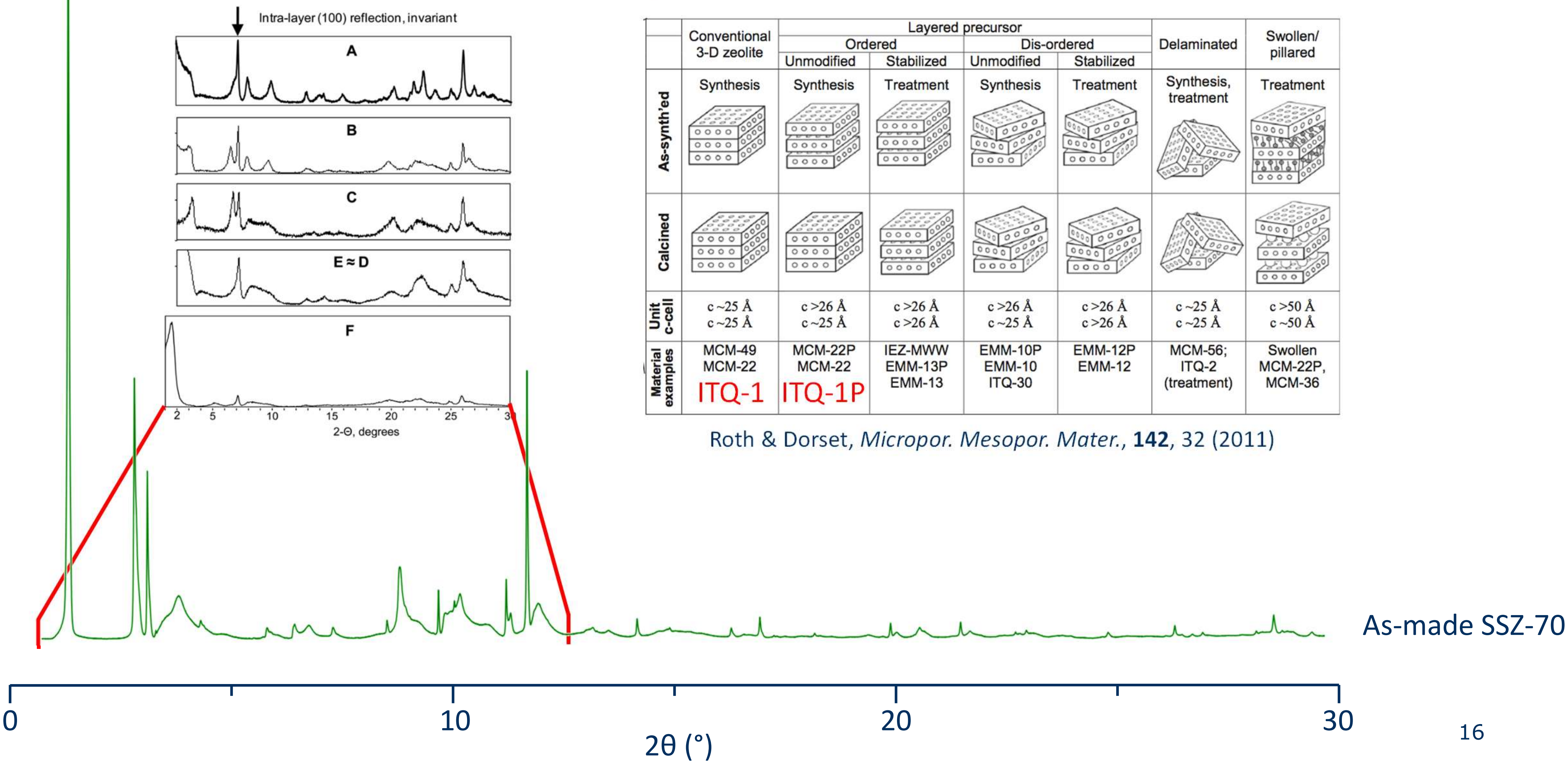


Along [001]



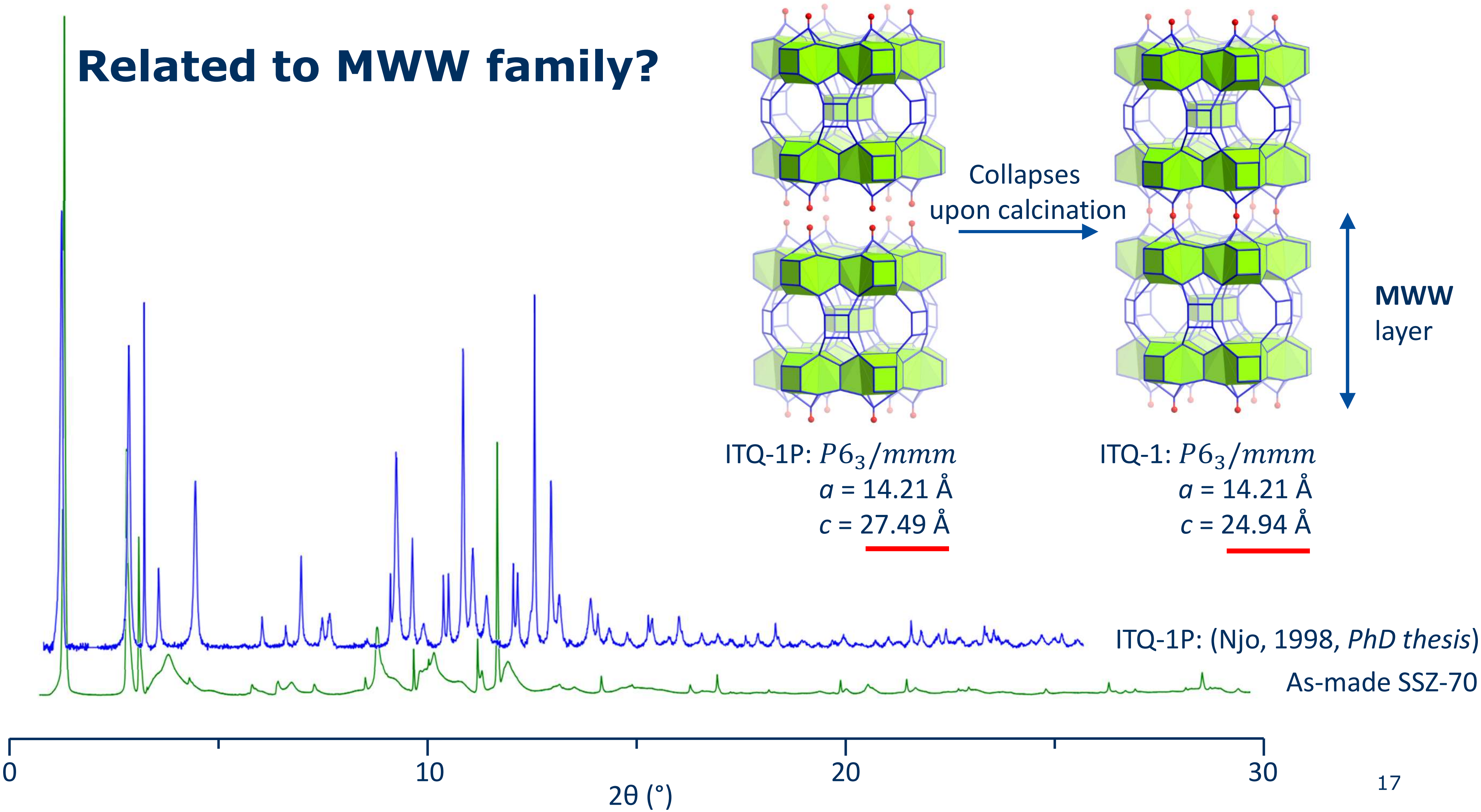
Along [100]

Related to MWW family?



