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CENTRE OF ADVANCED MATERIALS

27.11.2020

METODY ELEKTRONOVÉ MIKROSKOPIE PRO CHARAKTERIZACI ZEOLITOVÝCH KATALYZÁTORŮ

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CUCAM project

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EUROPEAN UNION
European Structural and Investment Funds
Operational Programme Research,
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MLÁDEŽE A TĚLOVÝCHOVY

Přehled

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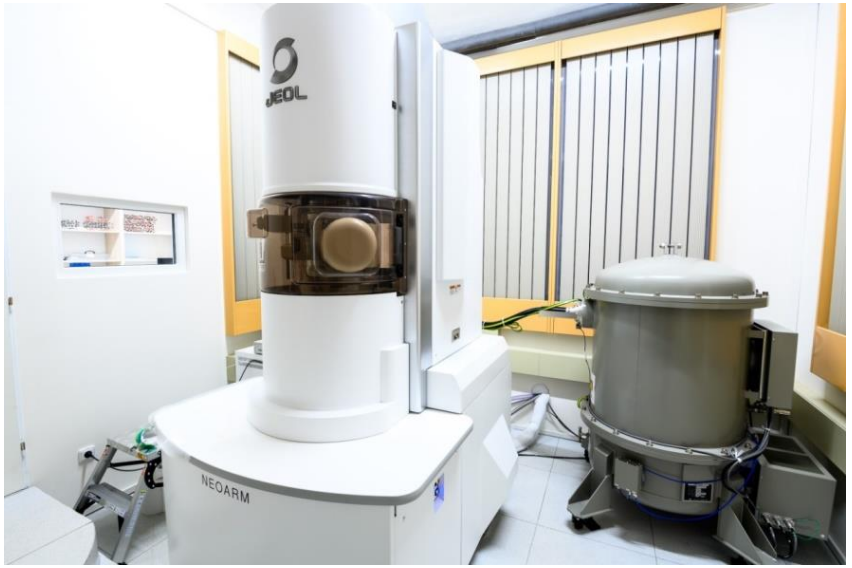
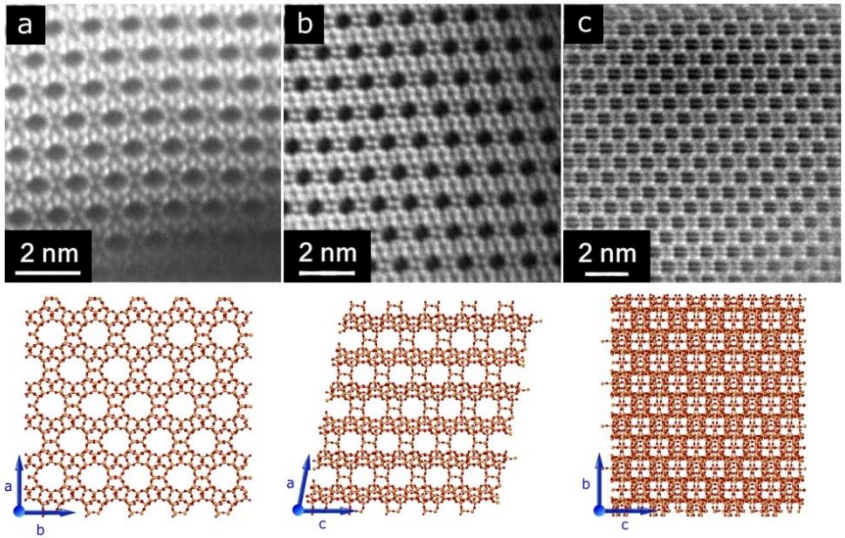
Elektronová mikroskopie

Zeolitové katalyzátory



Metody EM a související

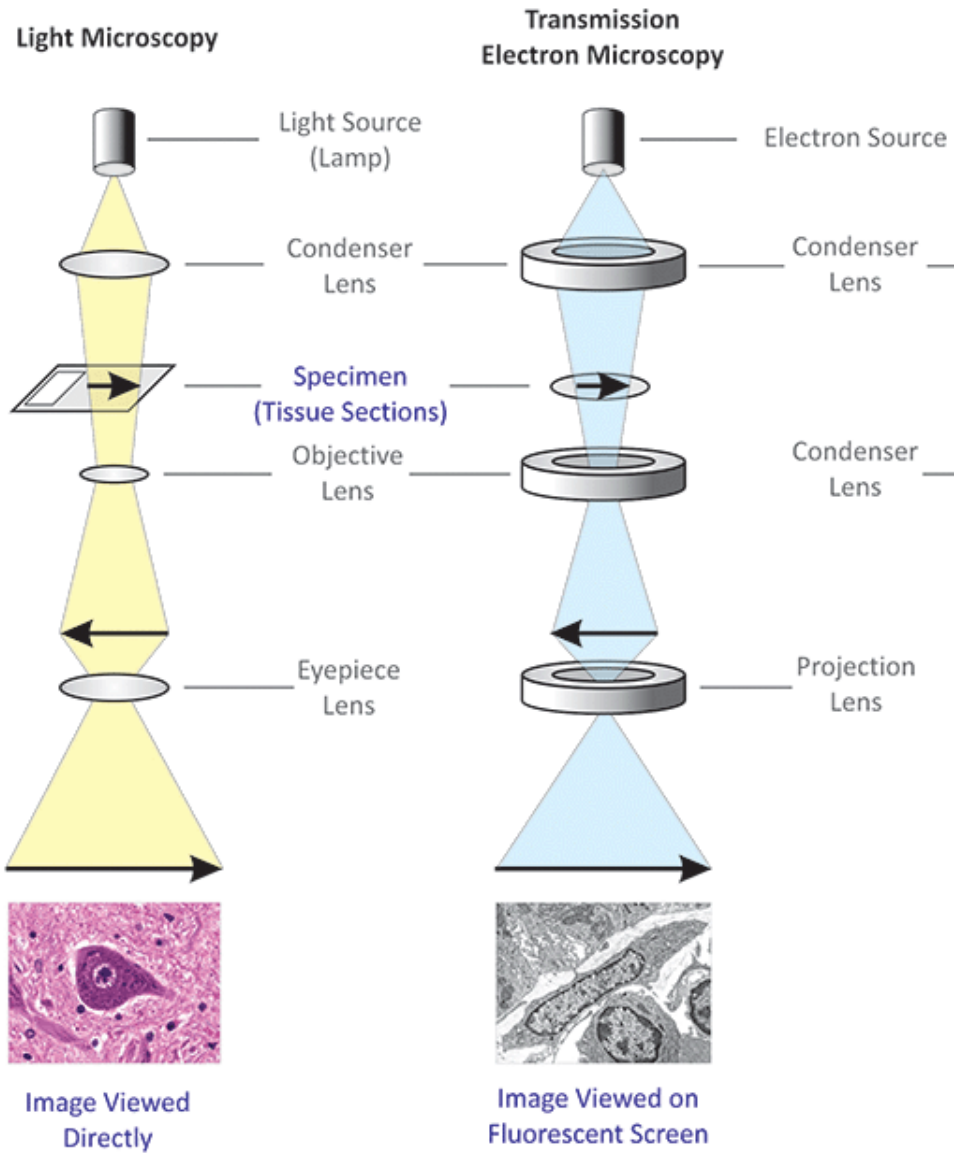


Syntéza zeolitu - ADOR

Elektronová difrakce

Vyhlídka

Electron microscopy



Resolution limits:

LM: 100 nm (10^{-7} m)

TEM: < 50 pm (5×10^{-11} m)

Increase by 4 orders of magnitude!

Key steps in EM

1924: French physicist **Louis de Broglie** (1892–1987) realizes that electron beams have a wavelike nature similar to light. Five years later, he wins the Nobel Prize in Physics for this work.

1931: German scientists **Max Knoll** (1897–1969) and his pupil **Ernst Ruska** (1906–1988) build the first experimental TEM in Berlin.

1933: **Ernst Ruska** builds first electron microscope that is more powerful than an optical microscope.

1941: **Manfred Von Ardenne** and **Bodo von Borries** patent - electron scanning microscope (SEM).

1981: **Binnig and Rohrer -** detailed images of atoms on the surface of a crystal of gold.

1986: **Binnig and Rohrer** share the Nobel Prize in Physics with the original pioneer of electron microscopes, **Ernst Ruska**.

https://www.explainthatstuff.com/electronmicroscopes.html

2017: Dubochet, Frank, Henderson share the Nobel Prize in Chemistry for development of **Cryo-Electron Microscopy**

Jak zeolity vypadají a co jsou?

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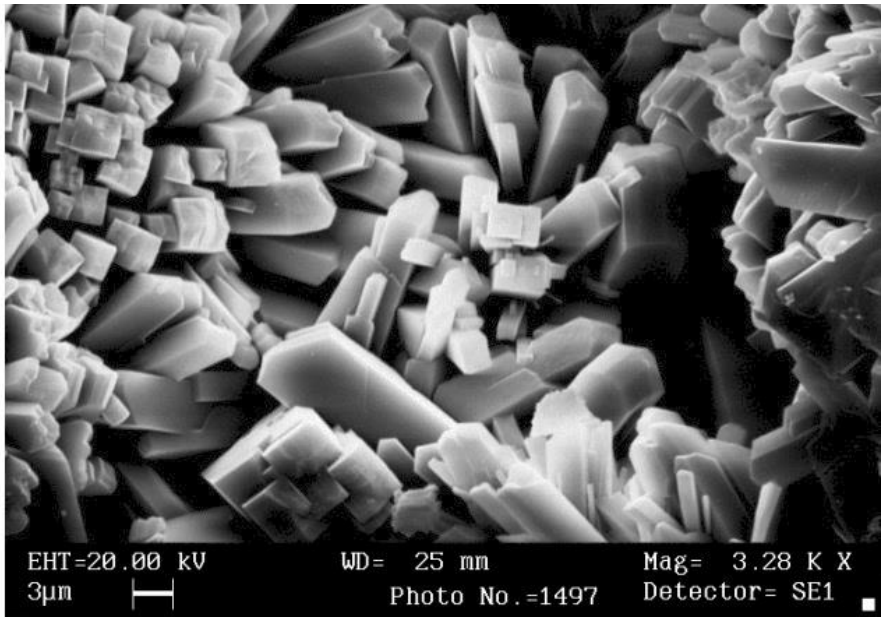
Zeolit

(řecky: zein – „vařit“ a líthos – „kámen“)

- **Mikroporézní krystalické hlinitokřemičitany složené z TO_4 tetraedrů propojených přes své vrcholy, kde T = Si, Al** (Ti, B, Ga, Ge, Fe …)
- Řada se jich nachází v přírodě (scolelit, mordenit, stilbit, phillipsit…)
- 248 struktur (IZA) – různá chemická složení mřížky – různé zastoupení kationtů…



Credit: Dr Jan Přech

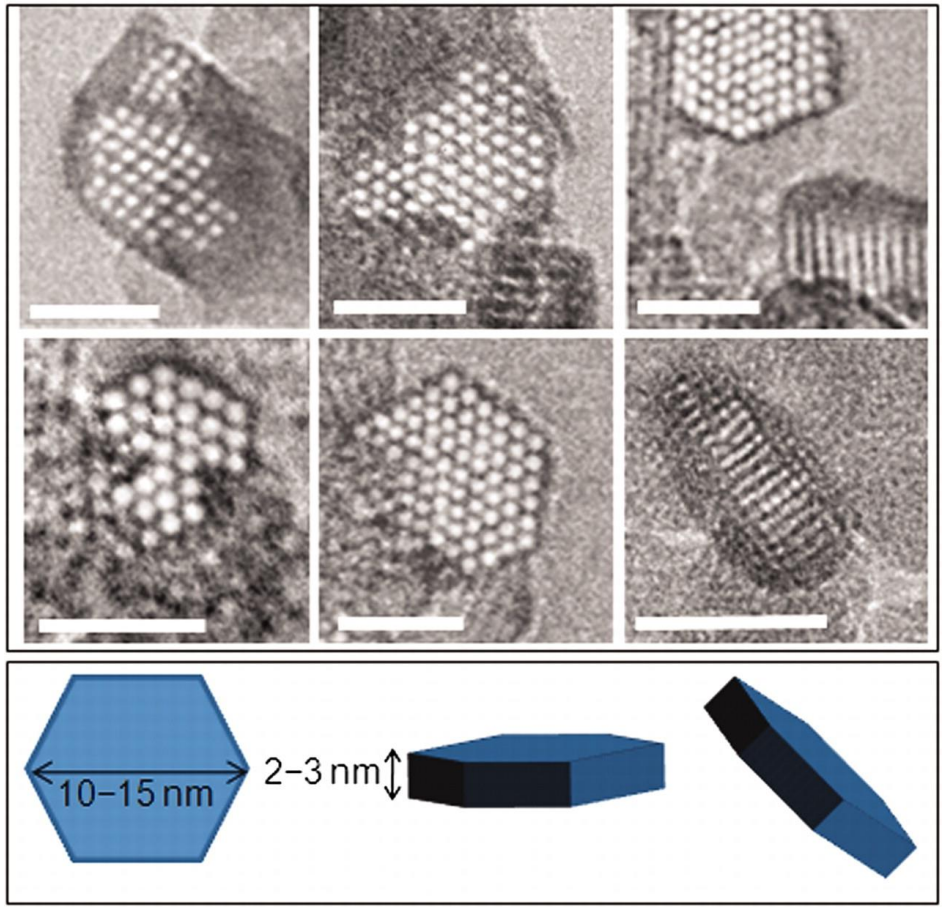
Zeolites

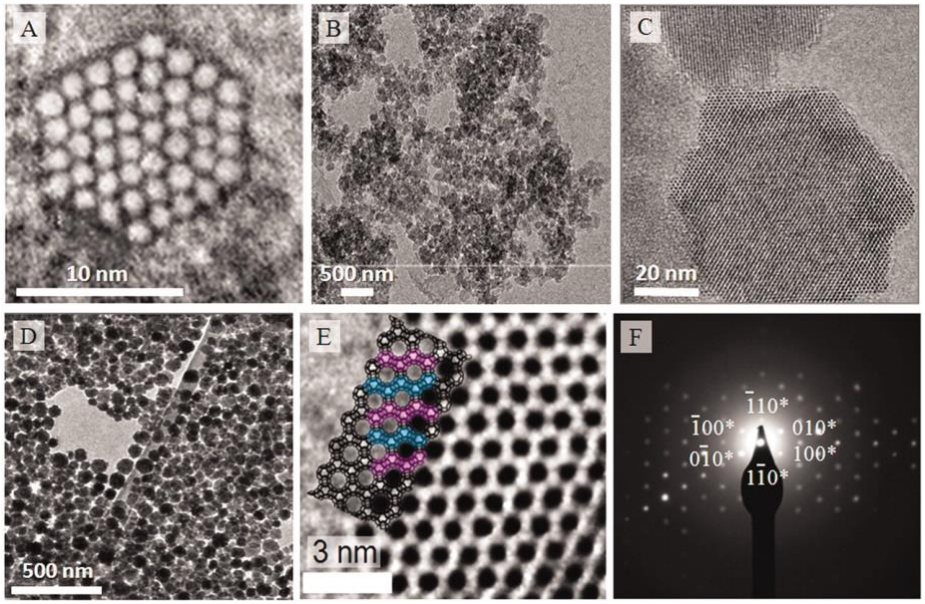
Porous aluminosilicates

Low electron-beam stability

Adsorbed water decreases stability

Low dose of electrons required





Mintova et al., ***Science***, 335, 6064, pp. 70-73

Hlazeni piva? – Zeolity!

