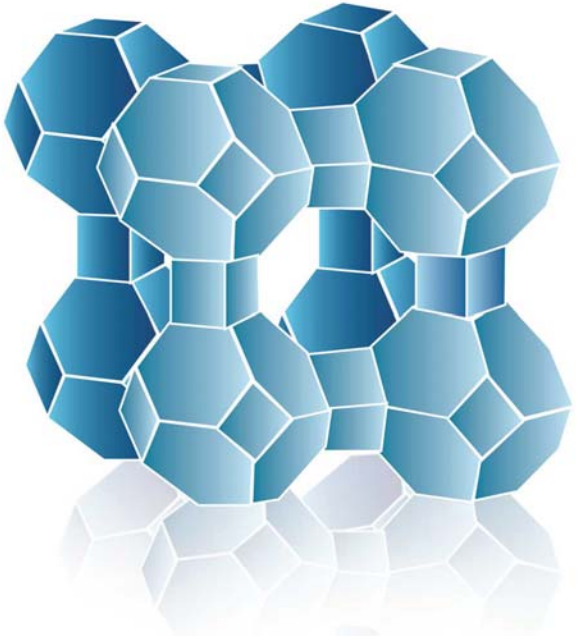
Synthesis of micro- and mesoporous materials



Jean-Philippe Tessonnier

Fritz Haber Institute of the Max Planck
Society, Berlin, Germany

Lecture Series
Heterogeneous Catalysis

Outline

Basic concepts on porosity and importance in catalysis

Porous materials in industry

How to design a hierarchical material? The example of silicates.

Short overview on other materials

Conclusion

Basic concepts on porosity

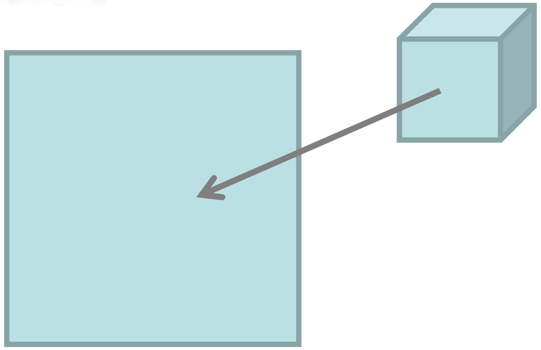
Porosity (and surface area) is generally required in heterogeneous catalysis:

- To improve the contact between the catalytic material and the reaction medium (gaseous or liquid)
- To achieve a good dispersion of the active phase on the surface of the support (avoid sintering)
- To increase the amount of active phase in your catalyst while keeping a good dispersion (increase the number of active sites)

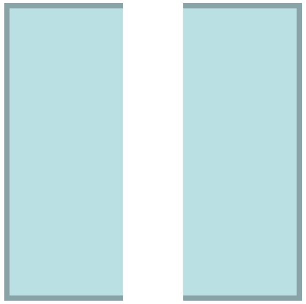
But also

- To allow only part of the molecules in the reaction mixture to react (sieving effect)
- To favor the formation of desired products by shape selectivity (transition state shape selectivity, tunnel shape selectivity)

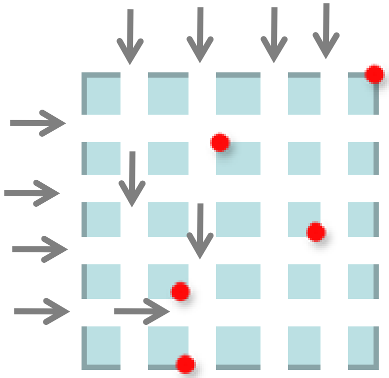
Contact between active sites and reactants