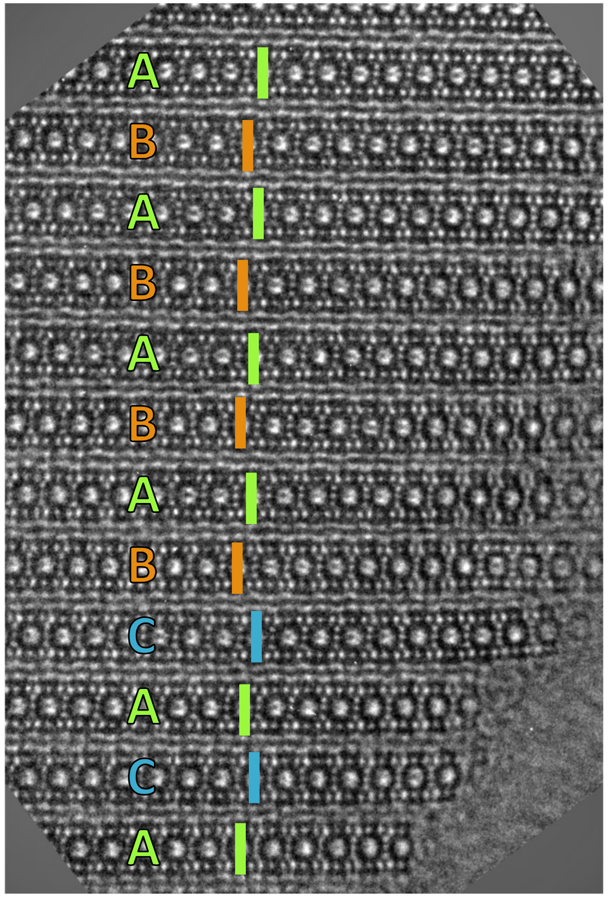
Roth & Dorset, *Micropor. Mesopor. Mater.*, **142**, 32 (2011)

Related to MWW family?



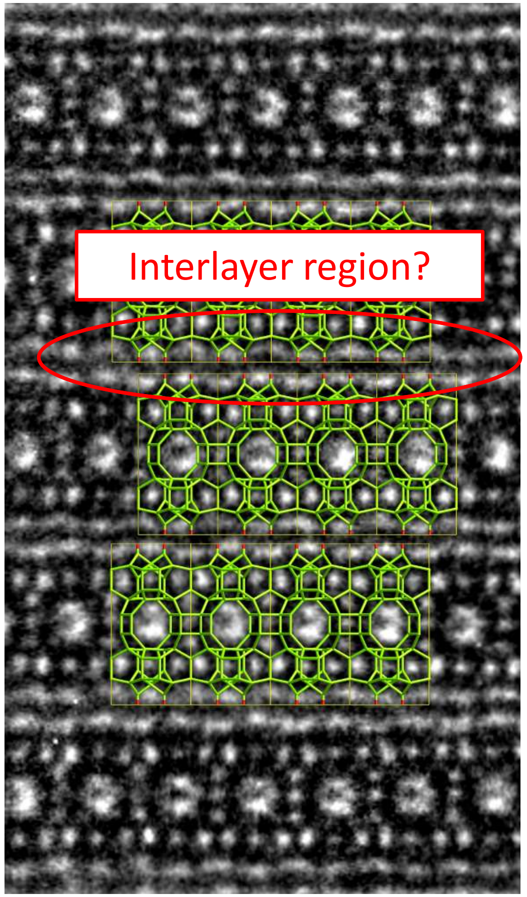
HRTEM (as-made)

Stacking disorder along [001]

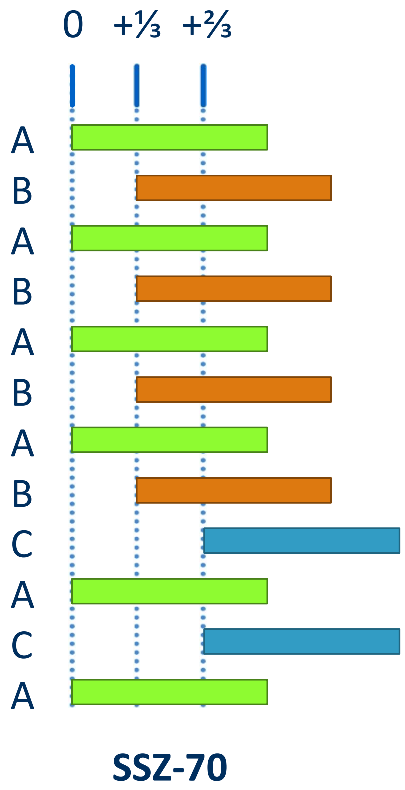


Collected by Wei Wan, Stockholm University, SE

MWW-layers



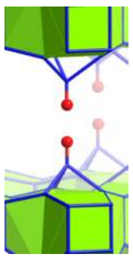
Stacking faults



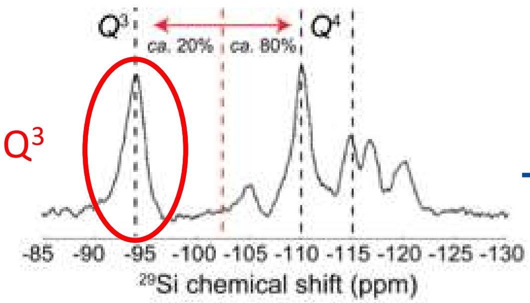
Solid-state ^{29}Si MAS NMR

As-made

Calcined

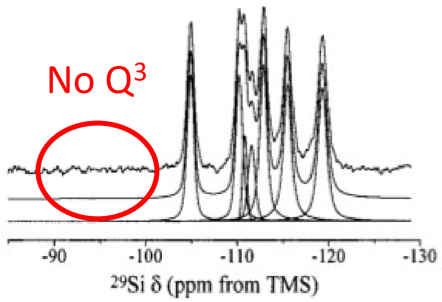


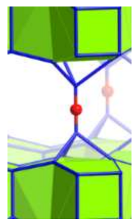
20% Q^3



ITQ-1

No Q^3

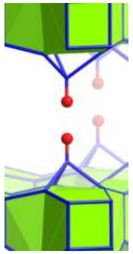




Hsieh, Aronson and Chmelka (2014)

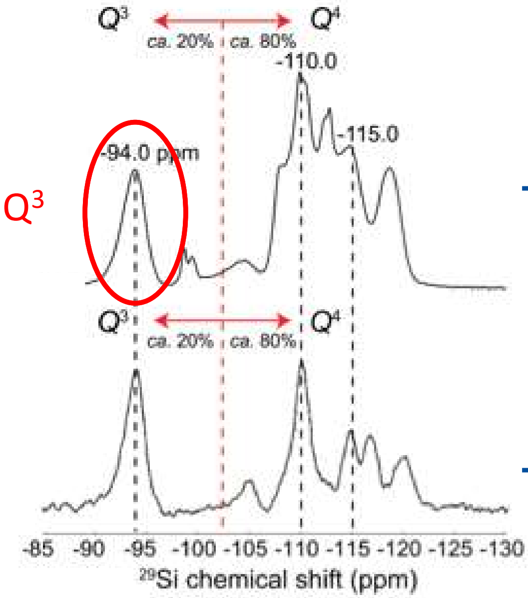
Archer *et al.*, **2010,** *Micropor. Mesopor. Mat.*, 130, 255
Camblor *et al.*, **1998**, *J. Phys. Chem. B*, 102, 44