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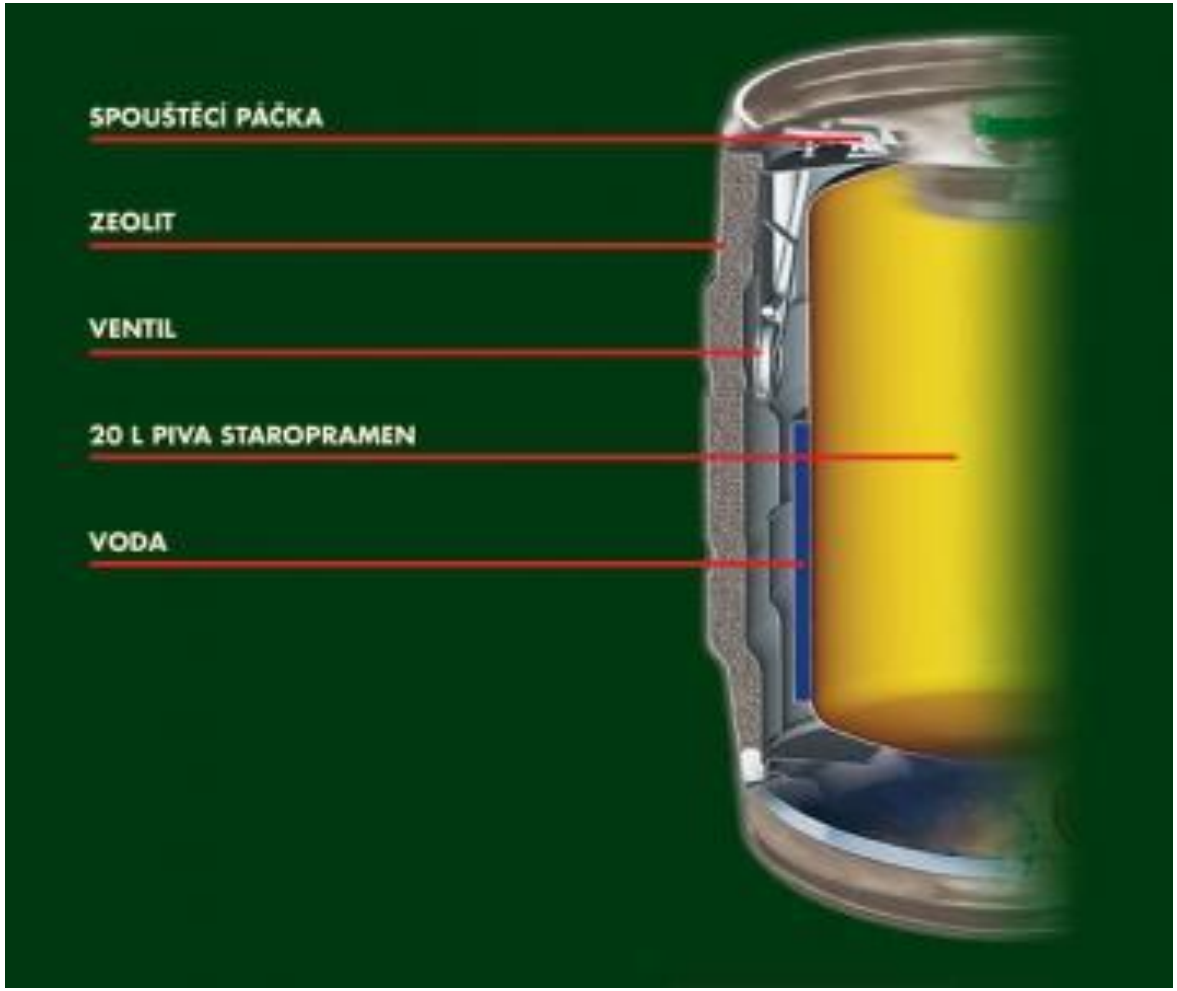
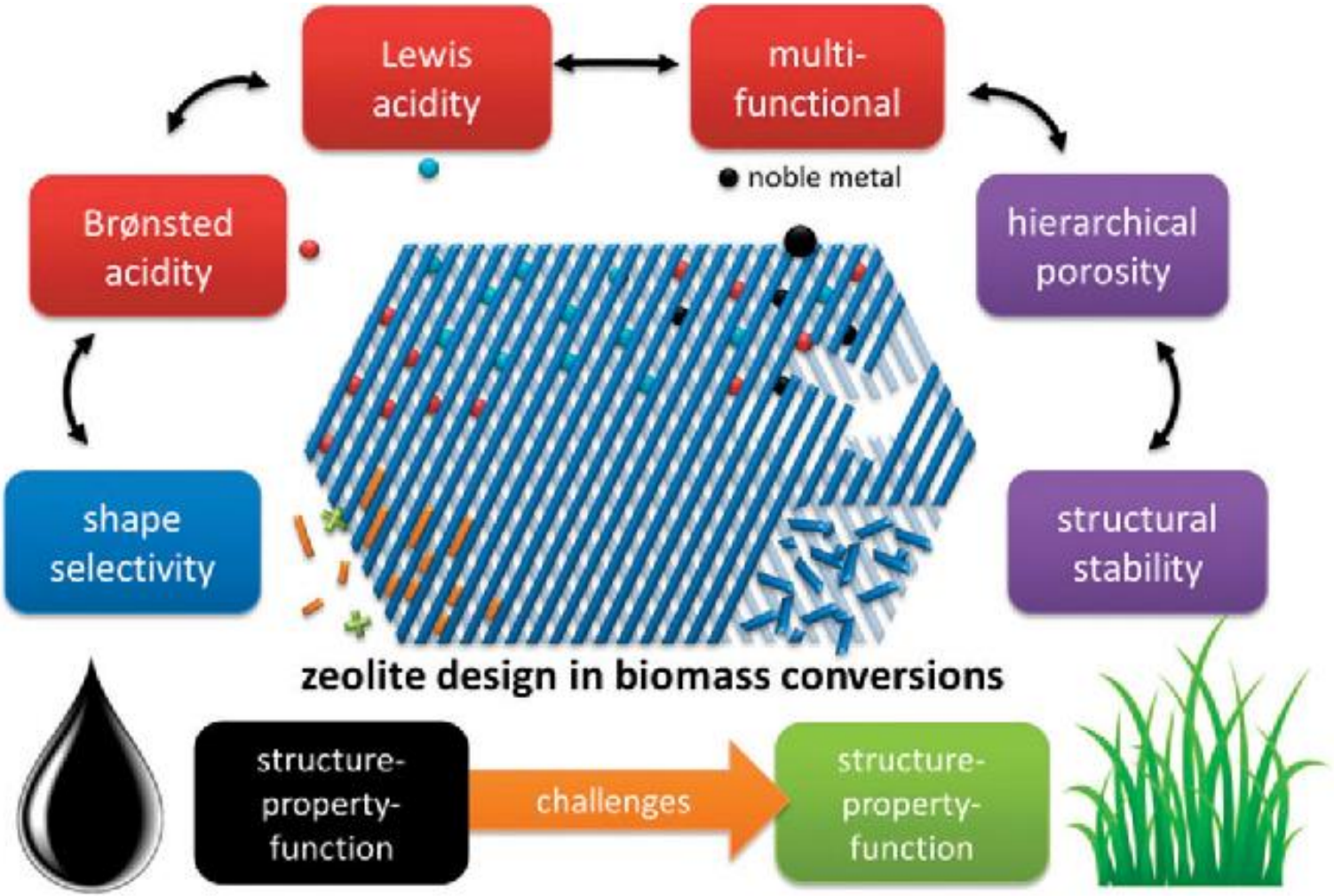


https://www.mmspektrum.com/novinka/pivni-kegy-s-integrovanym-chlazenim.html

Zeolity v katalýze



T. Ennaert et al., ***Chem. Soc. Rev.***, 2016,**45**, 584-611

Layered zeolites

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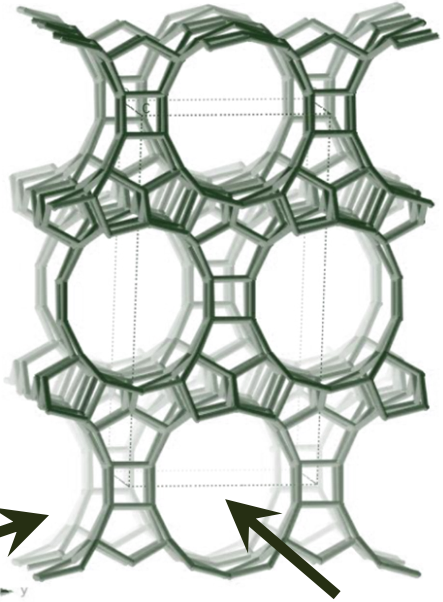


UTL

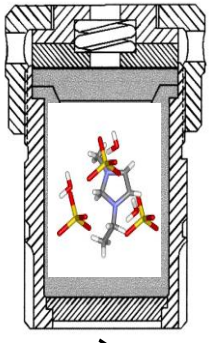
12-ring
0.85 x 0.55 nm

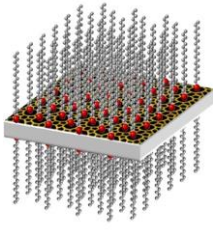
14-ring
0.95 x 0.71 nm

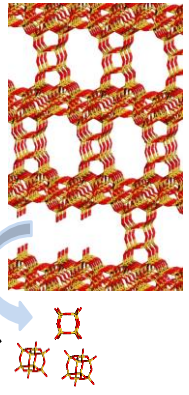
Hydrothermal synthesis

Rational design

Top-down







Strong acid centres

Defined micropores

Shape selectivity in catalysis

Roth W.J., Nachtigall P., Morris R.E., Čejka J., ***Chem. Rev.,*** 2014

Jaké mají zeolity vlastnosti?

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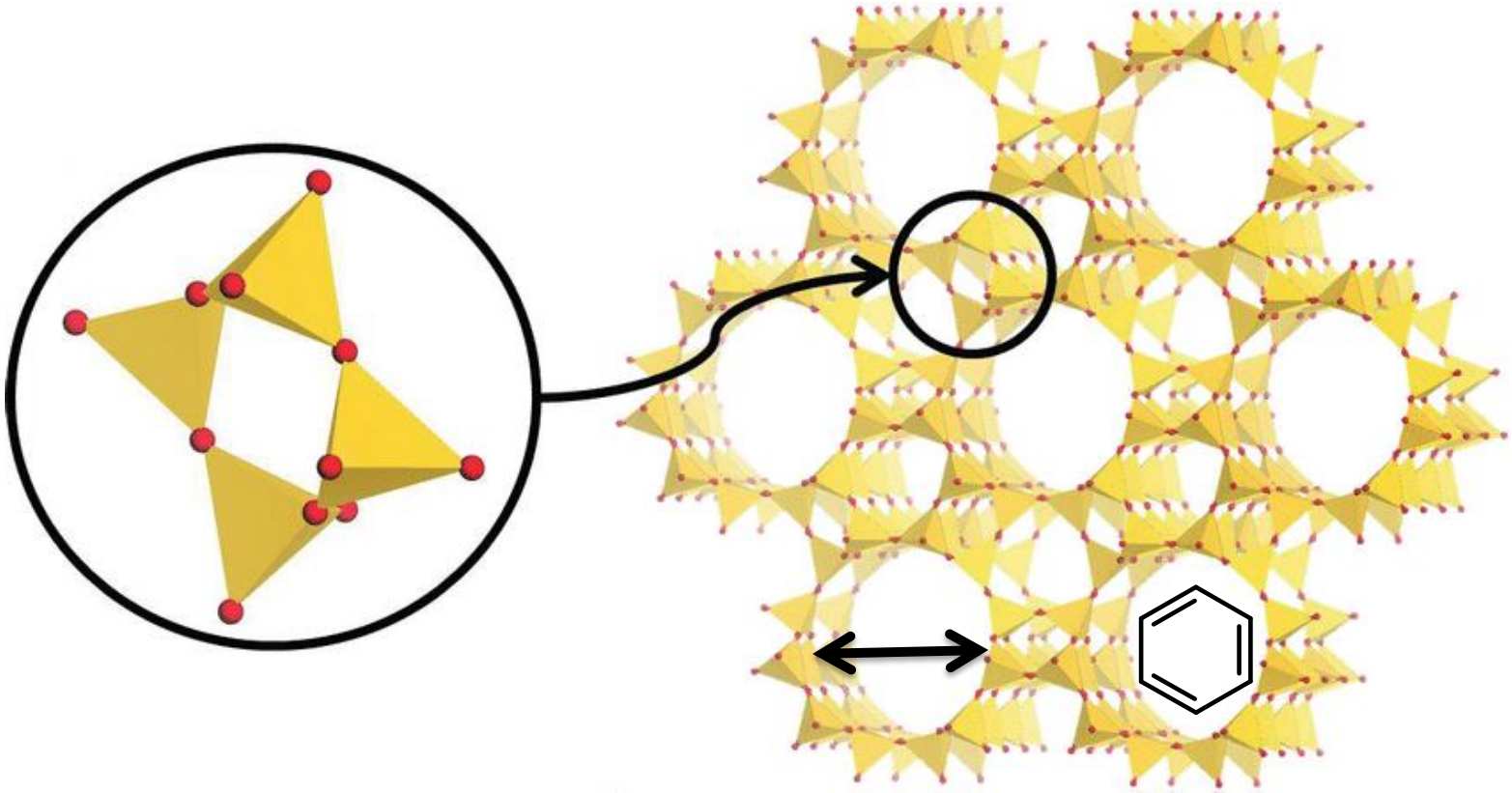
- Molekulové síto



Malé molekuly mohou difundovat skrz kanály, větší ne

Credit: Dr Jan Přech

Zeolite catalysts in scale

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Plant

10 m

Reactor

1 m

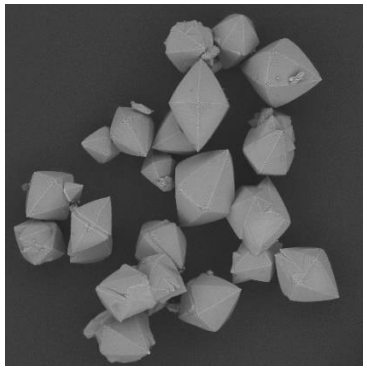
Extrudate

10 cm

Powder

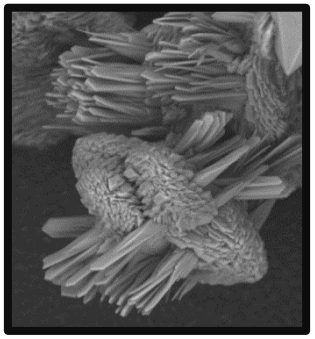
10 mm

Particles



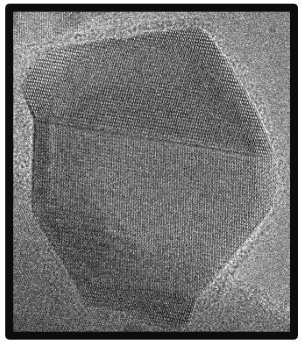
100 µm

Intergrowths



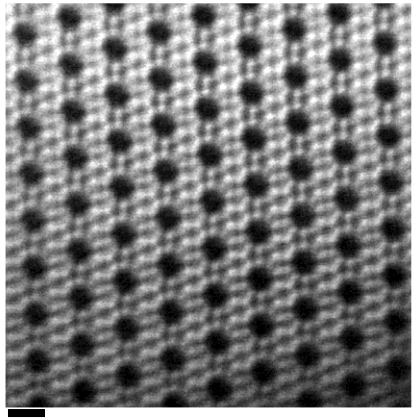
10 µm

Single crystal



10 nm

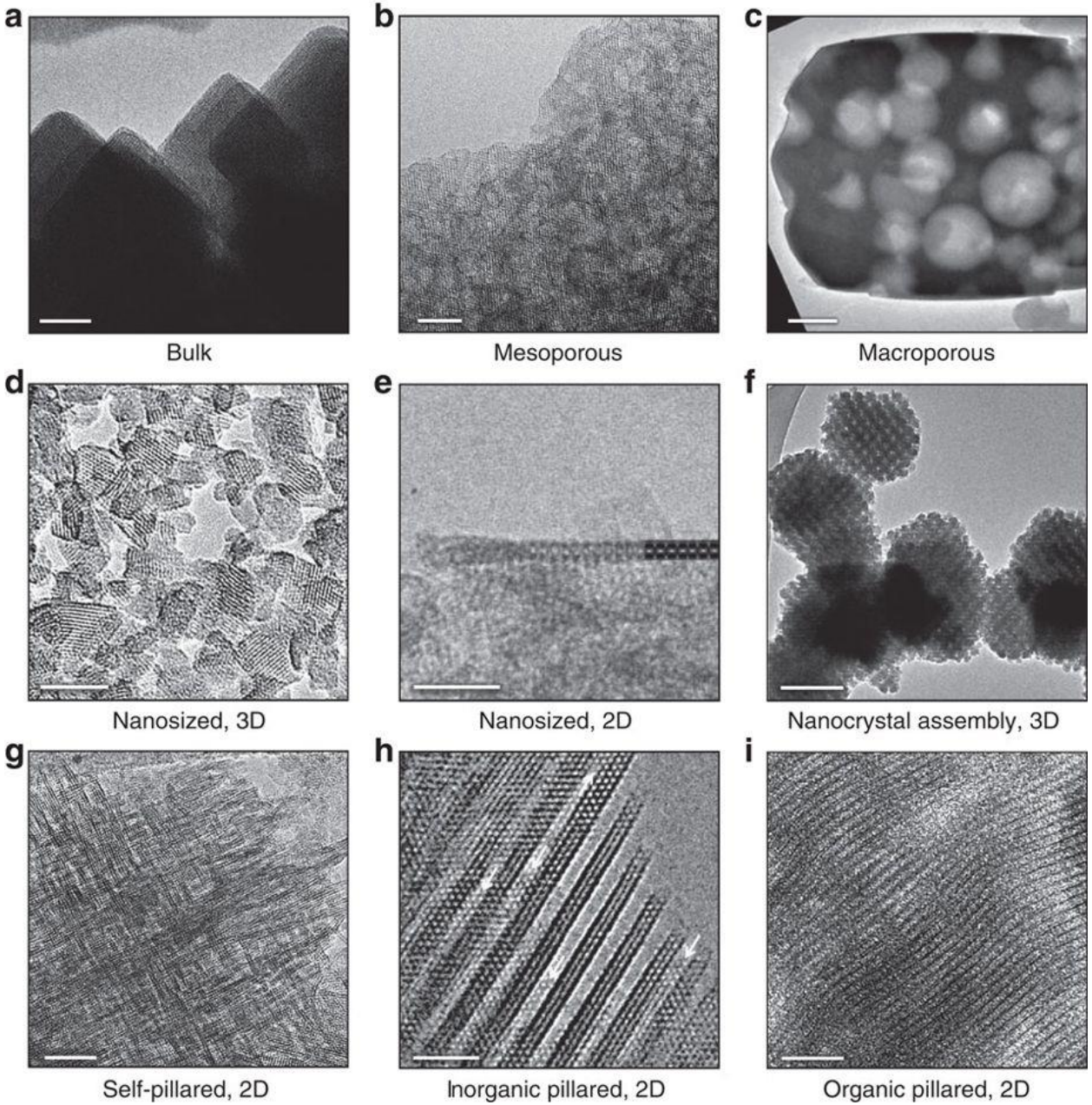
Pore structure



1 nm

D.N. Rainer, M. Mazur, **RSC Catalysis book series**, 2020

Variety of zeolite forms



Mitchell, S. *et al. Nat Commun* **6,** 8633 (2015)

Zeolites are no longer a challenge

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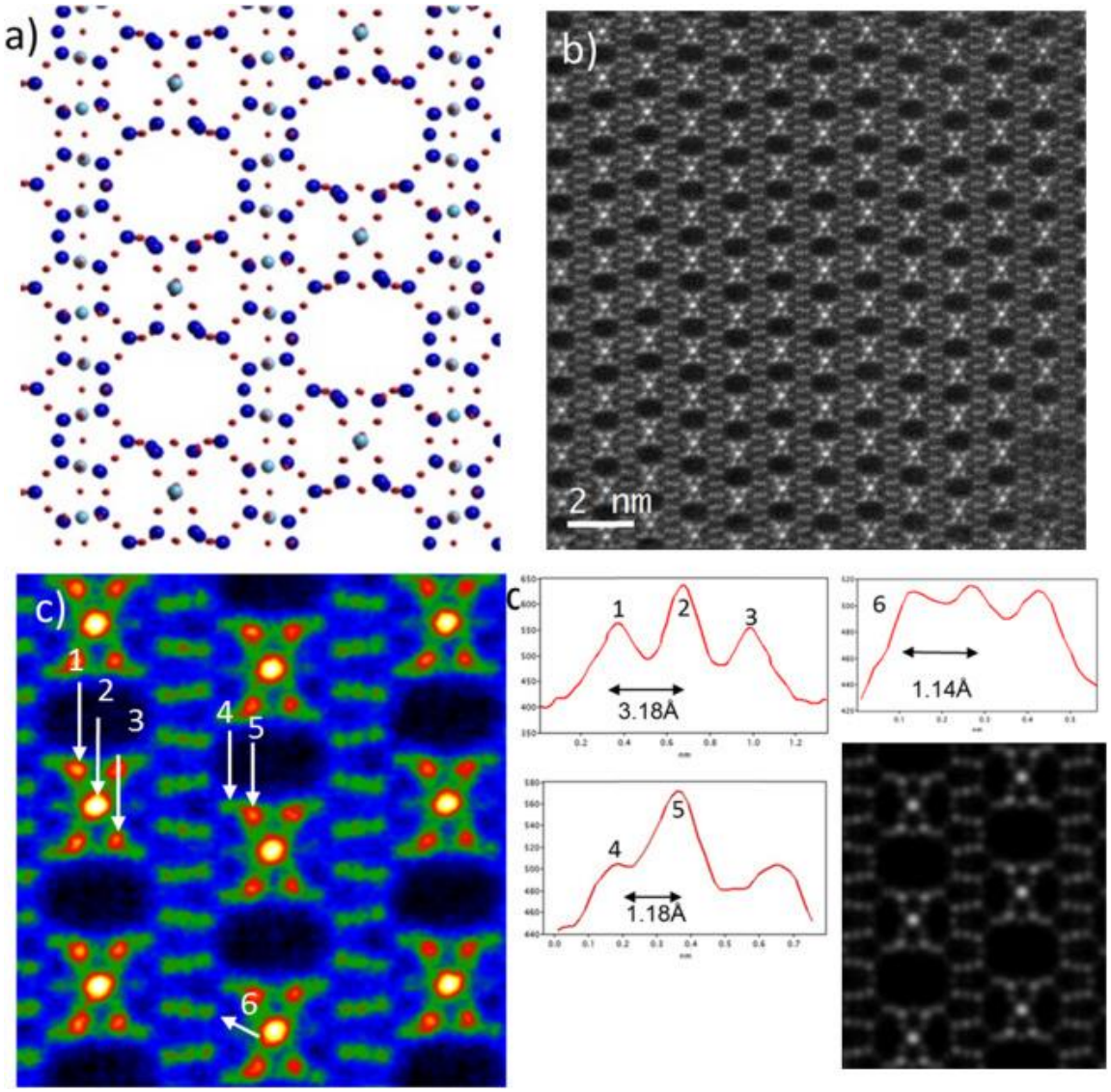

ETS-10

Alvaro Mayoral, Paul A. Anderson, Isabel Diaz, Zeolites are no longer a challenge: Atomic resolution data by Aberration-corrected STEM, Micron, 68, 2015, 146-151

Zeolites are no longer a challenge

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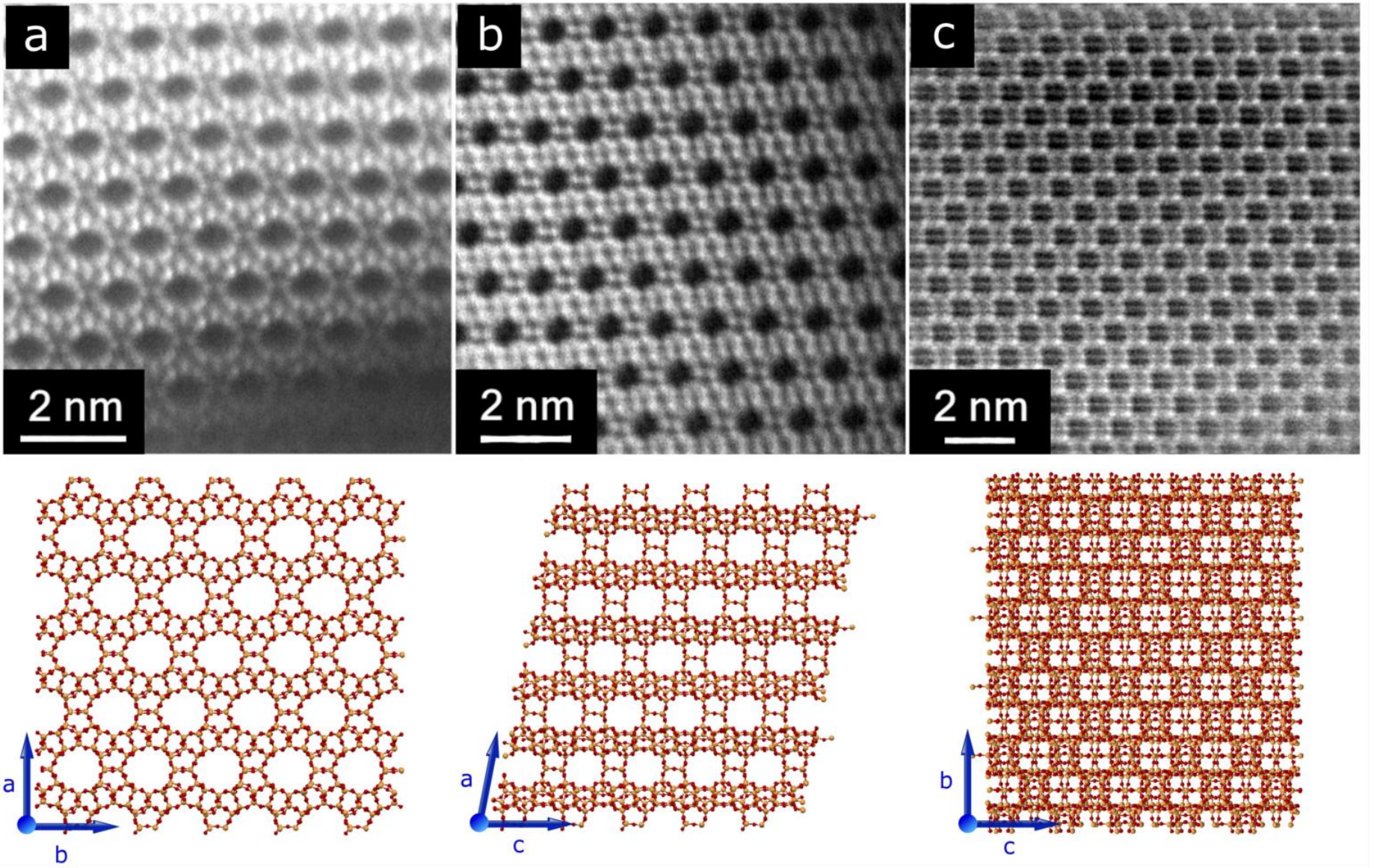
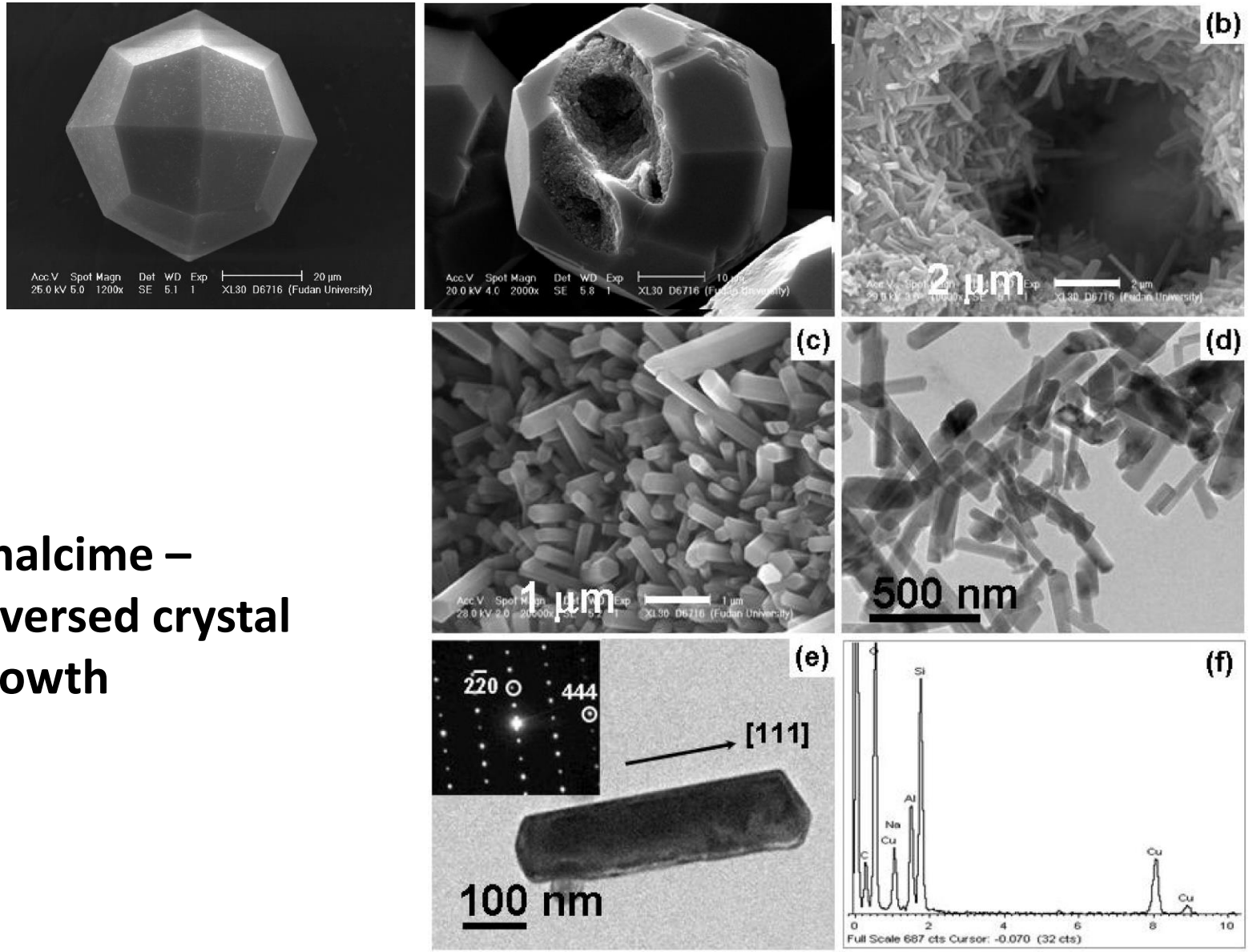


M. Mazur, V. Kasneryk, J. Přech, F. Brivio, C. Ochoa-Hernández, A. Mayoral, M. Kubů and J. Čejka, Inorganic Chemistry Frontiers, 2018, 5, 2746-2755.

Scanning Electron Microscopy



Analcime – reversed crystal growth

Q. Chen et al., ***J. Am. Chem. Soc.*** 2007, 129, 43, 13305-13312

Atomic Force Microscopy

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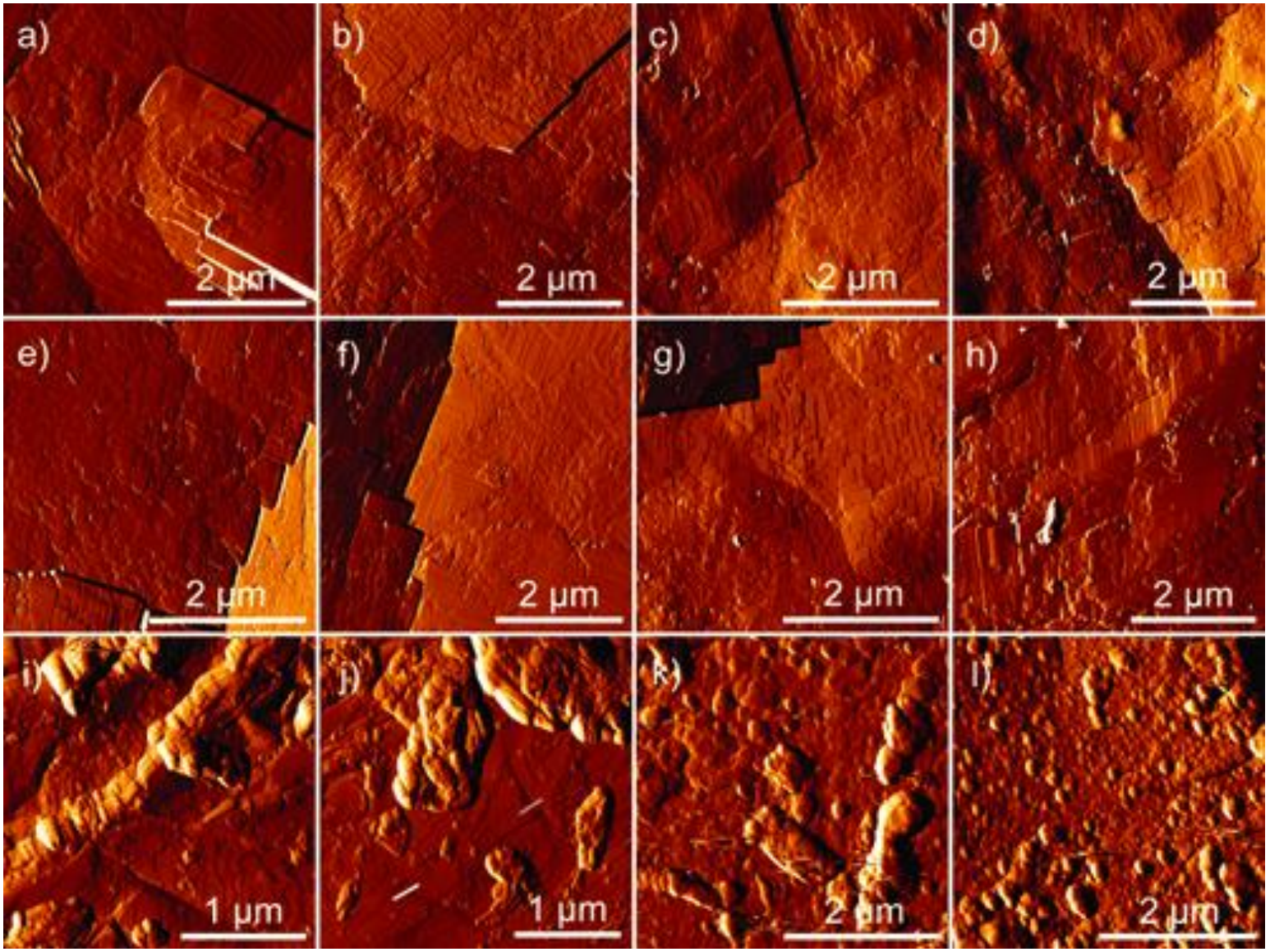

Smith, R. L., Eliášová, P. , Mazur, M. , Attfield, M. P., Čejka, J. and Anderson, M. W. (2014), Chem. Eur. J., 20: 10446-10450.

Combined methods

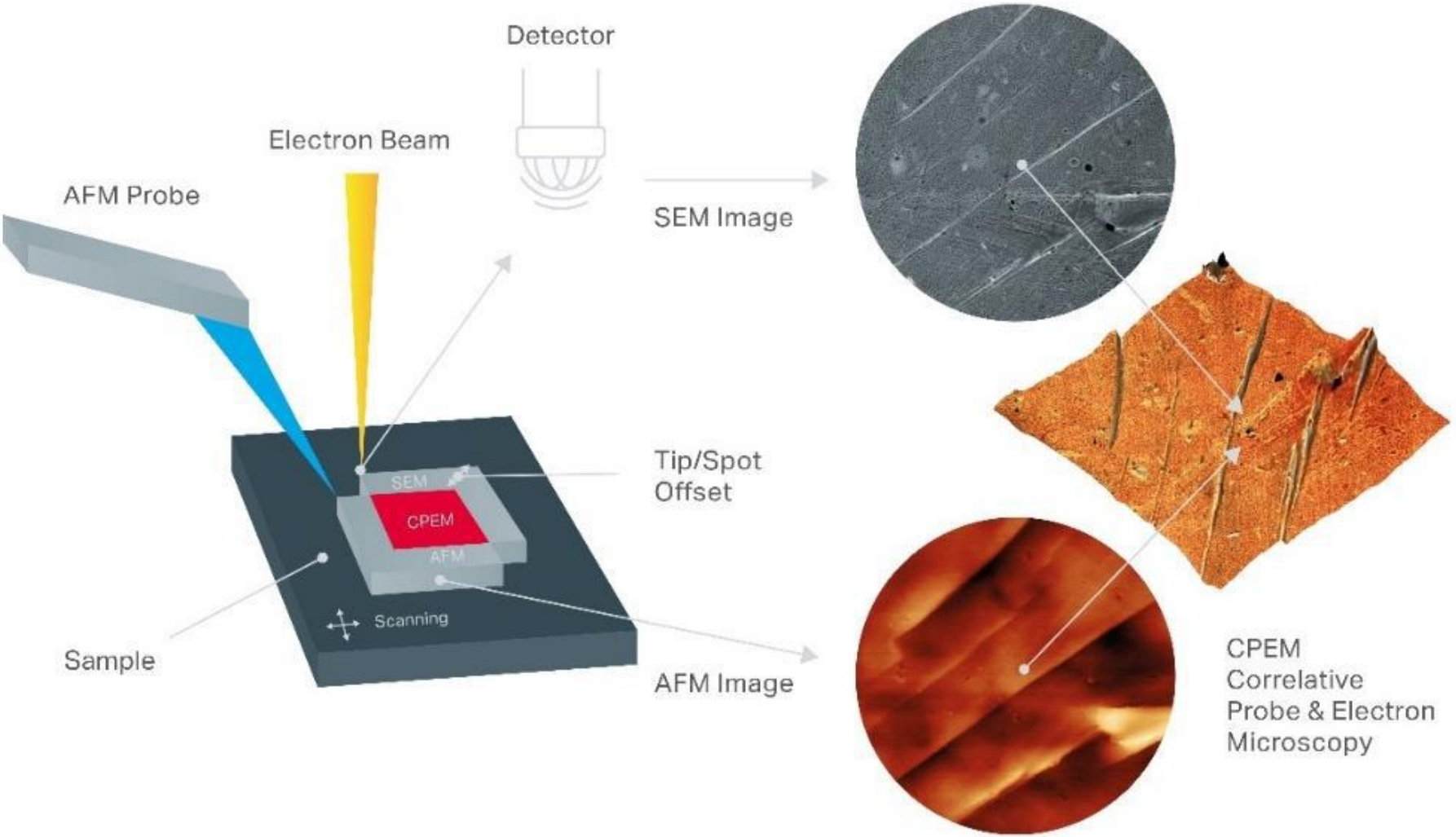

Image is shown with courtesy of NenoVision s.r.o. and Dr. Monika Vilémova and Institute of Plasma Physics of CAS.