Solid-state ^{29}Si MAS NMR



As-made

20% Q^3

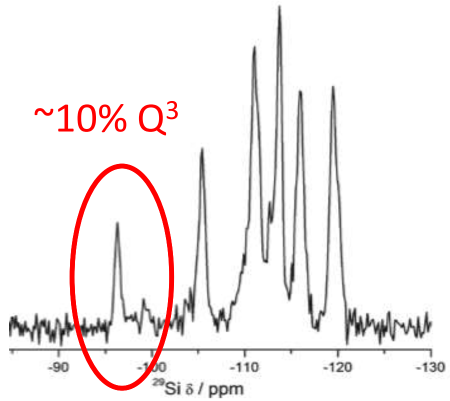


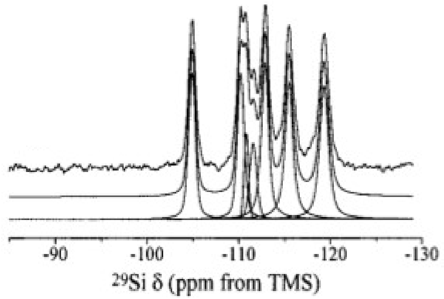
SSZ-70 →

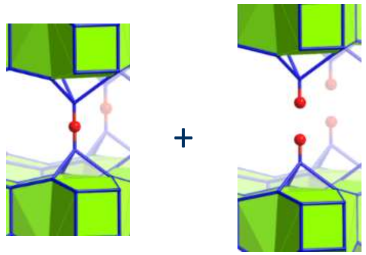
ITQ-1 →

Calcined

~10% Q^3



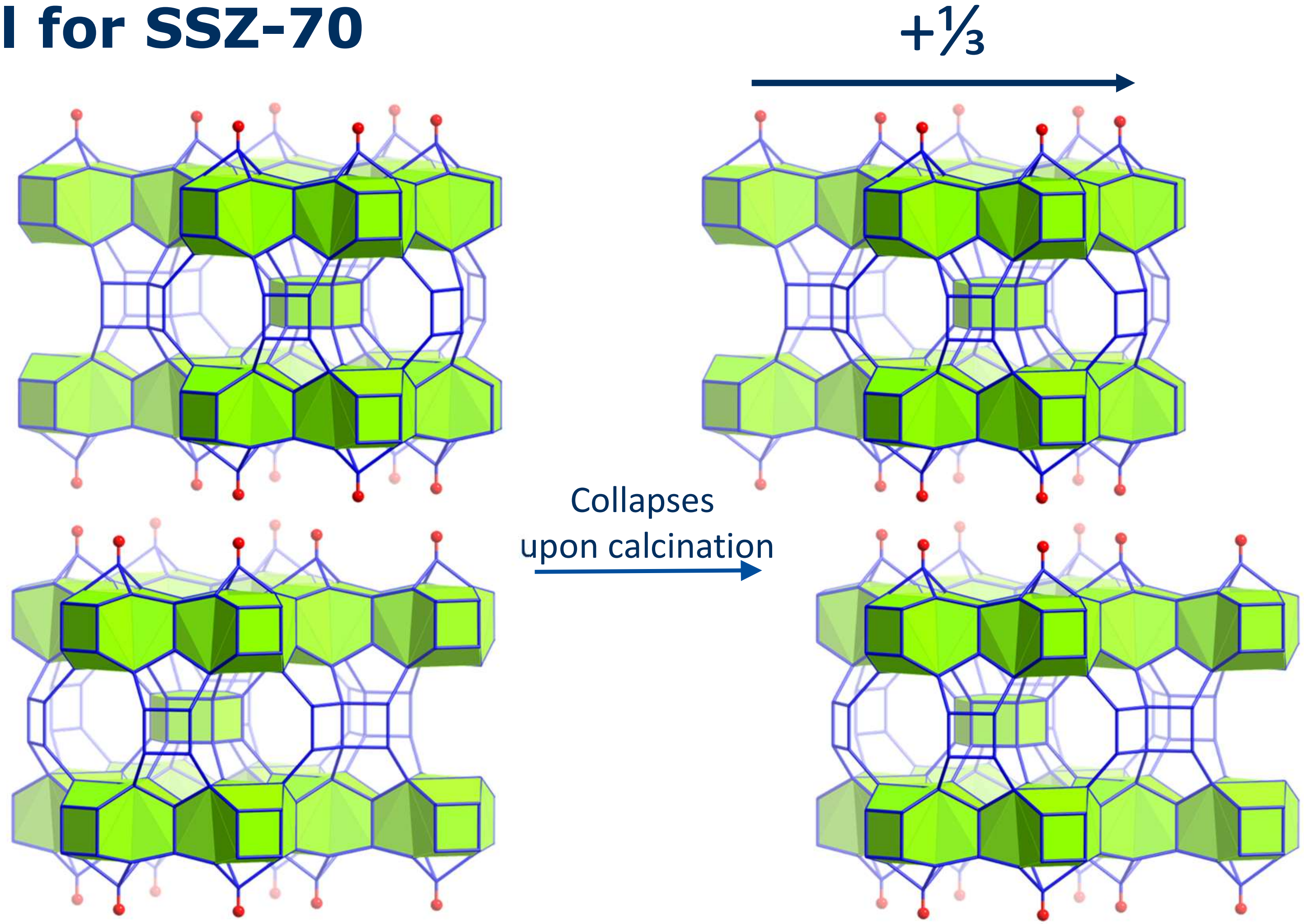




Hsieh, Aronson and Chmelka (2014)

Archer *et al.*, **2010**, *Micropor. Mesopor. Mat.*, 130, 255
Camblor *et al.*, **1998**, *J. Phys. Chem. B*, 102, 44