CPEM – AFM/SEM method

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Correlative Probe and Electron Microscopy (CPEM)

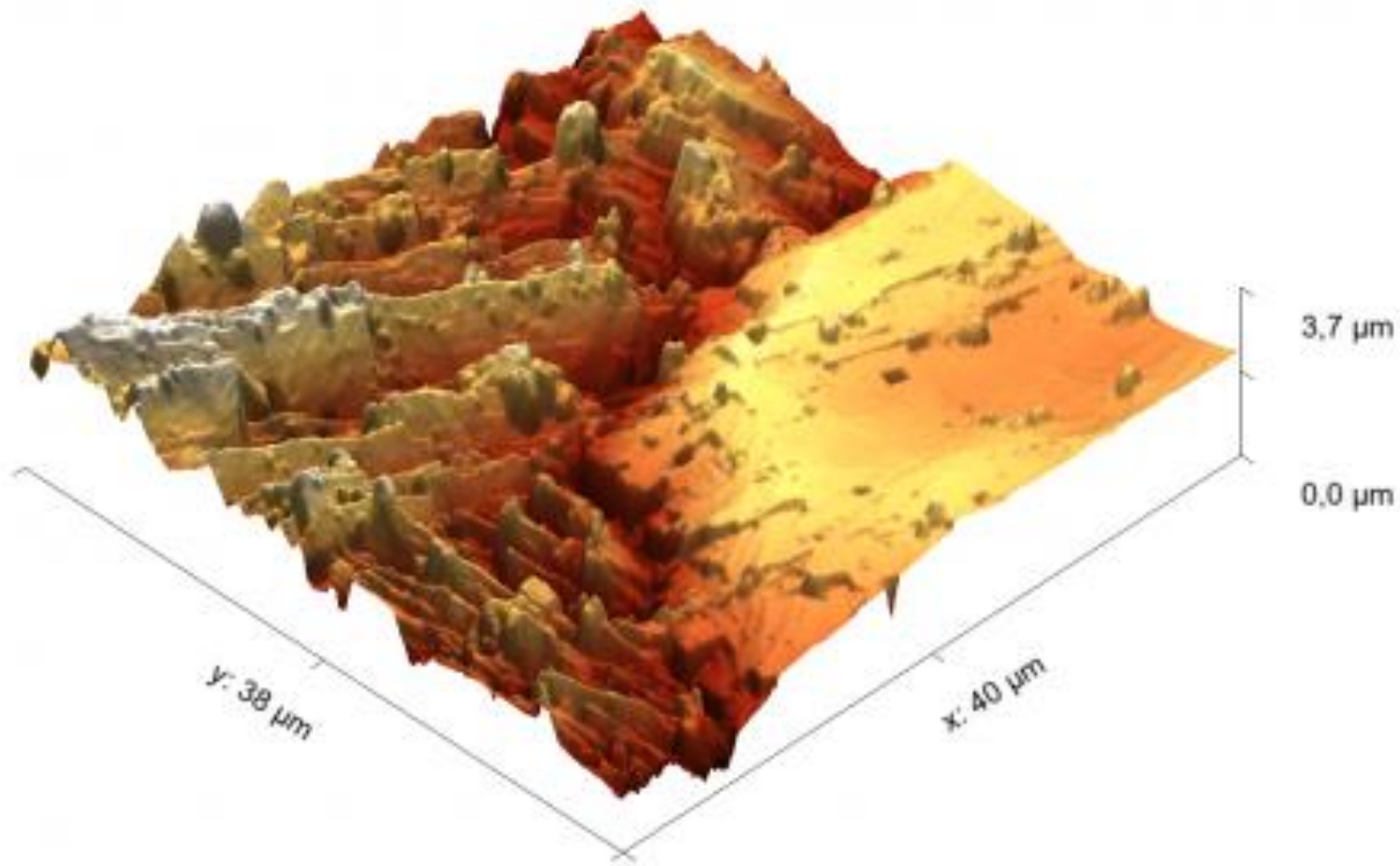

Image is shown with courtesy of NenoVision s.r.o.

Transmission electron microscopy

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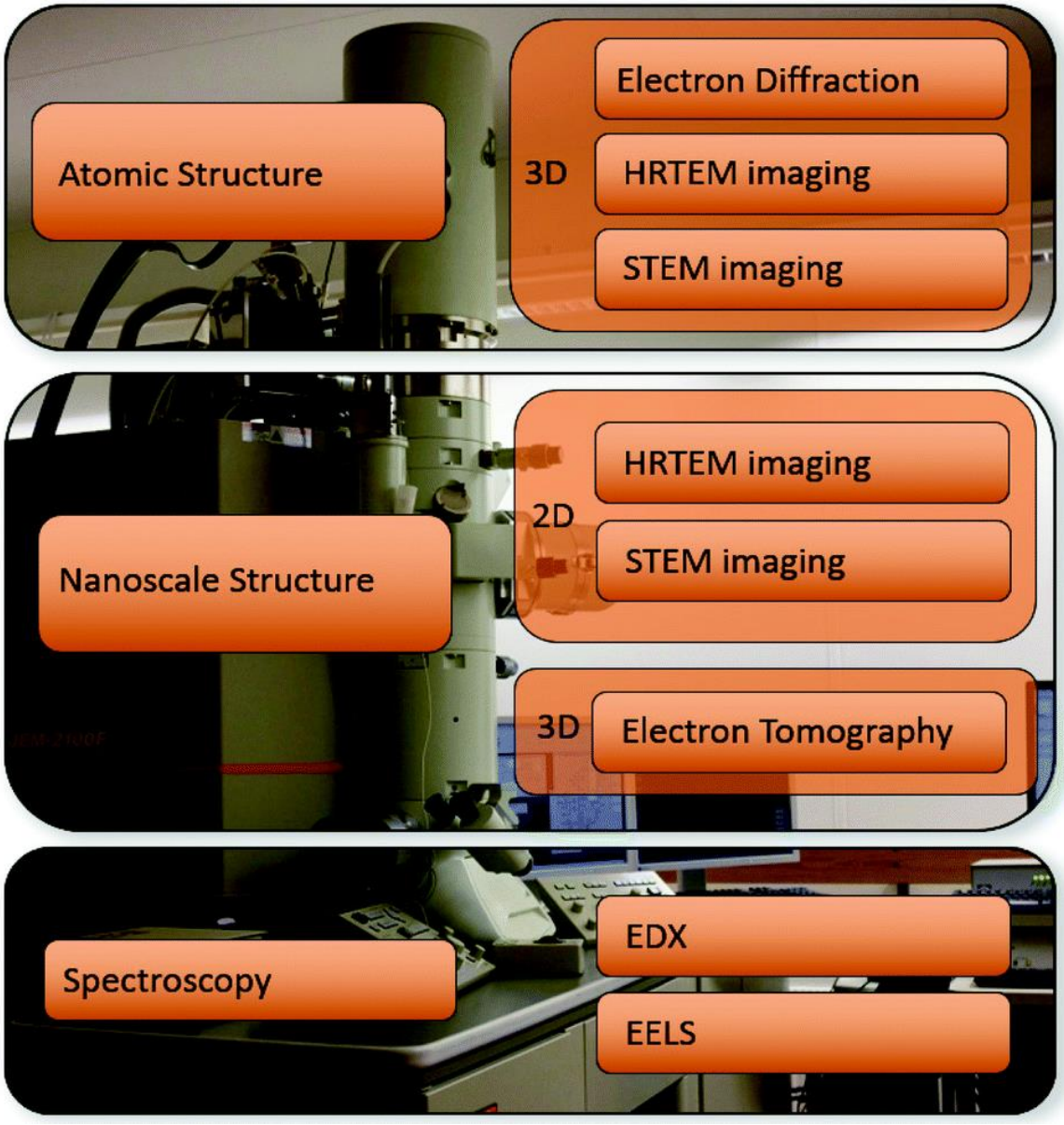
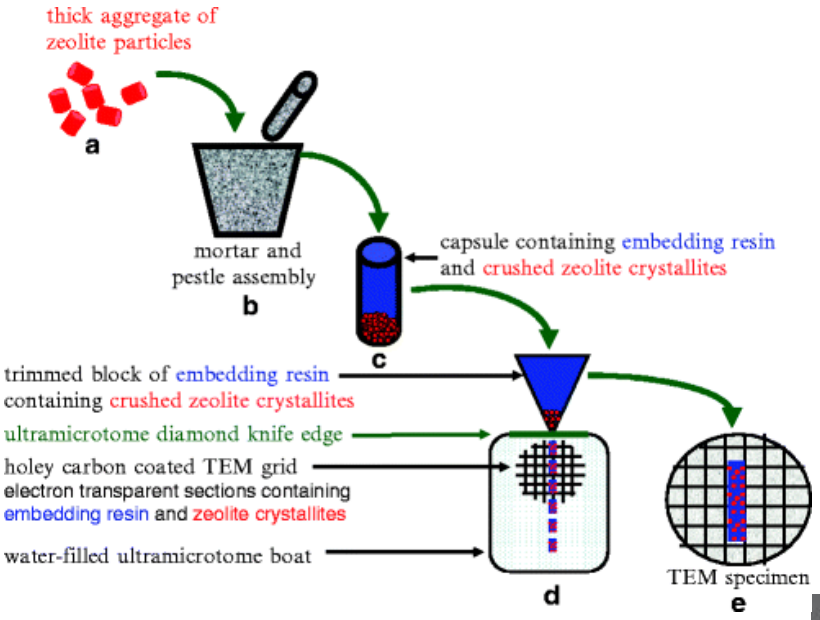


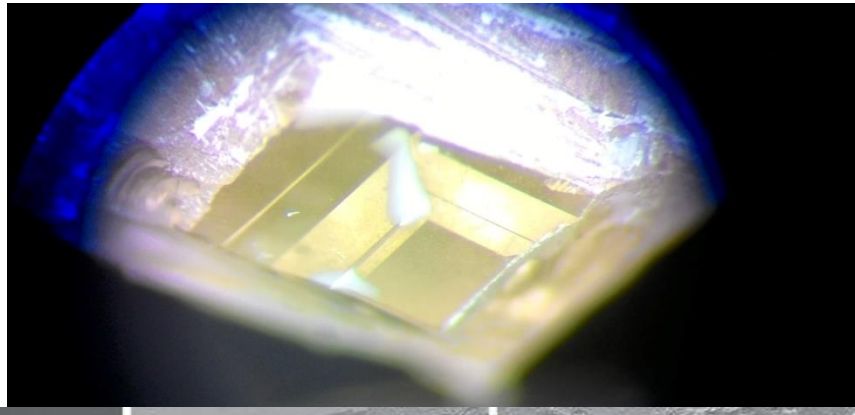
W. Wan et al., ***Inorg. Chem. Front.***, 2018,**5**, 2836-2855

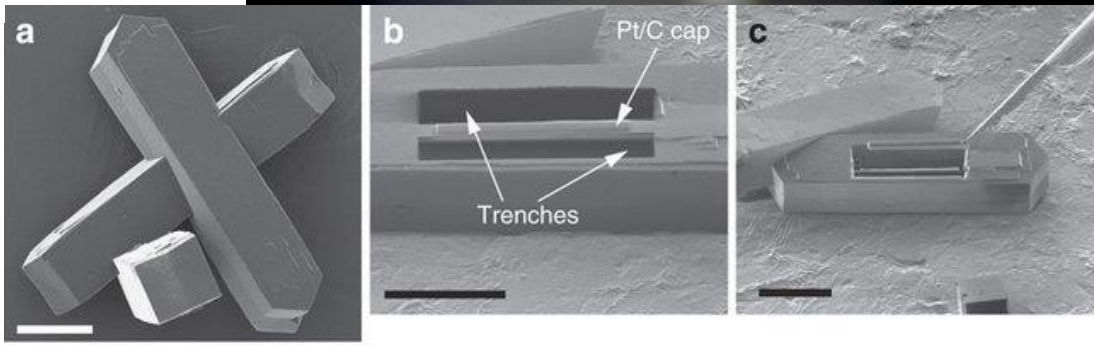
Sample preparation



Ultramicrotomy

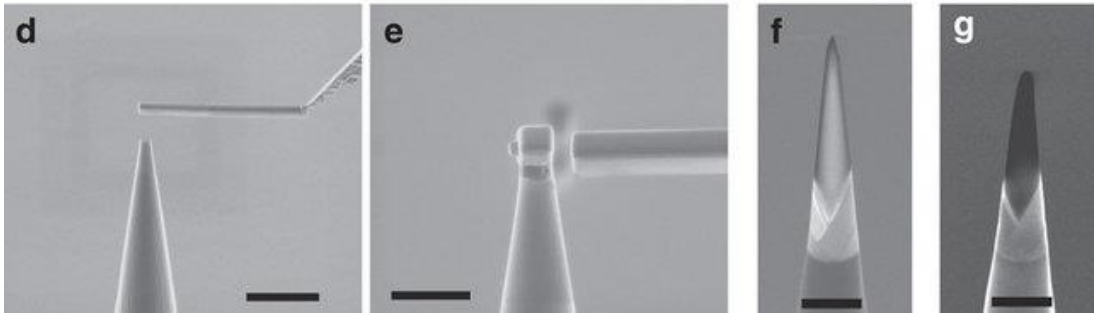
C.E. Kliewer, Zeolite Characterization and Catalysis pp 169-196





Focus Ion Beam (FIB)

Perea, D. et al. *Nat Commun* **6,** 7589 (2015)



Structure determination from TEM

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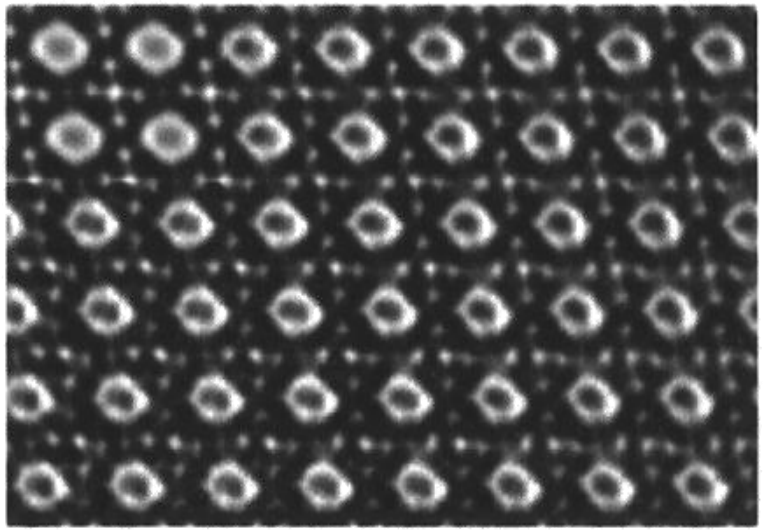
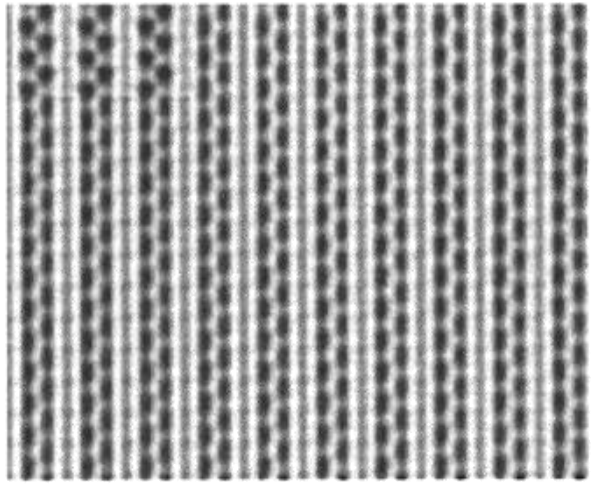
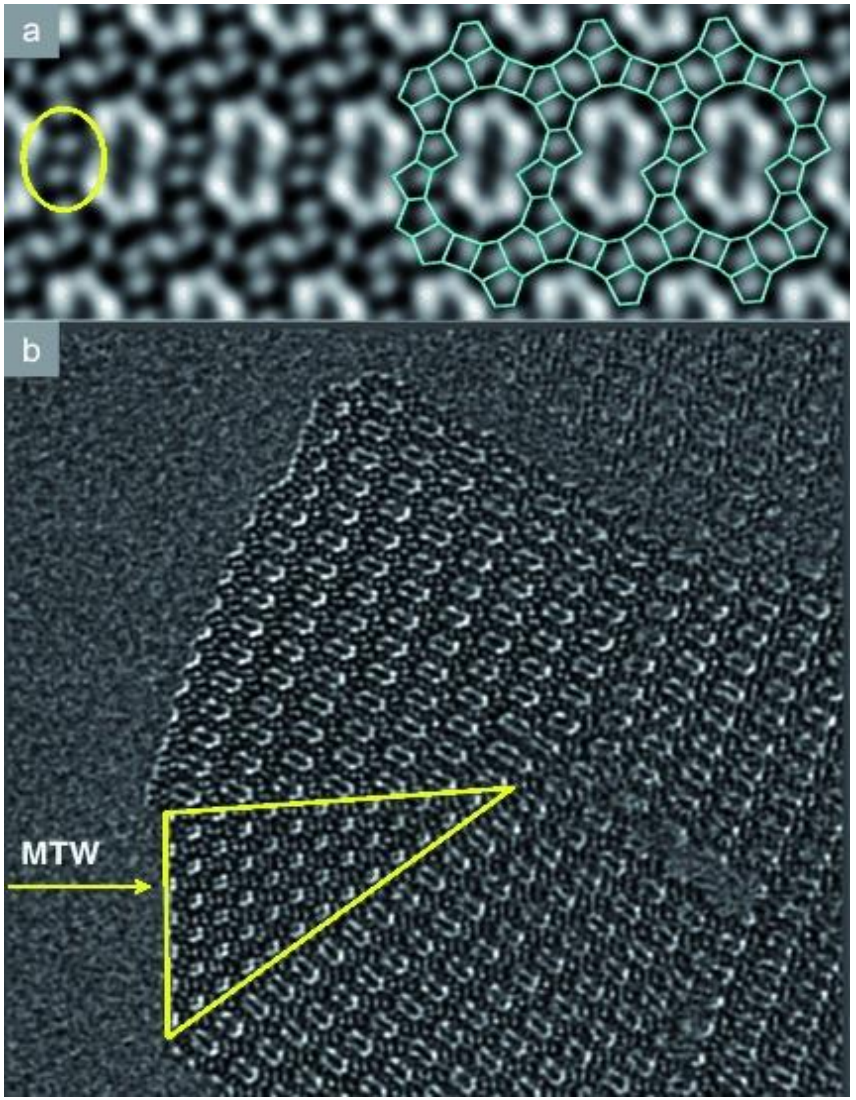




SSZ-48

P. Wagner, J. Phys. Chem. B 1999, 103, 39, 8245-8250



SSZ-61

Smeets, S. et al., Angew. Chem. Int. Ed., 53: 10398-10402.