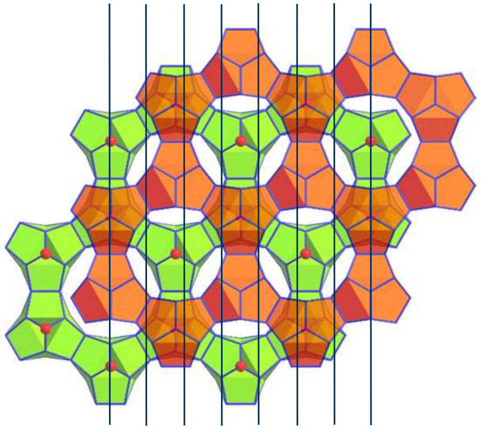
Model for SSZ-70



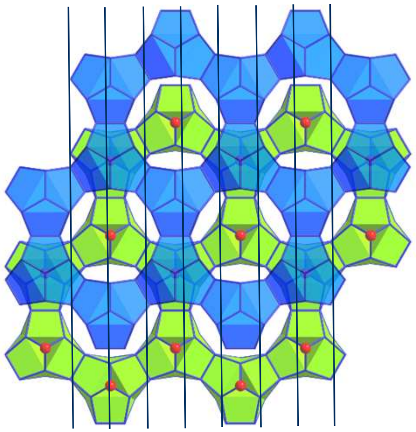
As-made SSZ-70

Calcined SSZ-70

Disorder model

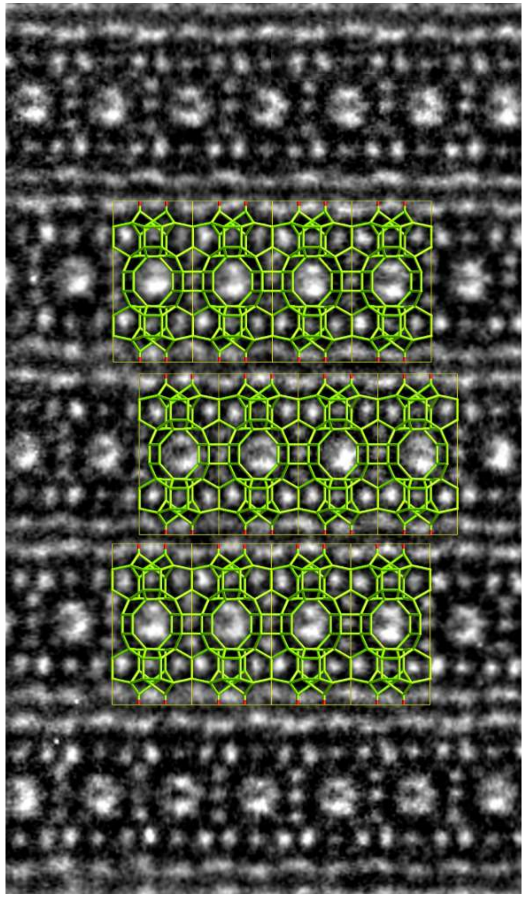


x+⅔, *y*+⅓



x+⅓, *y*+⅔

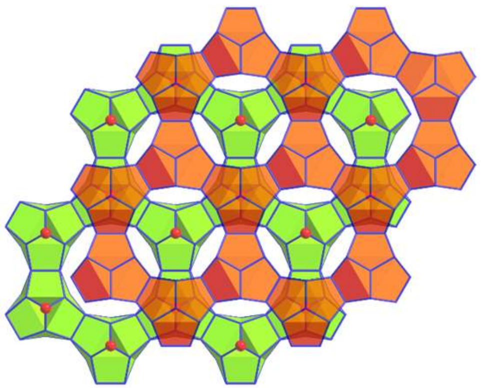
MWW-layers



Disorder model

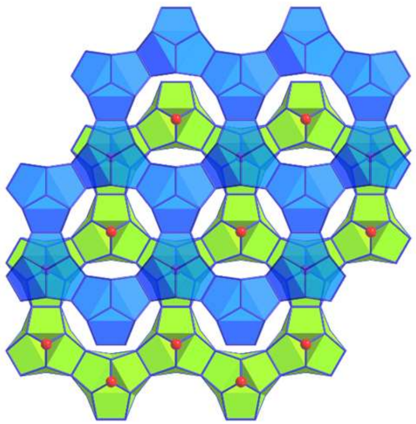
*Random arrangement of **MWW** layers*

$P(A \rightarrow A) = 0\%$
$P(A \rightarrow B) = 50\%$
$P(A \rightarrow C) = 50\%$



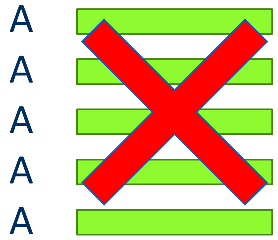
$x+\frac{2}{3},\ y+\frac{1}{3}$

$P(A \rightarrow B) = 50\%$

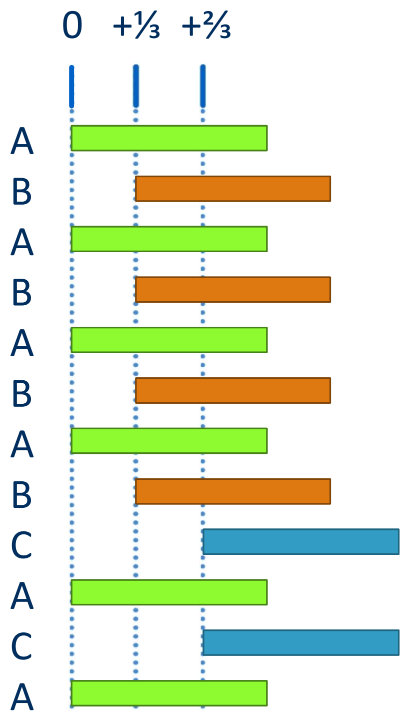


$x+\frac{1}{3},\ y+\frac{2}{3}$

$P(A \rightarrow C) = 50\%$

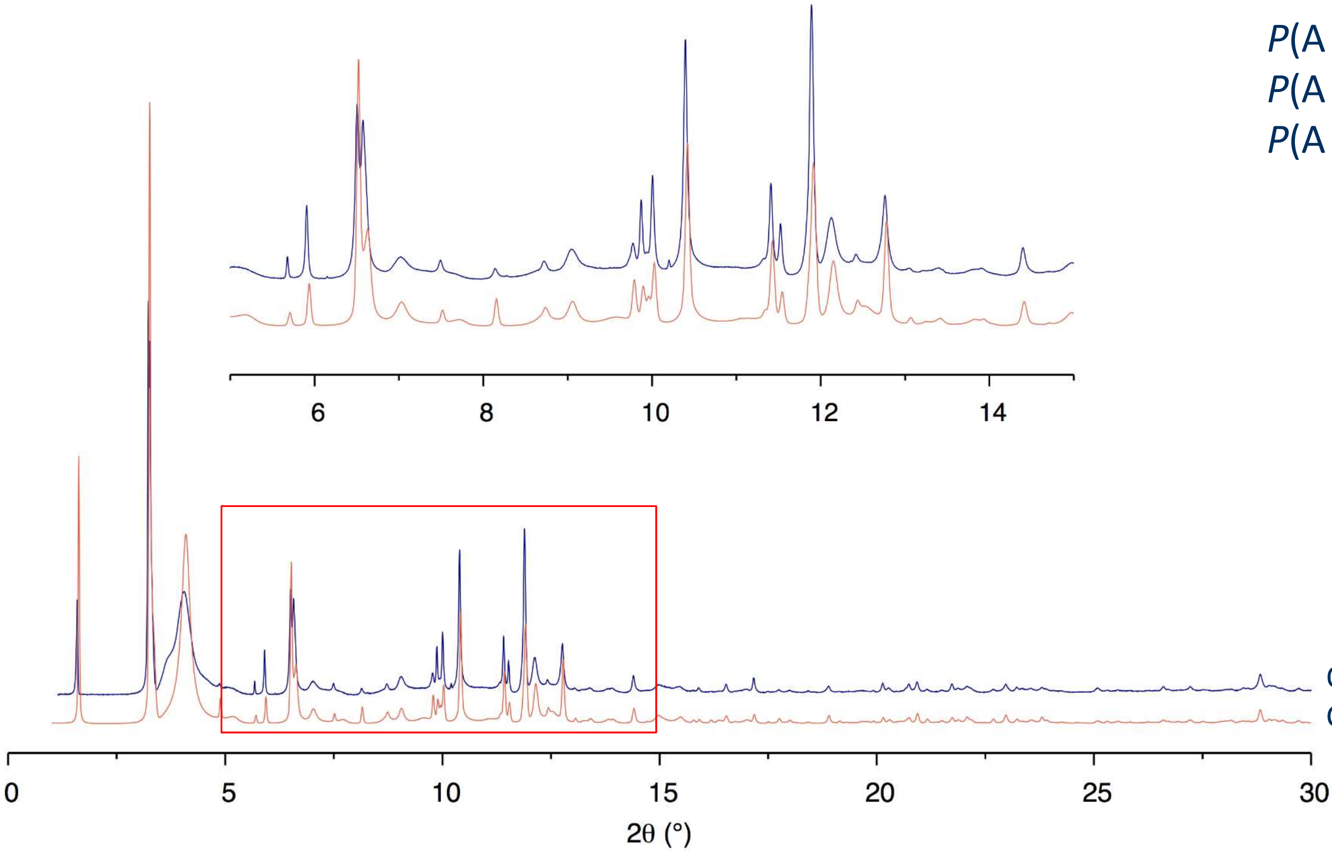


ITQ-1



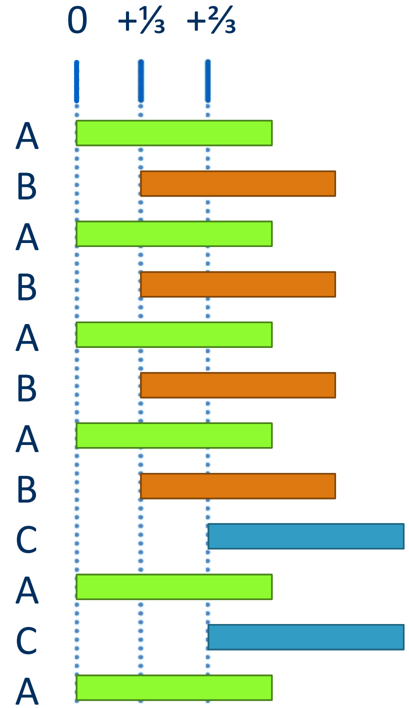
SSZ-70

Simulations using DiFFaX



Random arrangement of ***MWW*** *layers*

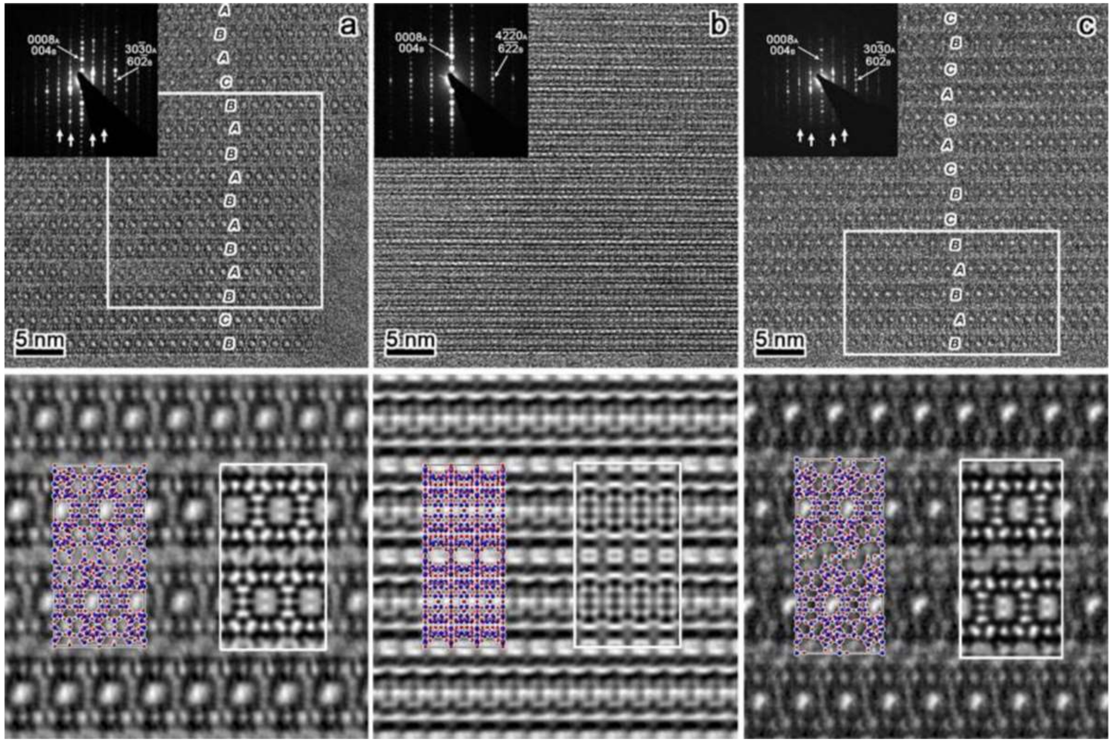
P(A → A) = 0%
P(A → B) = 50%
P(A → C) = 50%

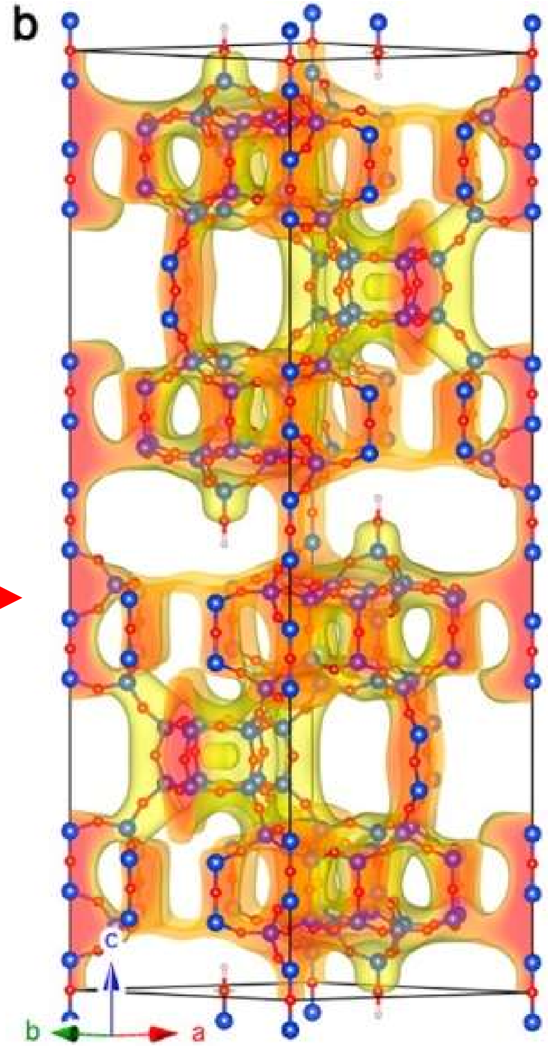


SSZ-70

DiFFaX: Traecy *et al.*, **1991**, *Proc. R. Soc. Lond. A*, 433, 499

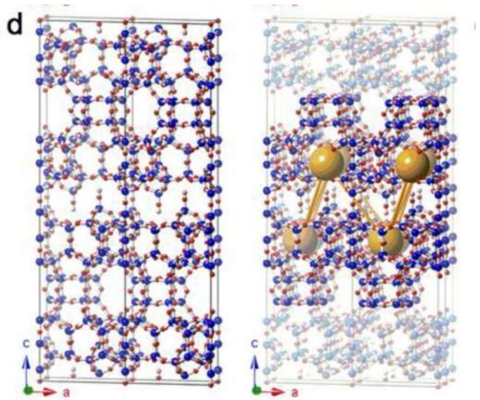
A different approach (ECNU-5)



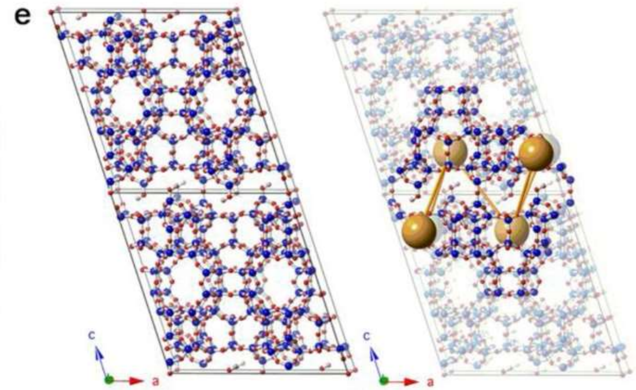


Xu *et al.*, **2015**, *Chem. Mater.*, 27, 23, 7852-7860

A different approach (ECNU-5)