Electron Tomography - tilt

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Thermofisher (FEI), Eindhoven, NL, test measurements

Electron Tomography - slices

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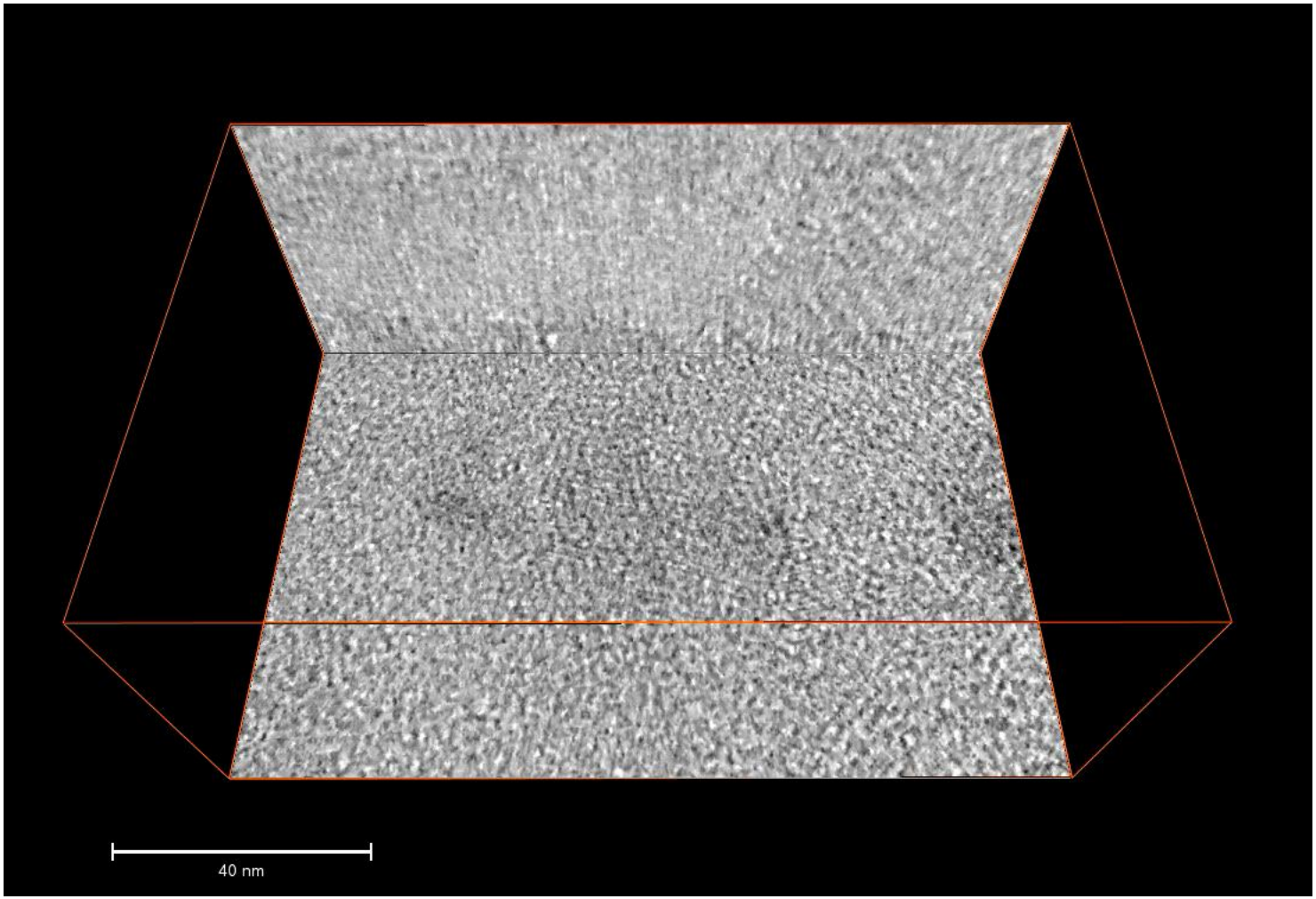
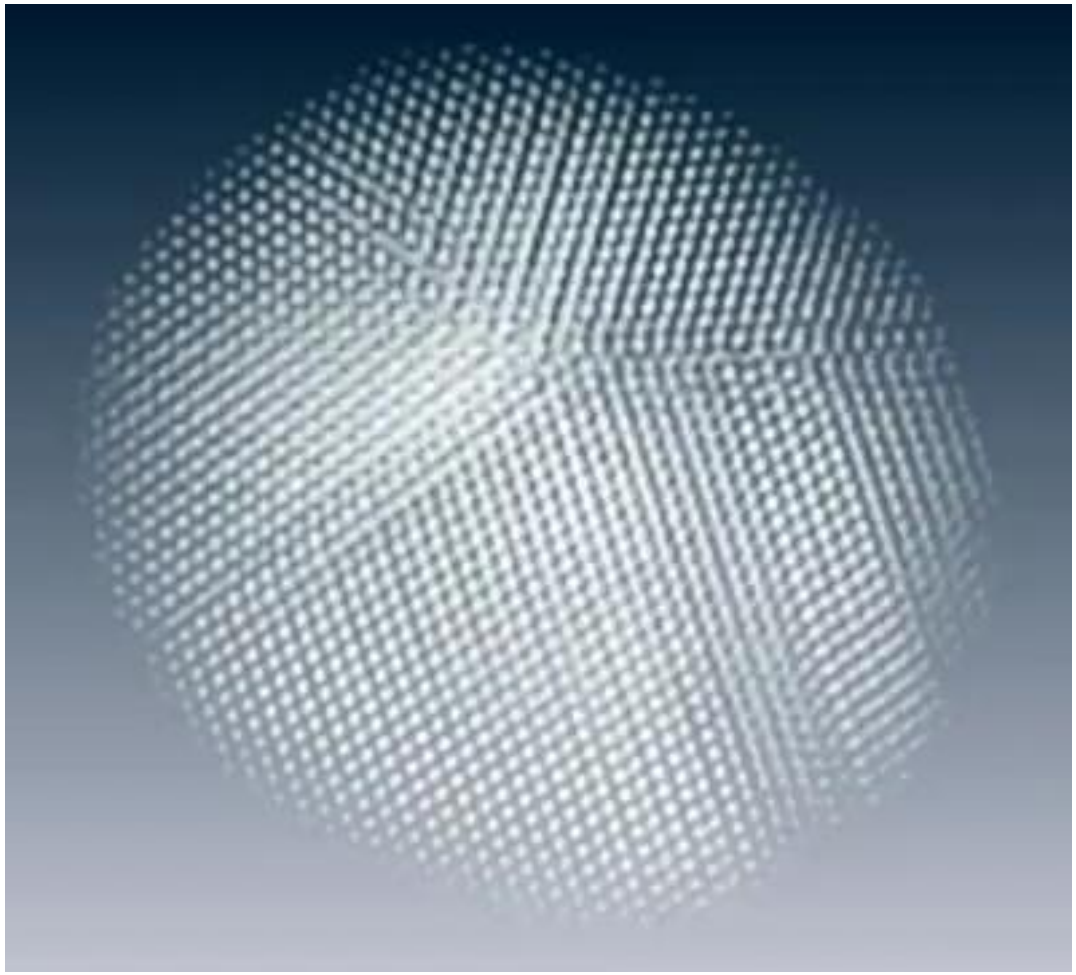


Thermofisher (FEI), Eindhoven, NL, test measurements

Atomic Electron Tomography



Source: https://www.eurekalert.org/multimedia/pub/54422.php

ADOR – česká metoda syntézy

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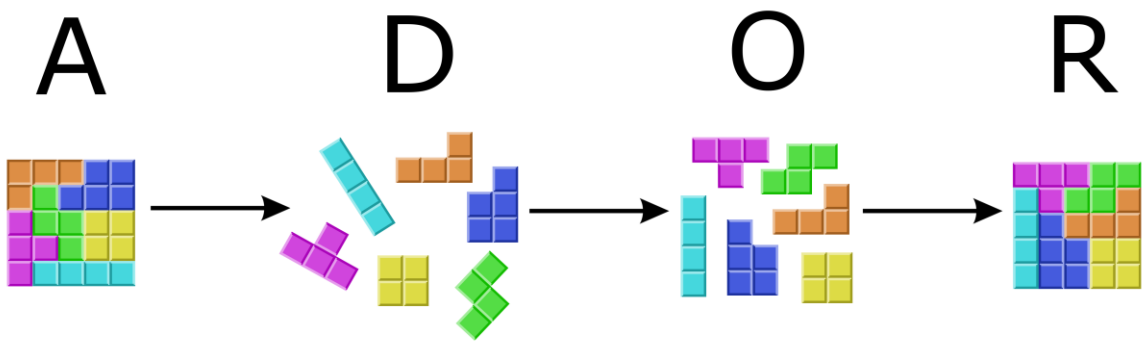
The **ADOR** (**A**ssembly-**D**isassembly-**O**rganization-**R**eassembly) process involves the synthesis of 3D germanosilicate during first step. Then, selective disassembly of it to form a layered material followed by organization of layers and reconnection of them to get new zeolite.

The ADOR is a way for the preparation of layered zeolite precursors, that can be further modified to get the **related zeolitic architectures**.
12 new topologies were revealed so far.



Roth et al., ***Nature Chem.***, 2013, **5**, 628–633

Mazur et al., ***J. Mater. Chem. A***, 2018,**6**, 5255-5259

ADOR zeolites with nanoparticles

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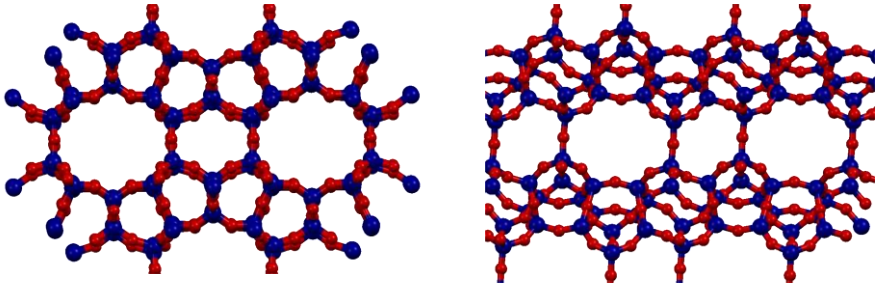
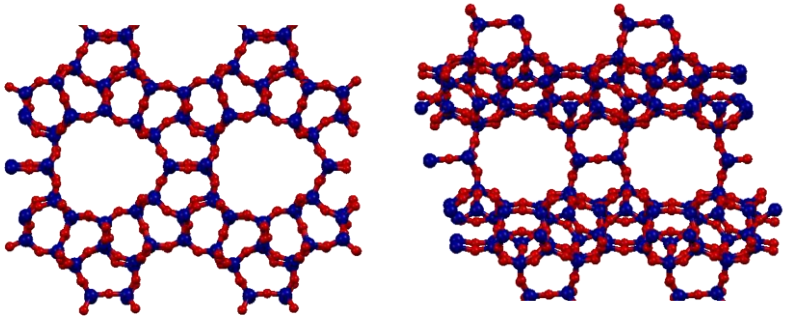
IPC-4 (**PCR**)



10-ring: 6.1 Å × 5.1 Å
8-ring: 4.7 Å × 3.5 Å

IPC-2 (**OKO**)



12-ring: 7.0 Å × 5.6 Å
10-ring: 6.1 Å × 4.7 Å

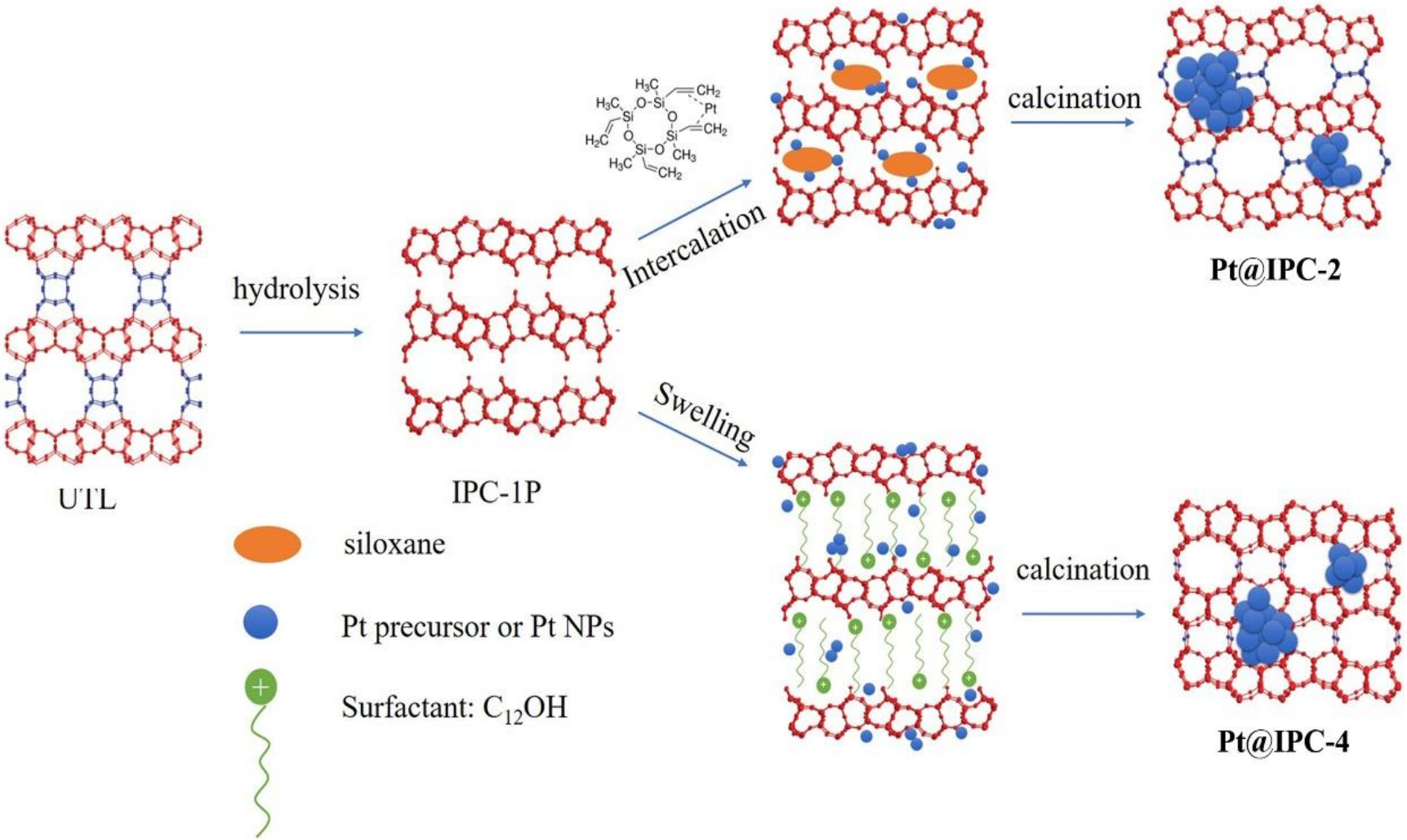
P. Eliasova et al. **Chem. Soc. Rev.**, 2015

Encapsulation of Pt NPs into the IPC-2 and IPC-4 zeolites

Shape-selective hydrogenation

Y. Zhang et al. **Microporous Mesoporous Mater.**, 279, 2019, 364

ADOR zeolites with nanoparticles



Y. Zhang et al. **Microporous Mesoporous Mater.**, 279, 2019, 364

Tvarová selektivita

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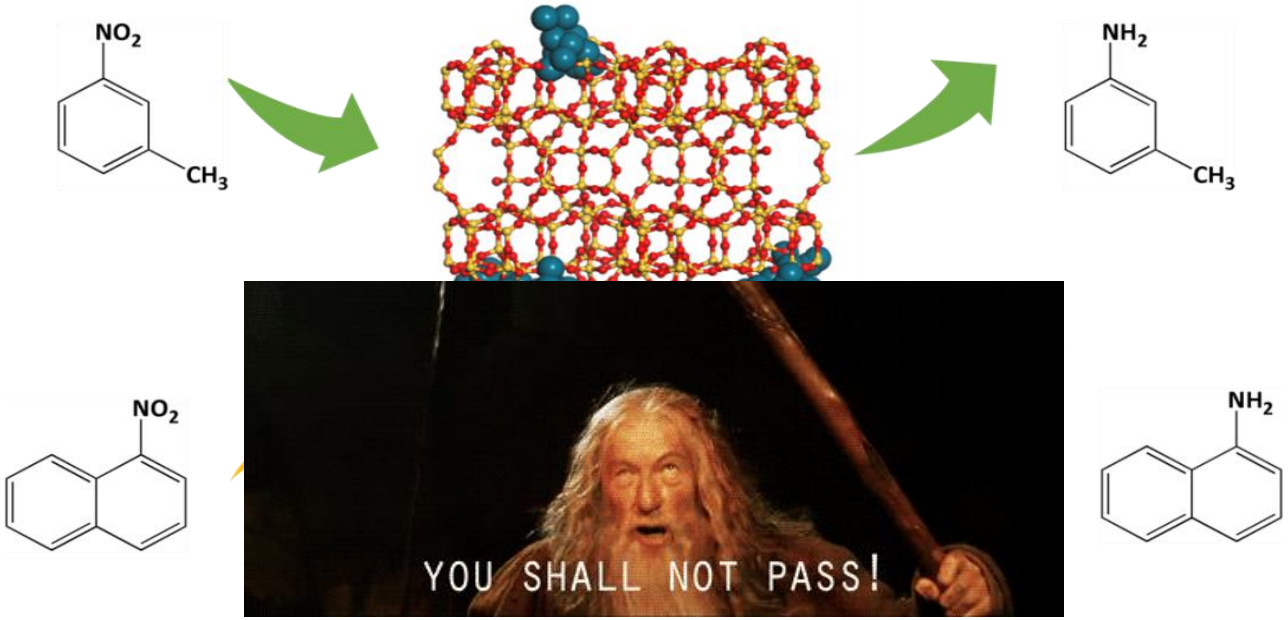
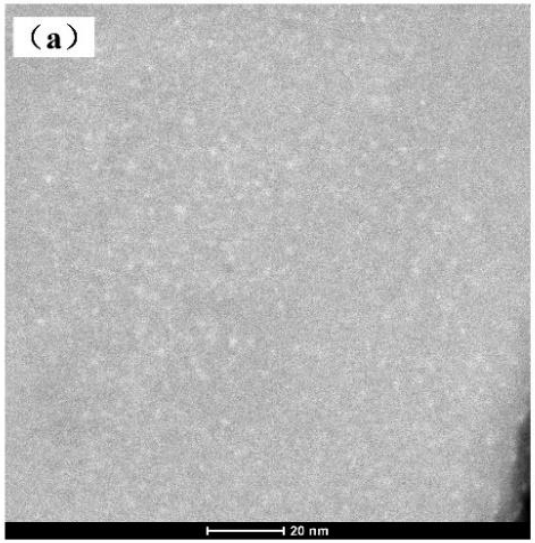
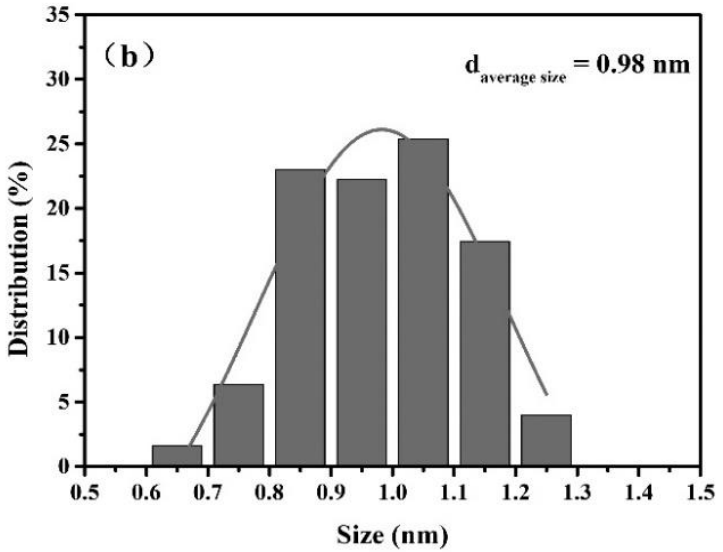
Confirmed shape selectivity!