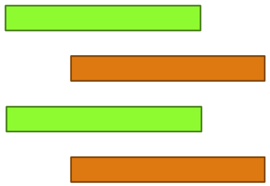


Polymorph A: $C2/m$

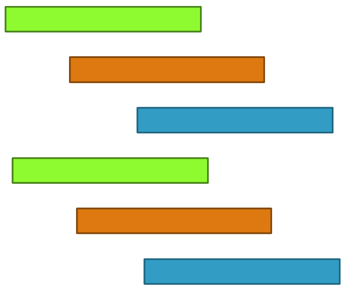


Polymorph B: $P6_3/mmc$

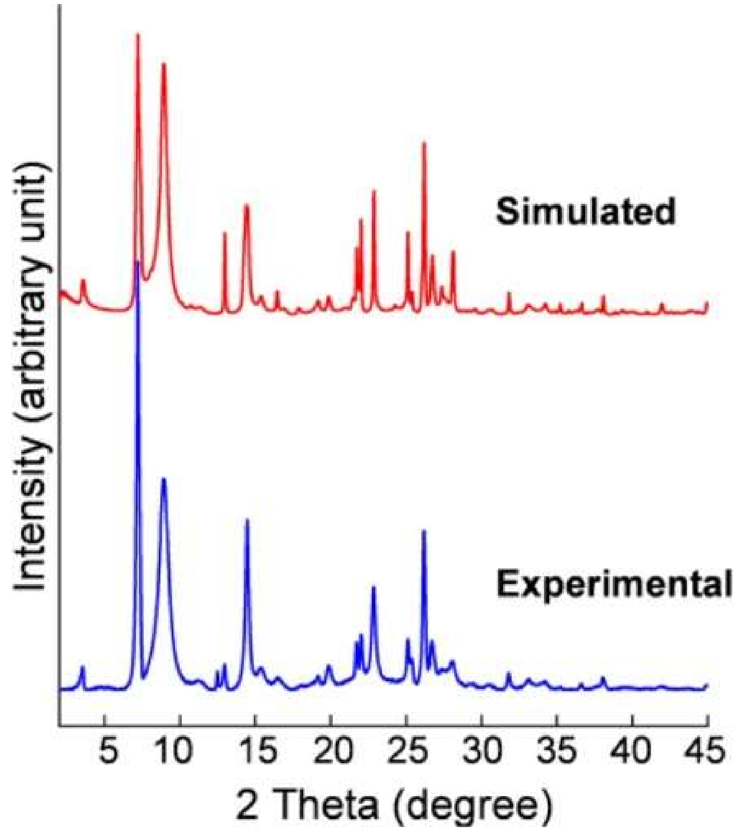
ABAB



ABCABC

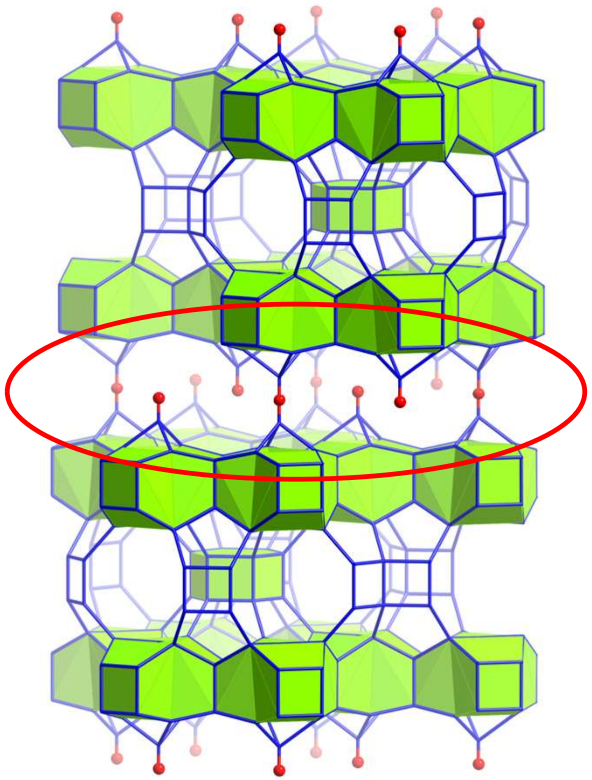


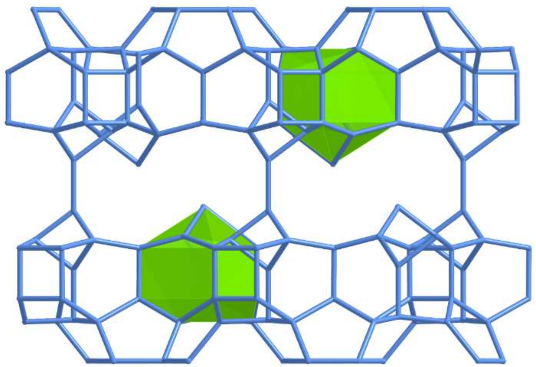
DiFFaX Simulations

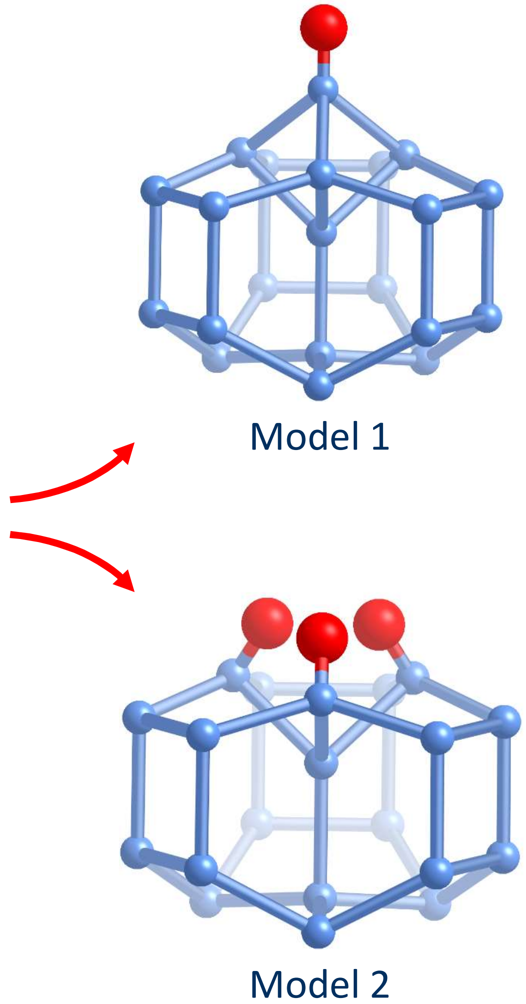


Xu *et al.*, **2015**, *Chem. Mater.*, 27, 23, 7852-7860