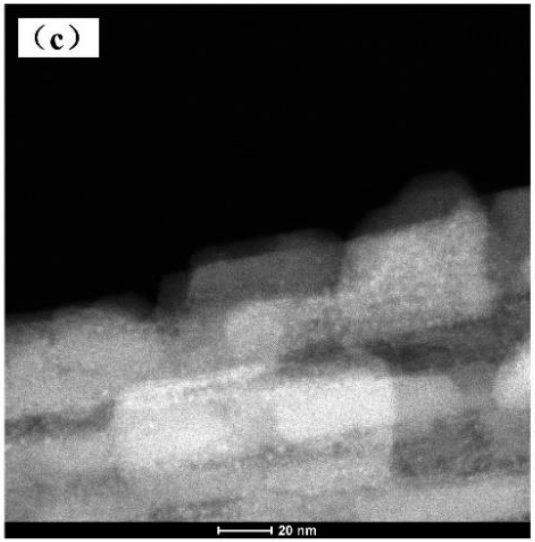


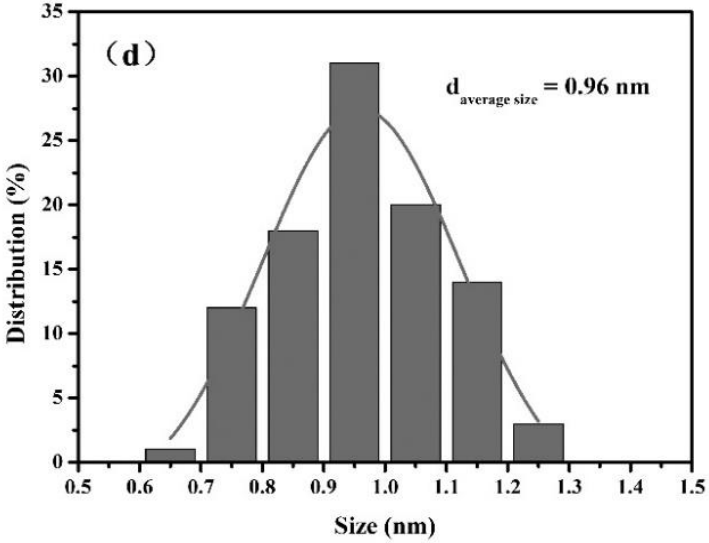
Y. Zhang et al. **Mater. Today Nano**, 2019, in press

ADOR zeolites with nanoparticles









Y. Zhang et al. **Microporous Mesoporous Mater.**, 279, 2019, 364

Subnanometric Pt

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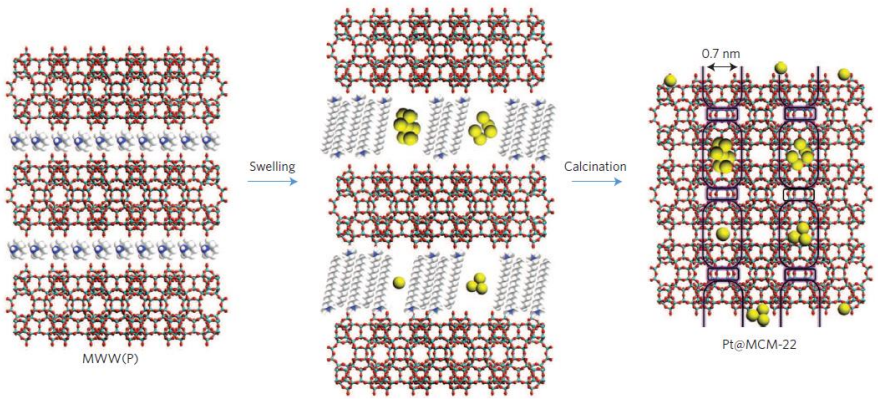
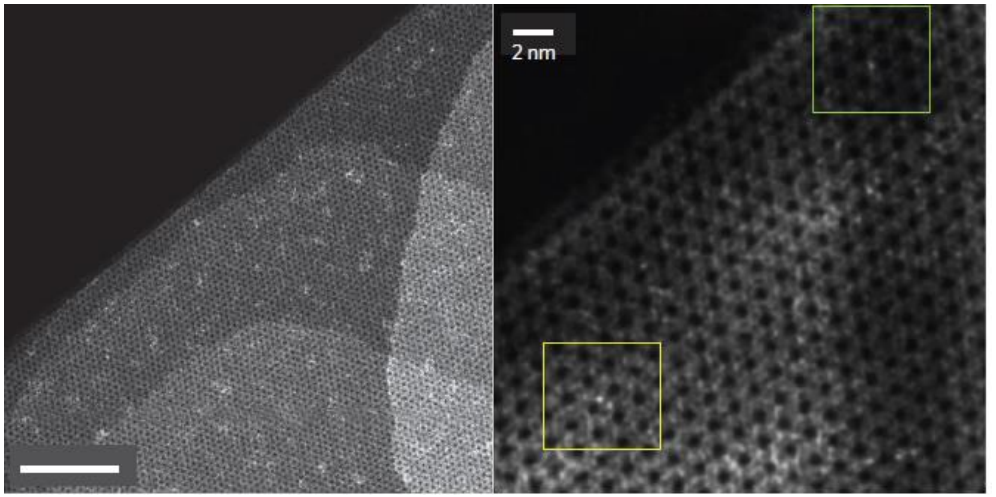
New method to generate subnanometric platinum from 2D to 3D zeolite





Corma et al.

Nat. Mater., **2017**, 16, 132-138 *Nat. Commun.*, **2018**, *9,* 574

Shape-selective hydrogenation

Our idea:

Different length of surfactants

Different d-spacing

Different Size of Pt NPs

MCM-22P swollen with Pt NPs

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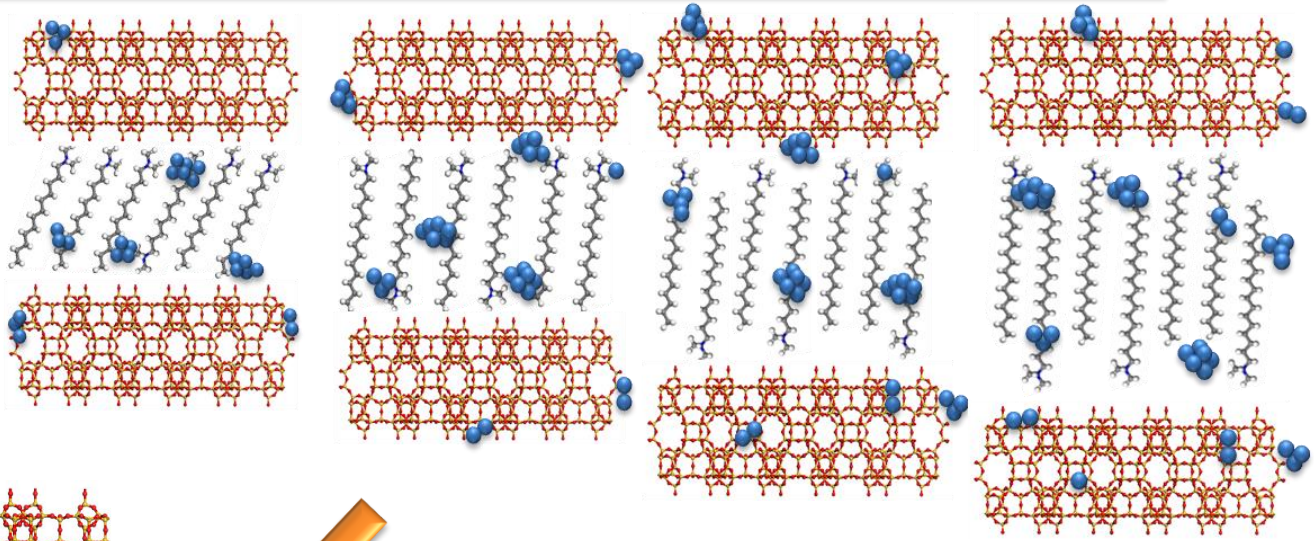
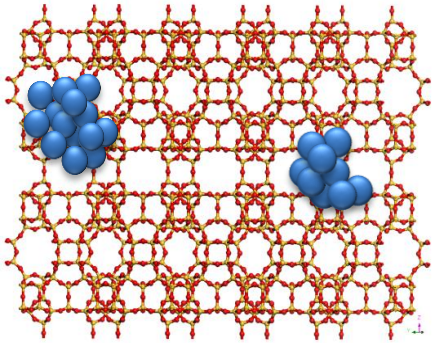
	C_{12}^+ - OH^-	C_{14}^+ - OH^-	C_{16}^+ - OH^-	C_{18}^+ - OH^-
Length of surfactant	1.53 nm	1.56 nm	2.06 nm	2.25 nm
Interlayer distance	1.06 nm	1.72 nm	2.59 nm	2.89 nm





Y. Zhang et al. **Catal. Today**, 324, 2019, 135

MCM-22 with Pt NPs

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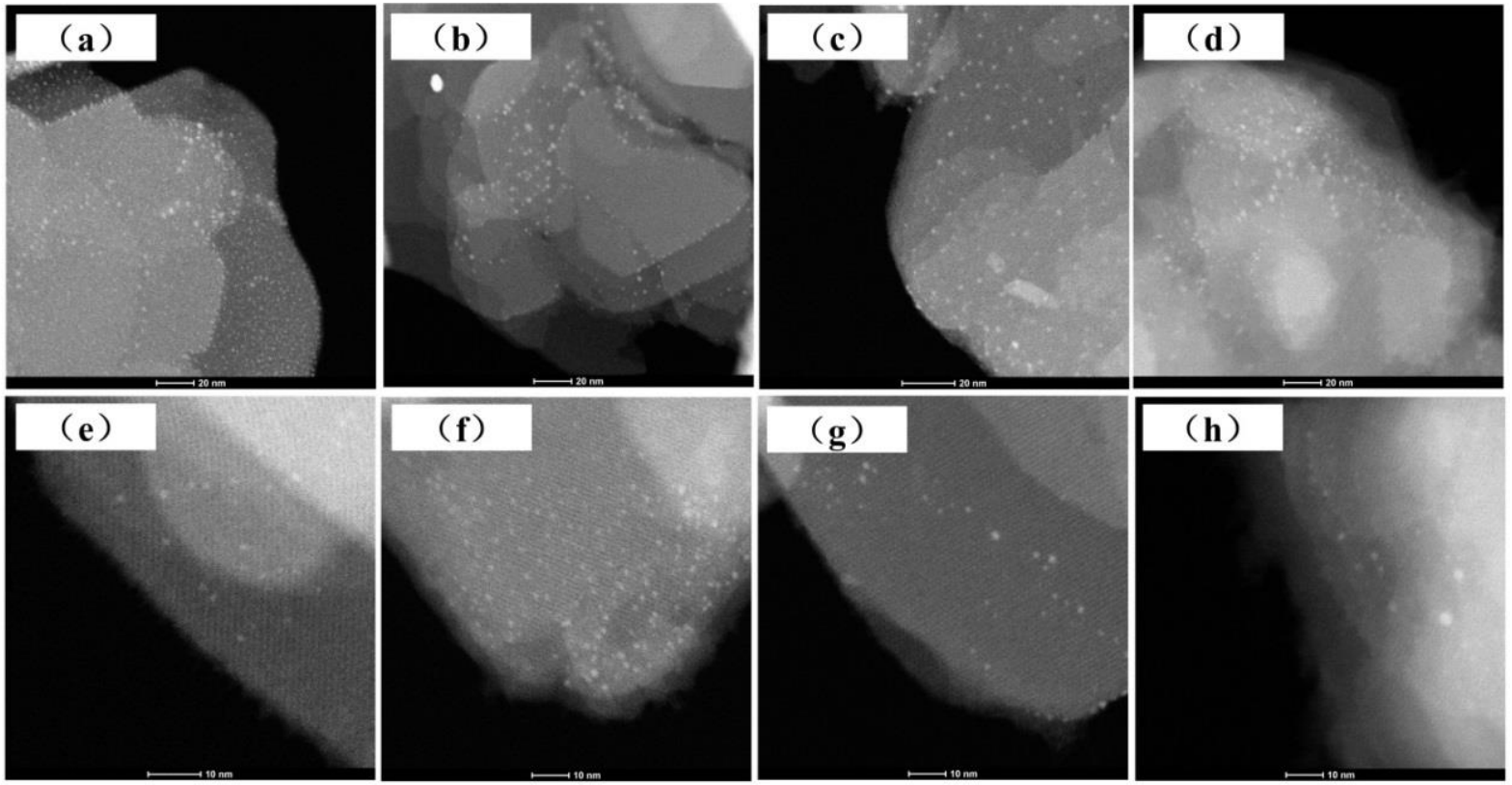
MCM-22-C_{12}OH-Pt **MCM-22-C_{14}OH-Pt** **MCM-22-C_{16}OH-Pt** **MCM-22-C_{18}OH-Pt**



- The uniform distribution of Pt NPs
- The size of the Pt NPs increases with the length of swelling agent

Y. Zhang et al. **Catal. Today**, 324, 2019, 135

Nanoparticles size distribution

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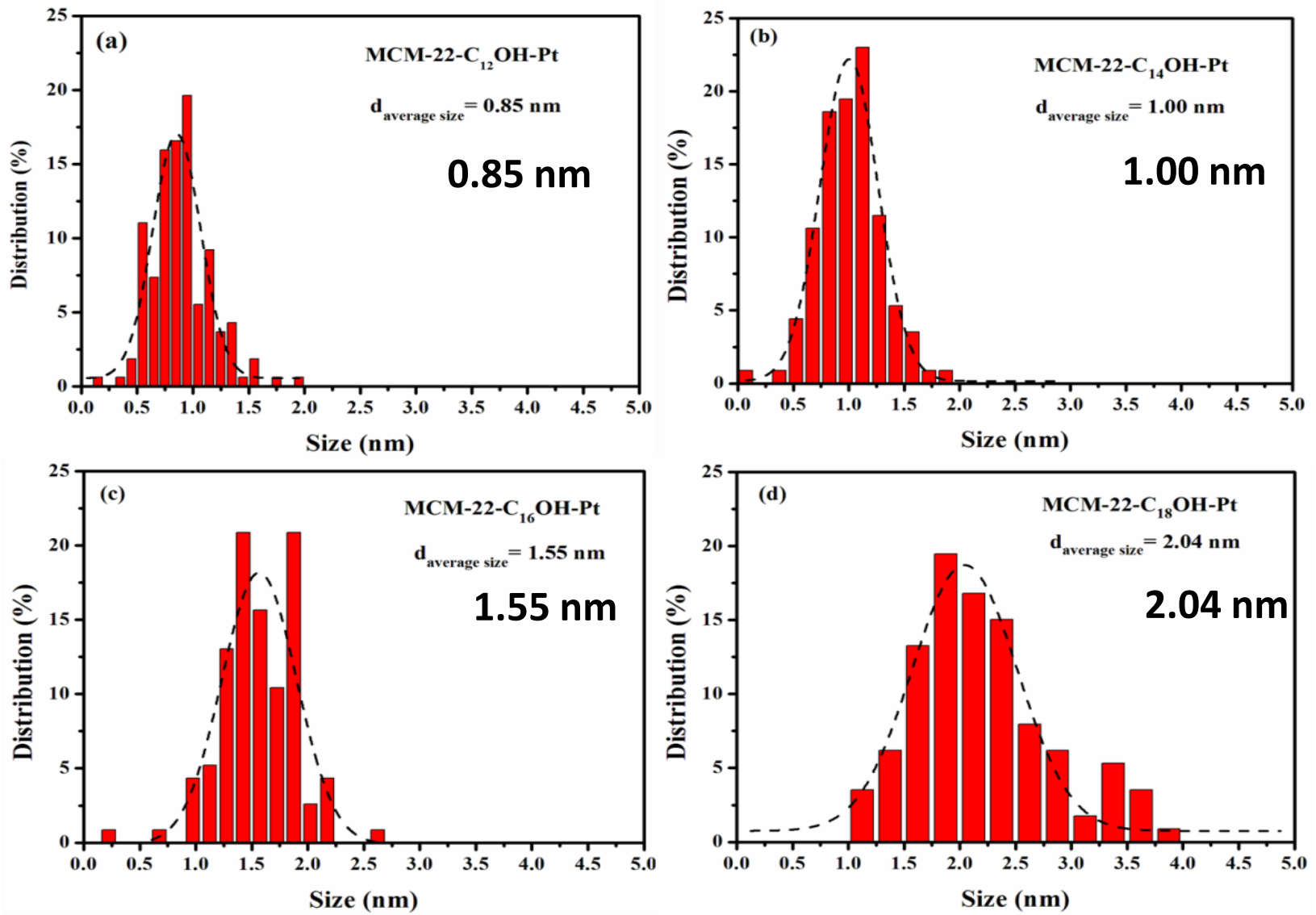

Y. Zhang et al. **Catal. Today**, 324, 2019, 135

Location of NPs

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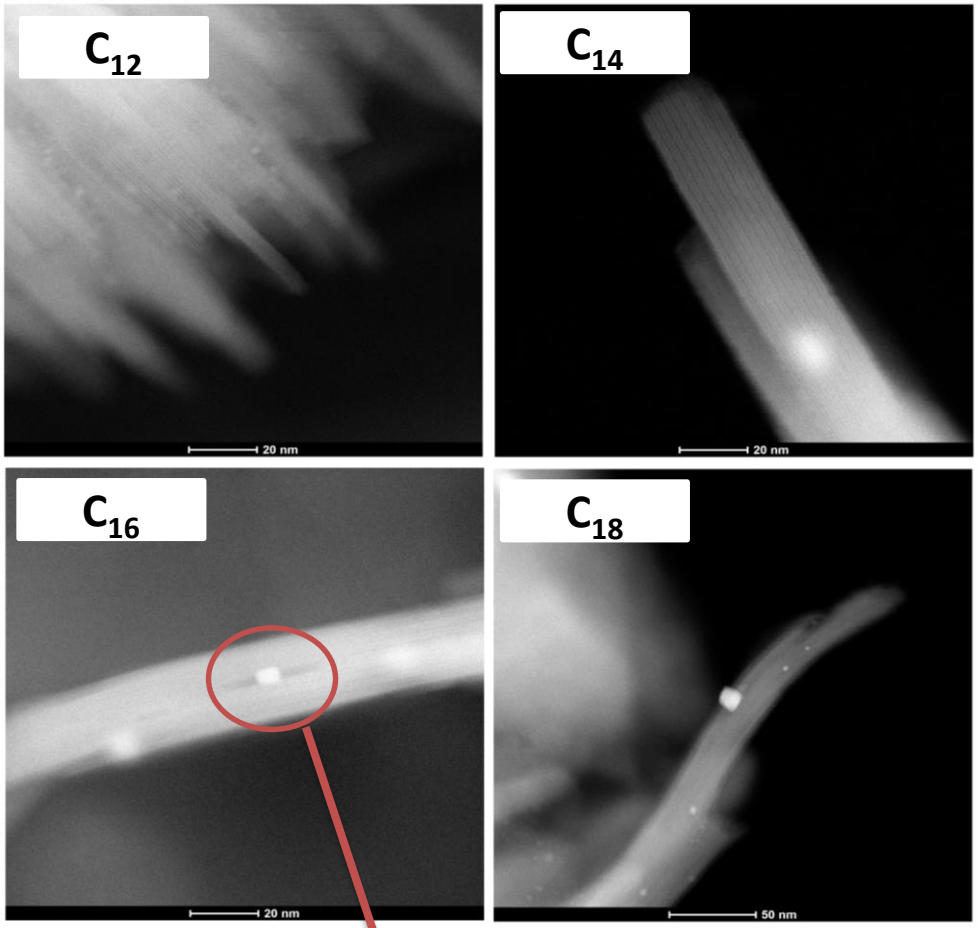
MCM-22 samples with Pt NPs



Pt NPs are merged into bulk MCM-22

Some Pt NPs are bigger than the voids and channels of MCM-22 structure which creates some defects in the framework

Need for the synthesis optimisation

NP stuck in between layers of MCM-22 disallowing full connection

Y. Zhang et al. **Catal. Today**, 324, 2019, 135

Spent catalyst imaging

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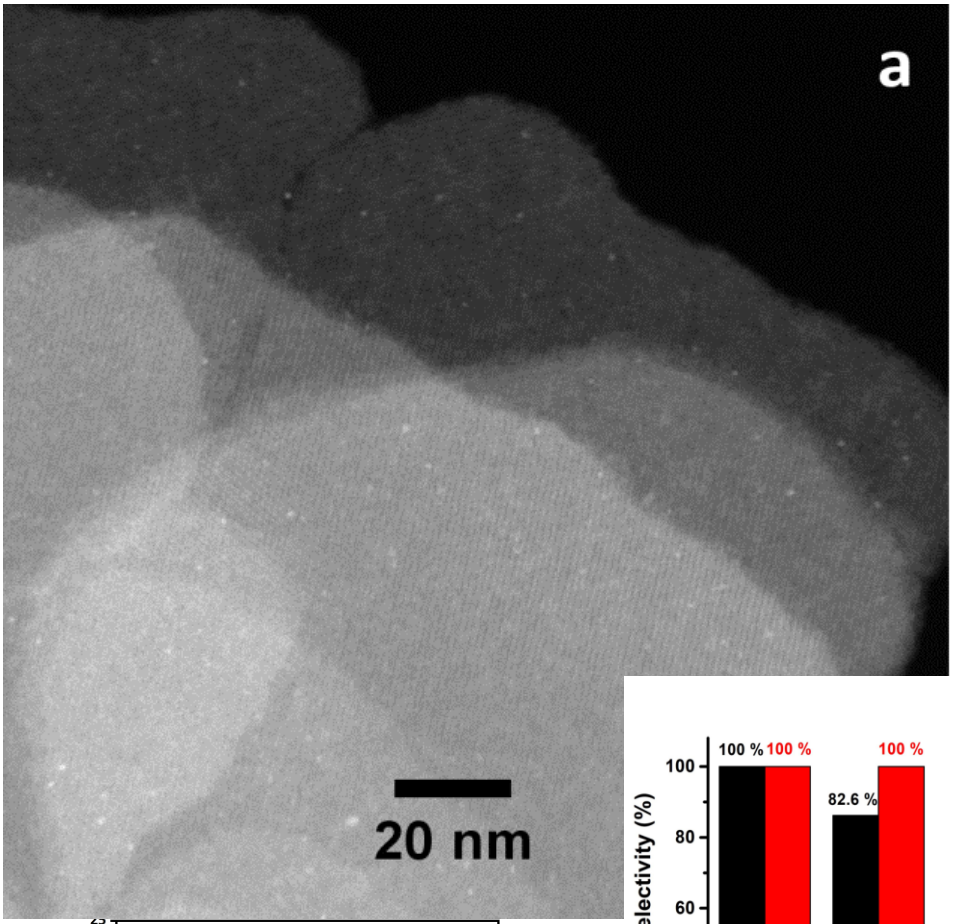

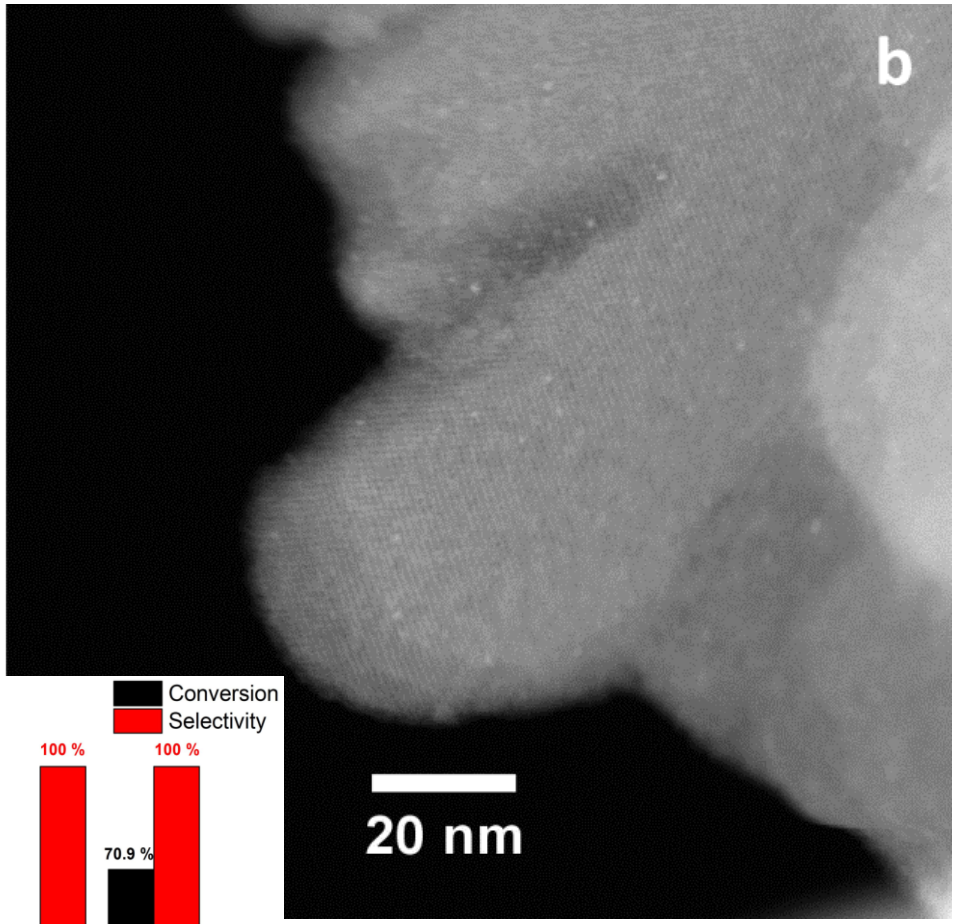

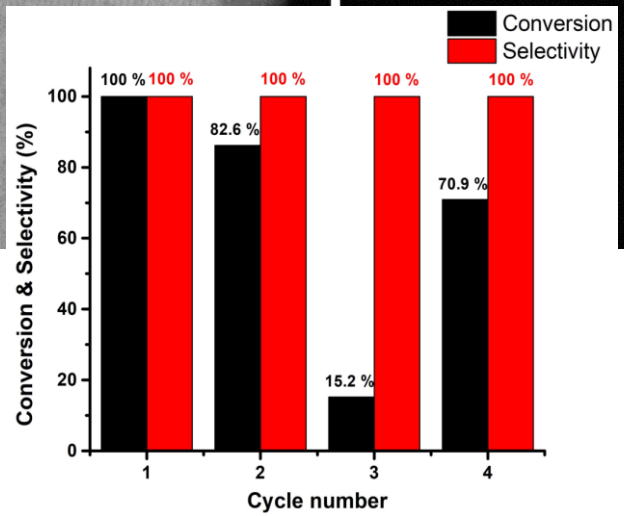

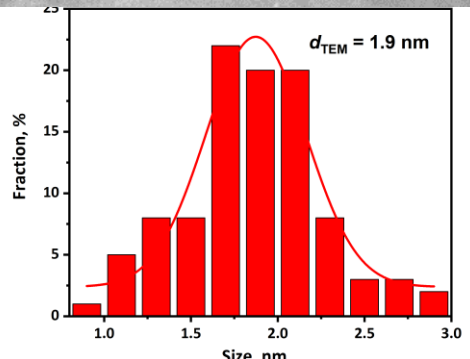

Y. Zhang et al. **Mater. Today Nano**, 2019, in press

Cryo-EM

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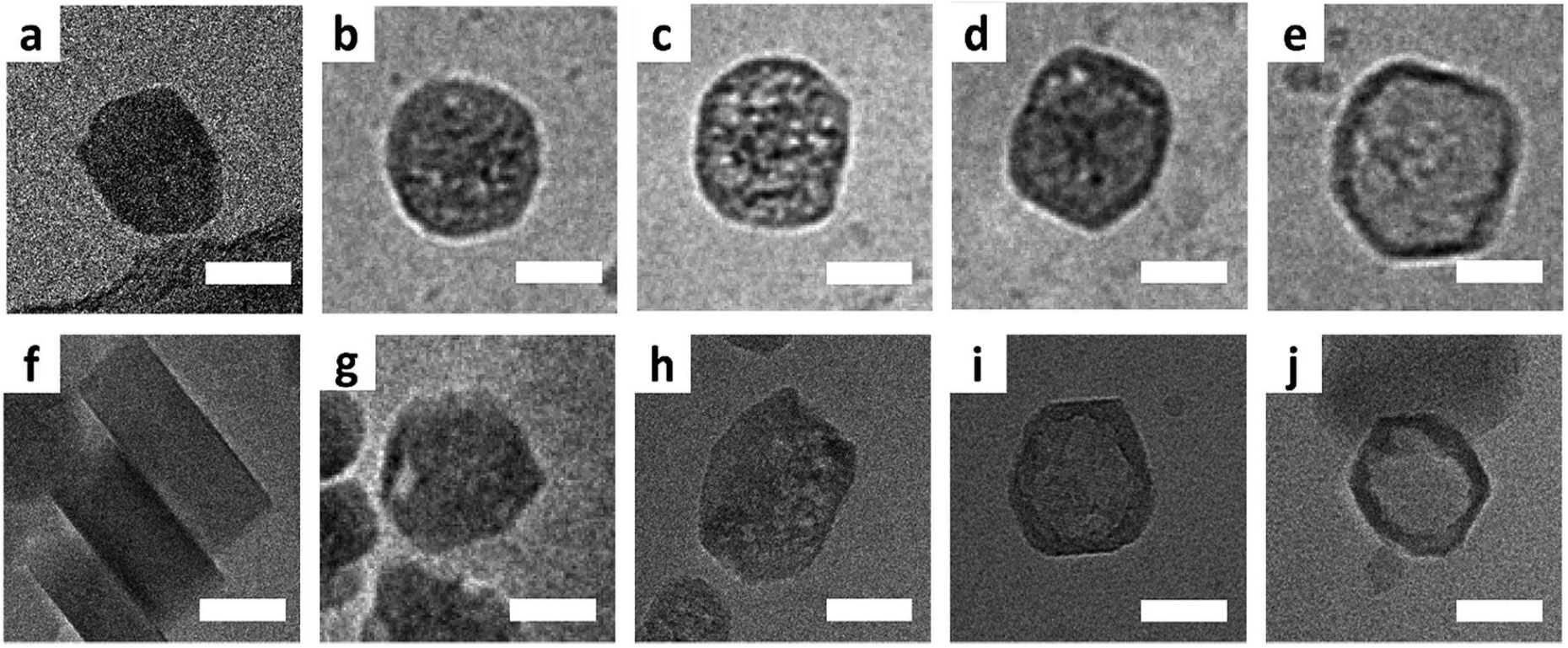

T. Li et al., ***J. Mater. Chem. A***, 2019,**7**, 1442-1446

MFI

Chemistry Nobel 2017 went to Jacques Dubochet, Joachim Frank, and Richard Henderson.

Cryo-EM

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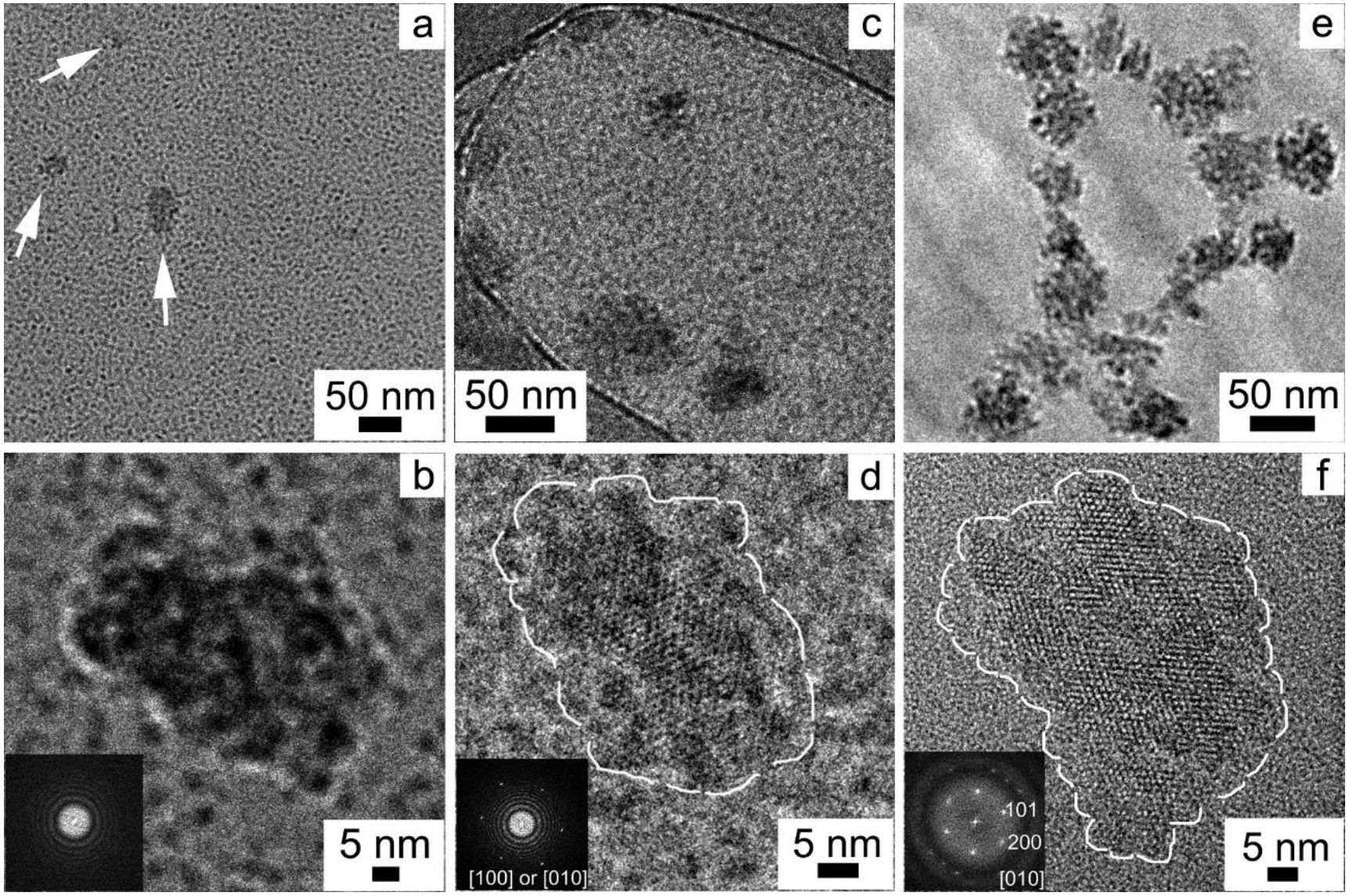