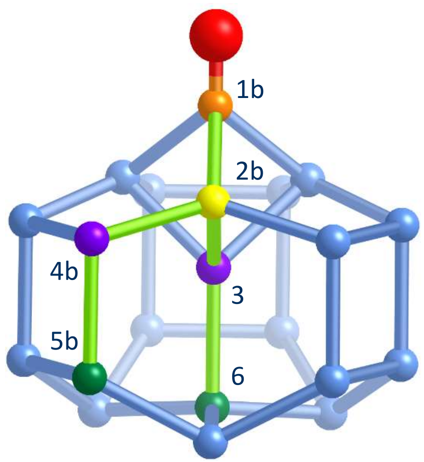
Interlayer region



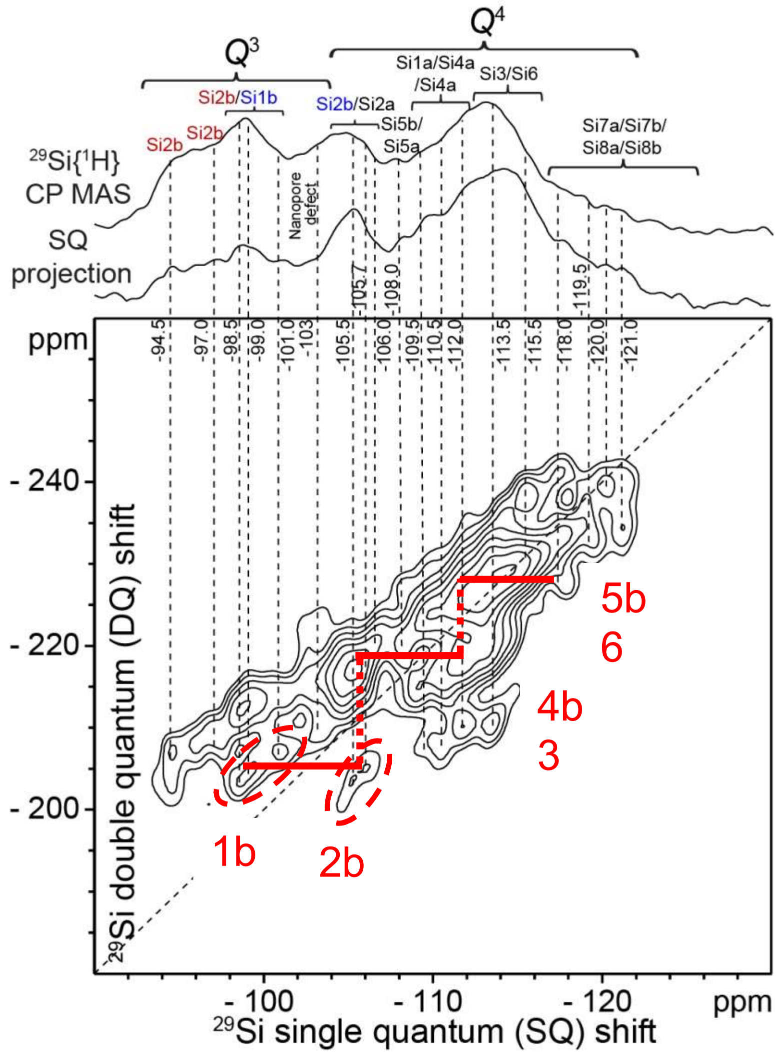




2D DNP-enhanced
J-mediated $^{29}Si\{^{29}Si\}$ NMR



Model 1



2D DNP-enhanced
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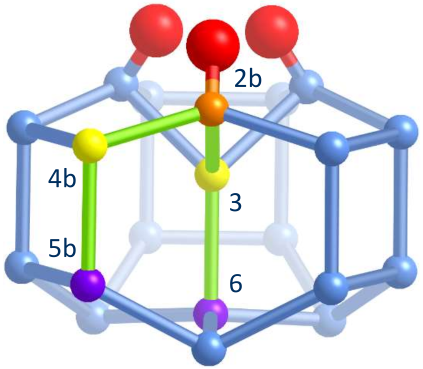
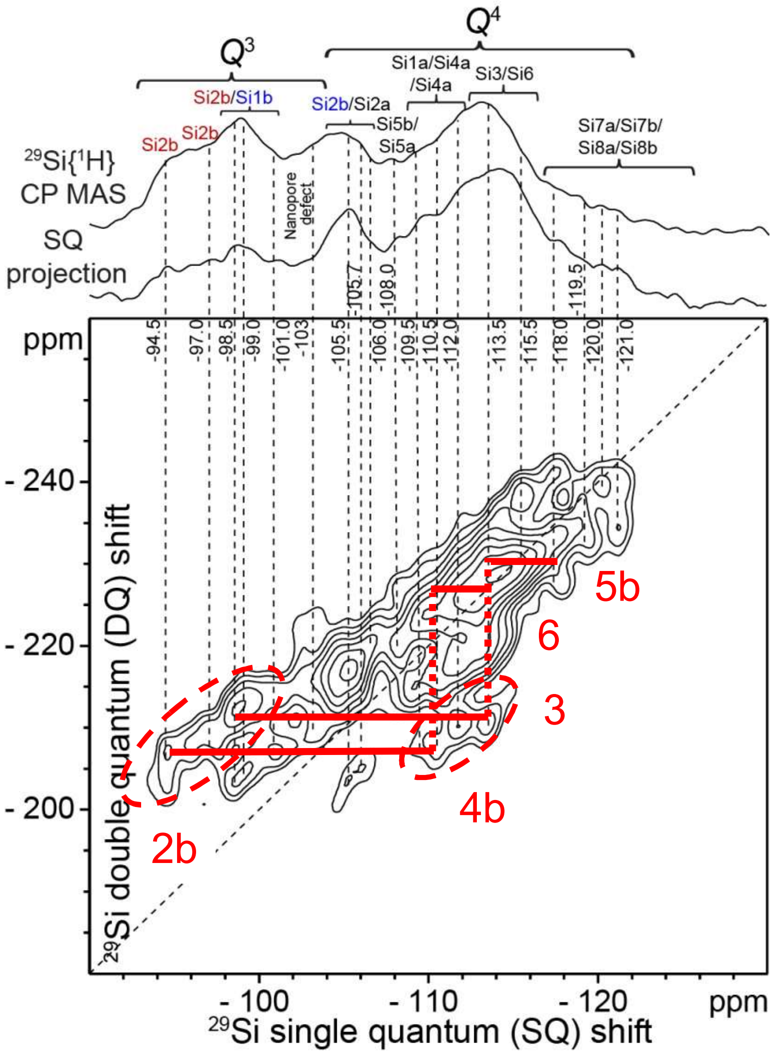
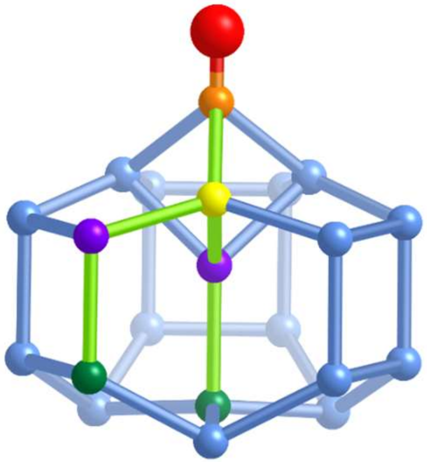


Model 2

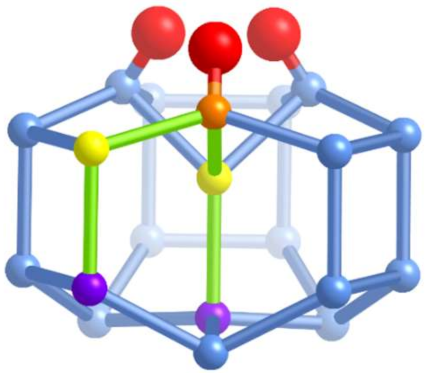


Interlayer region



Model 1

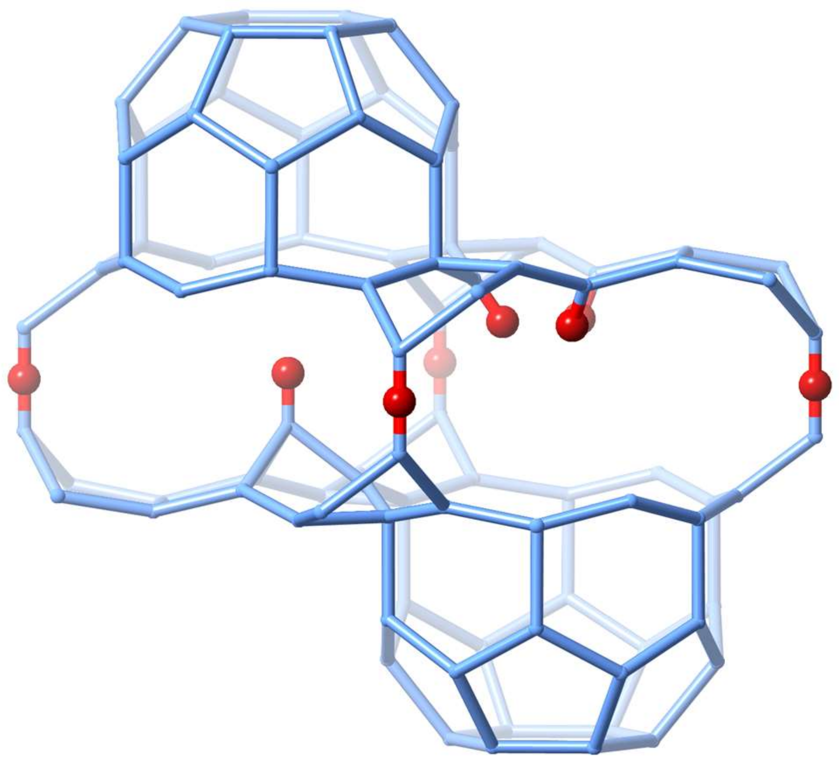
50%



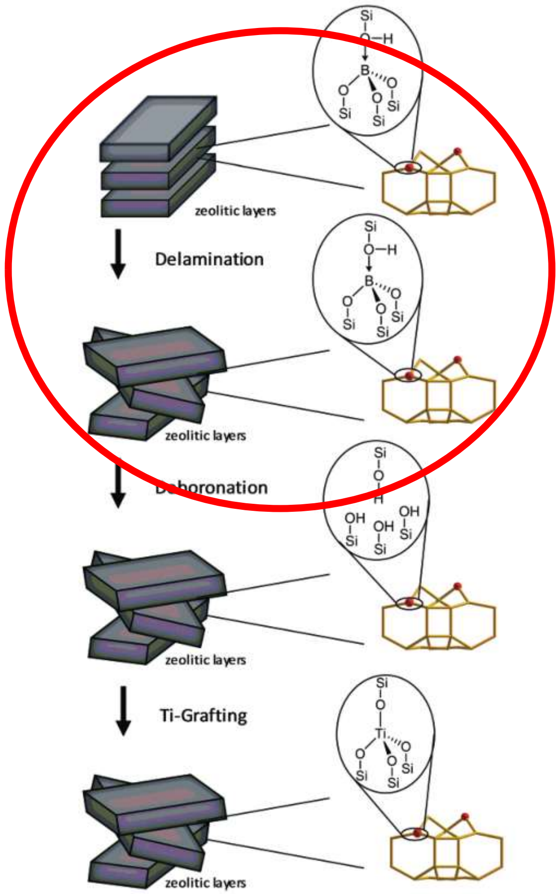
Model 2

50%

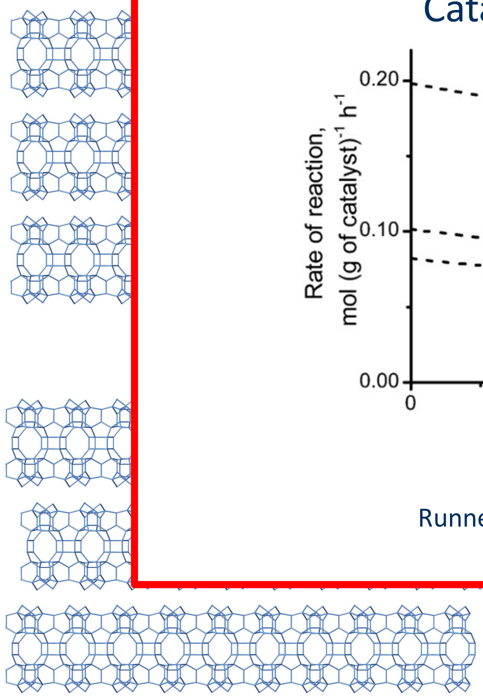
Structure of calcined SSZ-70



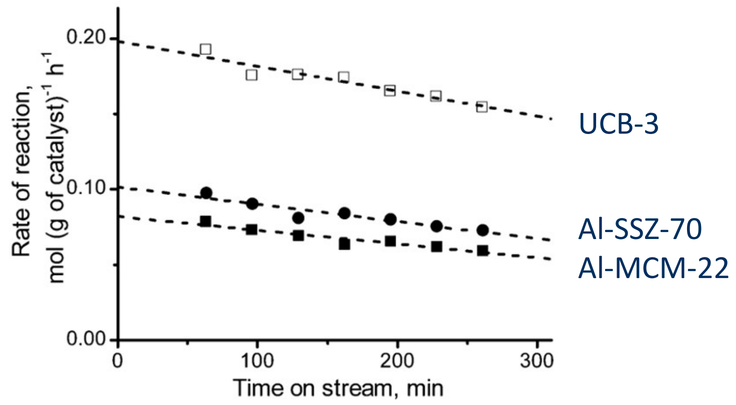
New understanding of a successful catalytic material



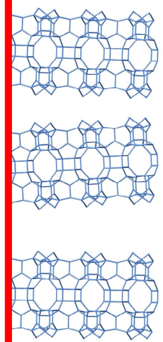
Ouyang, *et al. Dalton Trans*. 2014, 43, 10417
Aigner, *et al.*, *React. Chem. Eng*. 2017, 2, 852
Aigner, *et al.*, *React. Chem. Eng.*, 2017, 2, 842



Catalysis: aromatic alkylation



Runnebaum *et al.*, **2014**, *ACS Catal.*, 4, 2364



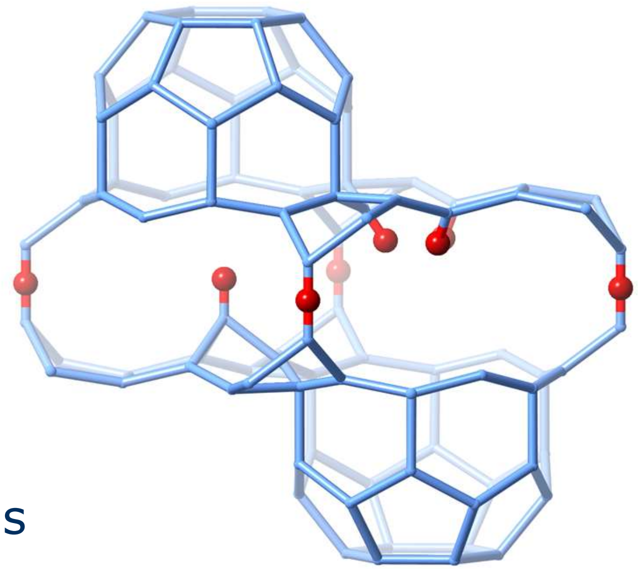
SSZ-70 (as-synthesized)

Weaker linkages in SSZ-70

- Easier to delaminate using mild conditions
- Intrinsic structure remains intact
- High degree of surface area

Conclusions

- Structure of SSZ-70 determined by combining methods
  - HRTEM → Short-range order
  - XRPD → Long-range order
  - 2D NMR → Nanostructure



- New stacking arrangement of **MWW**-layers
- Weaker linkages can help explain enhanced catalytic behaviour of SSZ-70 and derived materials
- Smeets *et al.*, *J. Am. Chem. Soc.* (2017), 139:16803