MFI

S. Kumar et al., ***J. Am. Chem. Soc.*** 2008, 130, 51, 17284-17286

Electron diffraction

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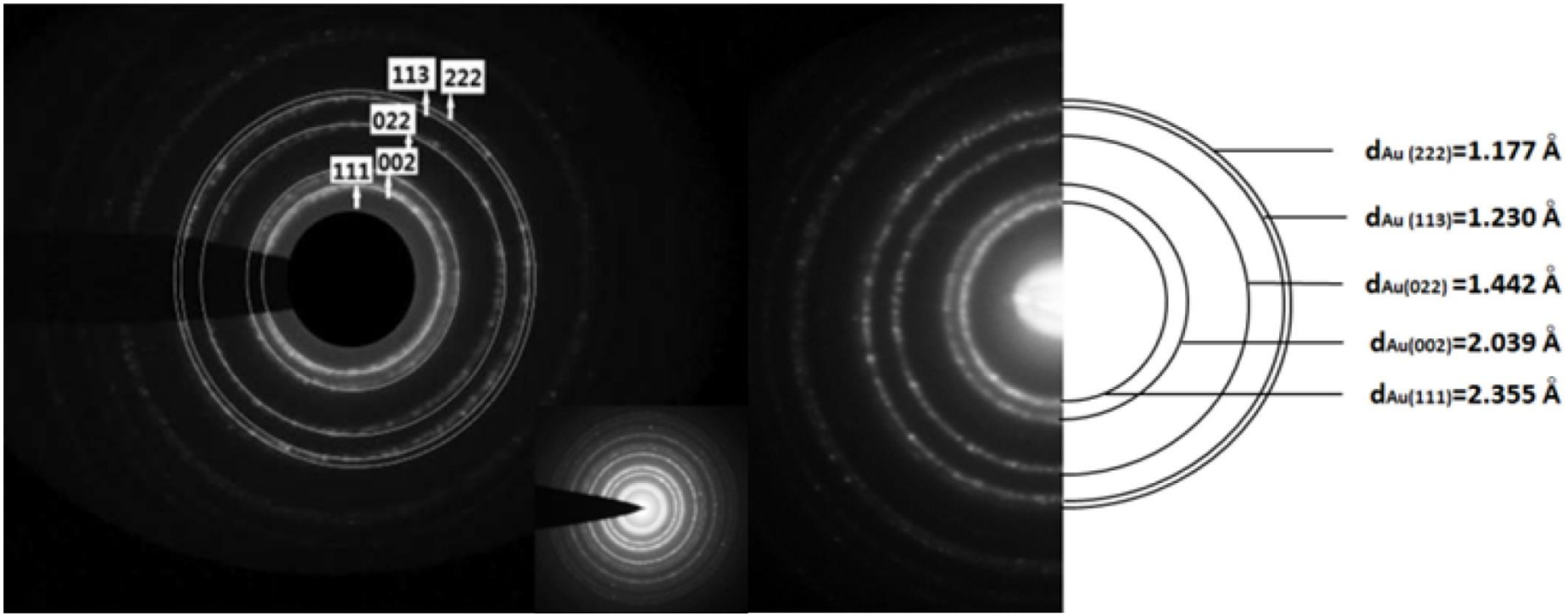
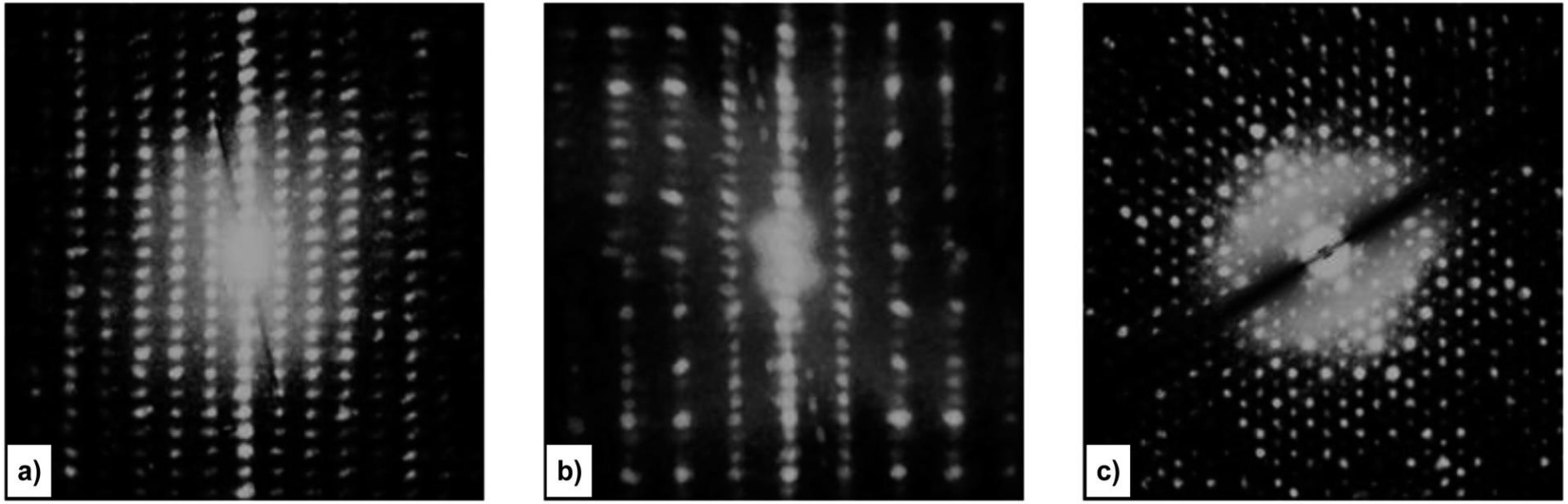
Electron diffraction technique utilizes the wave nature of electron in studying the crystal structure of the sample of interest in terms of chemical positions and nanoscale's atomic positions with high precision. This technique studies the phenomenon of the diffraction pattern resulting from the interference of a beam of electrons and the crystalline materials.



M. Asadabad et al. Modern Electron Microscopy in Physical and Life Sciences
DOI: 10.5772/61781

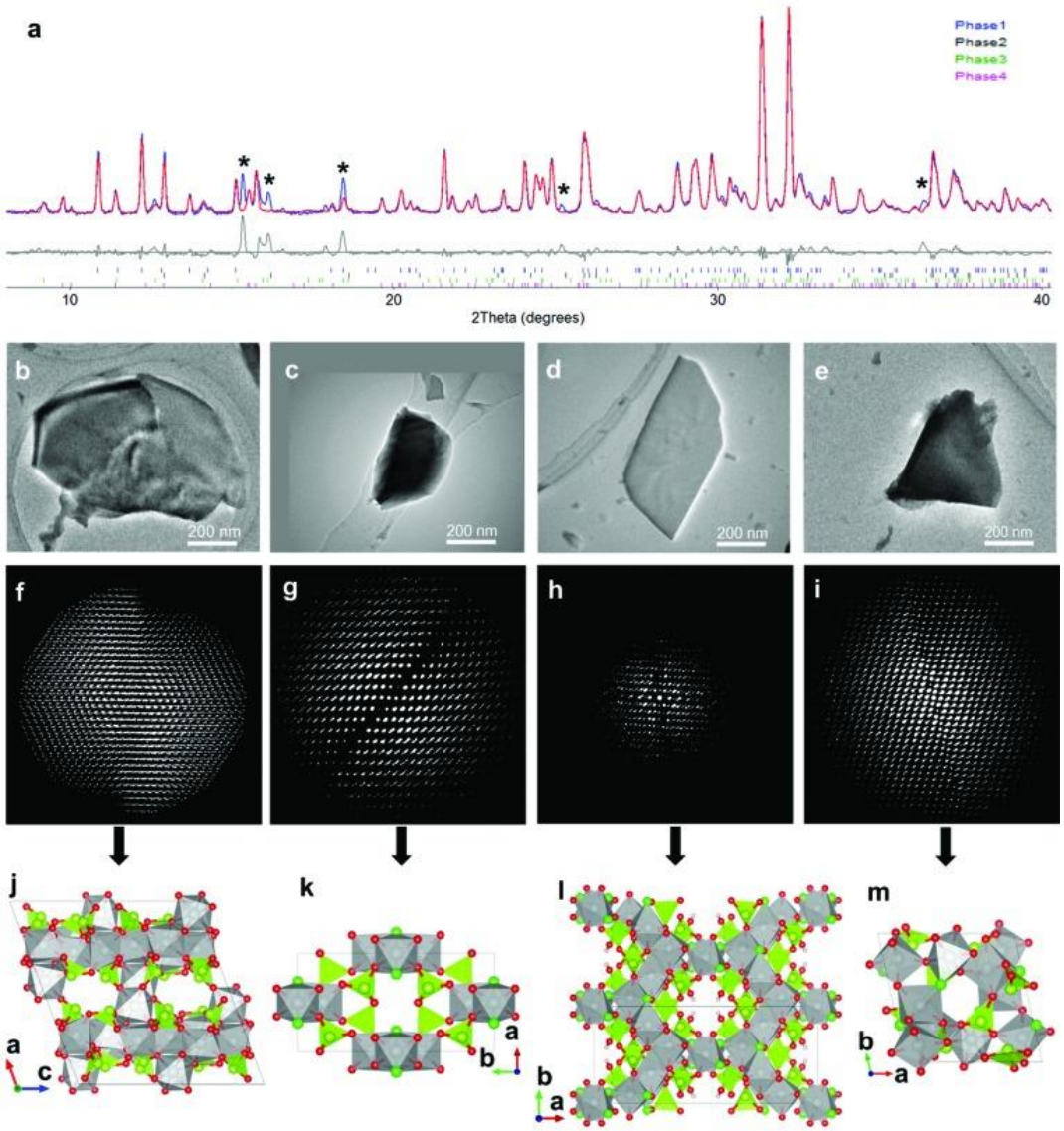
Structure determination from ED



Views along axis a* (a), axis b* (b), and axis c* (c) of the 3D ADT reconstructed volume of zeolite IM-17 (**UOV**)

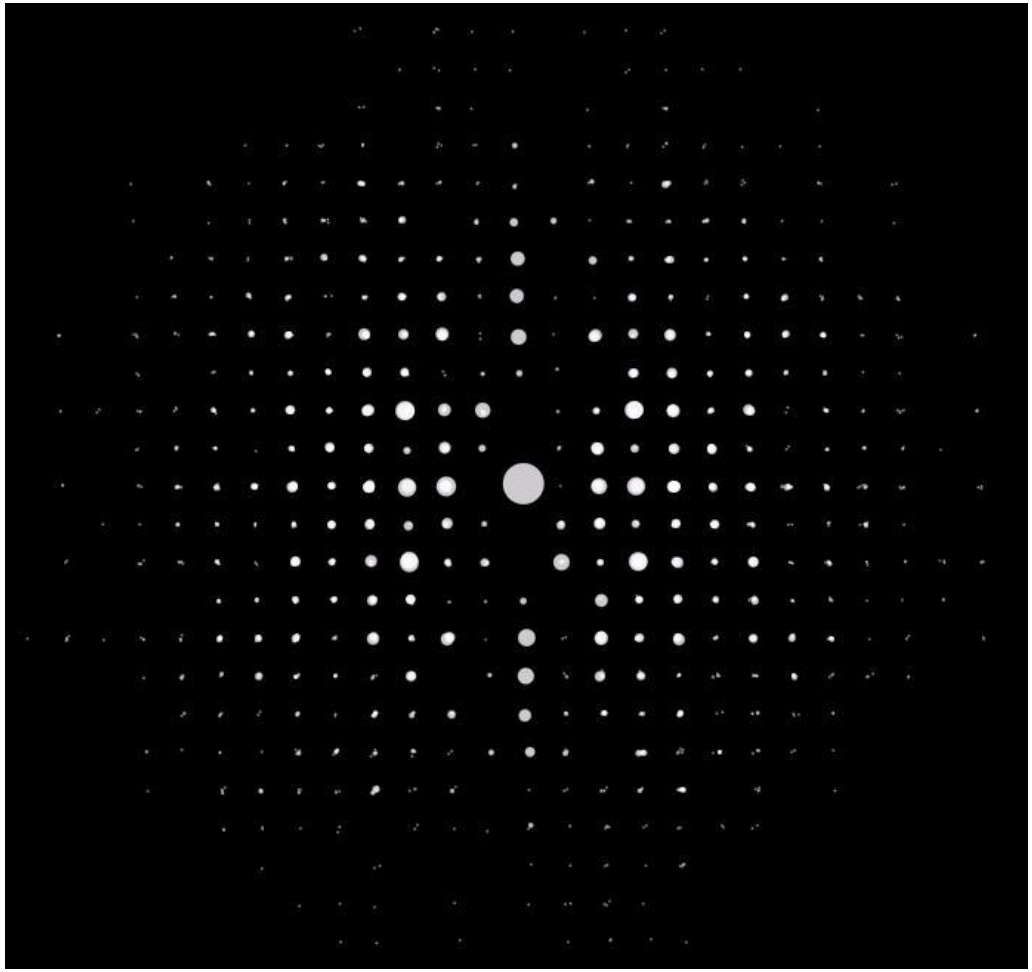
Y. Lorgoullioux et al., ***RSC Adv.***, 2014,**4**, 19440-19449

ED vs XRD

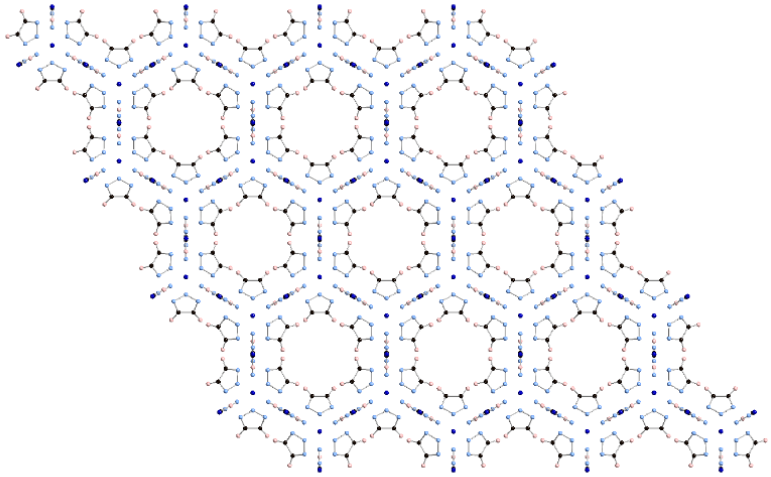


Yun, Y., Zou, X., Hovmoller, S. & Wan, W. (2015). IUCrJ 2, 267-282.

RED in use – MOF



3D data to create reciprocal lattice
→ Structure determination was possible



M. Infas H. Mohideen, et al. ***J. Mater. Chem. C***, 2019,**7**, 6692-6697

Serial Electron Diffraciton

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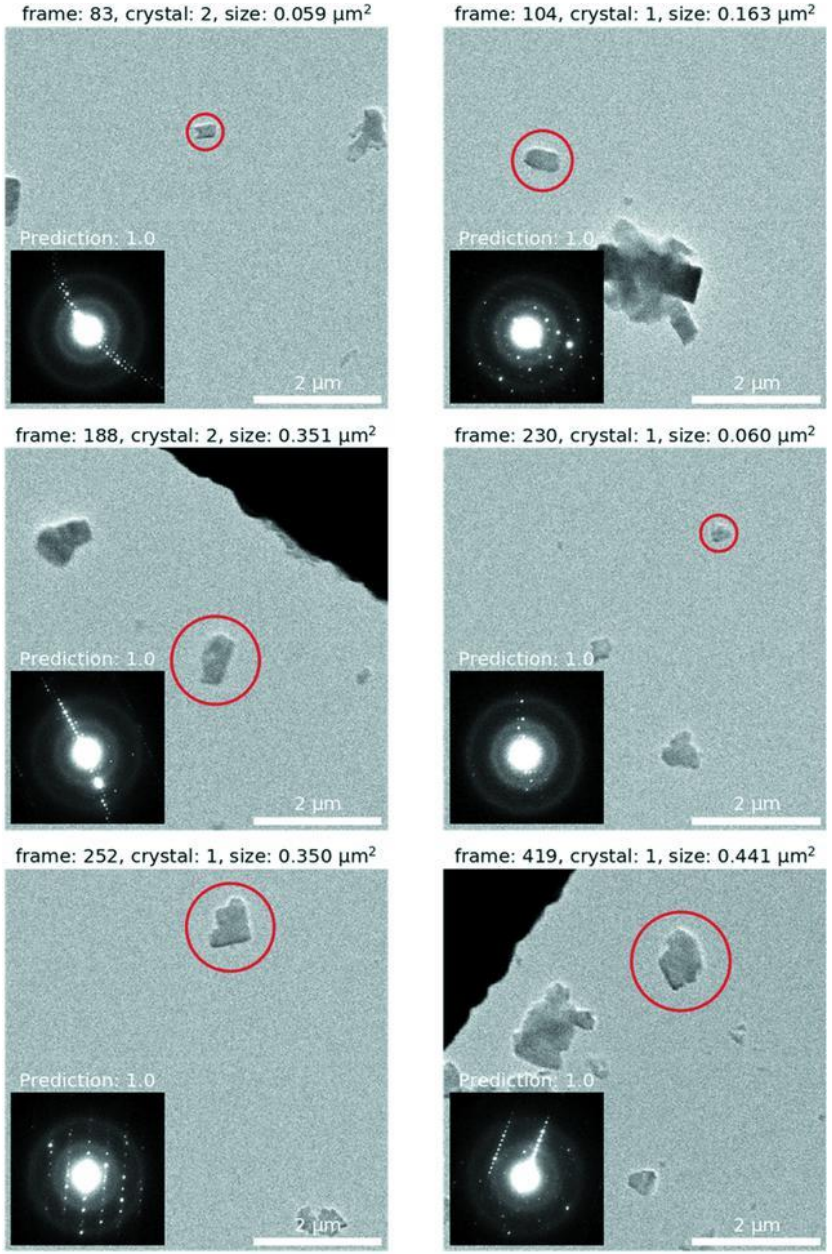

M. Cichocka *et al., J. Appl. Cryst.* (2018). **51**, 1652-1661

Vyhlídka

Metody elektronové mikroskopie se neustále vyvíjejí a jsou přístupnější a výkonnější

Jedná se o velmi přímé metody charakterizace katalyzátoru

Použití stále přesnější a automatizovanější přípravy vzorků před obrazovaním např. ultramikrotom / FIB, plazmové čištění

Charakterizace katalyzátorů je snazší a přesnější, např. sub-nanometrická částice kovů, stanovení struktury malých krystalů atd.

Rotační difrakční metody budou standardní metodou pro stanovení struktury

Poděkování

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Operational Programme Research,
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MINISTRY OF EDUCATION,
YOUTH AND SPORTS

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CUCAM projekt

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MLÁDEŽE A TĚLOVÝCHOVY