Surface area
of the cube: 6 a^2



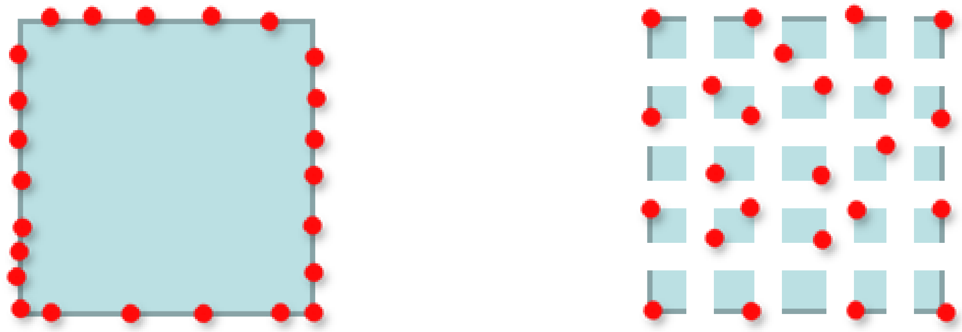
Gain: 2 a^2



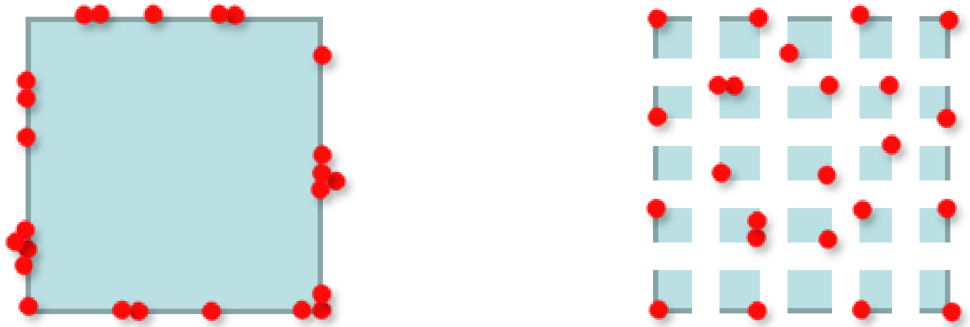
● Active site

Achieve a good dispersion and keep it

During catalyst synthesis:



Under reaction conditions:

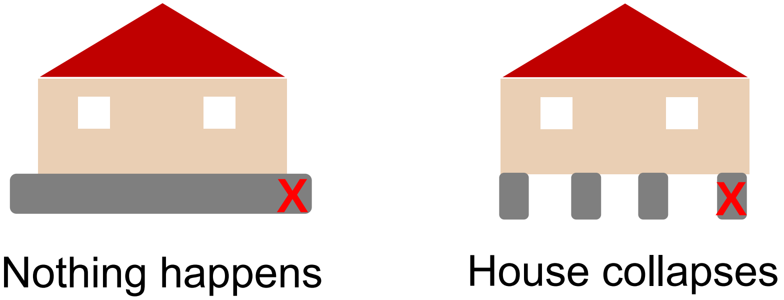


● Active site
24 for each sample

Drawbacks of porosity

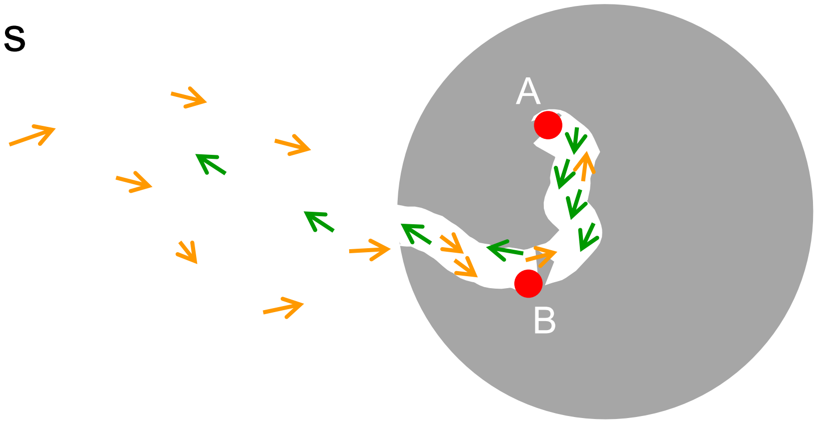
Low(er) mechanical strength

Serious problem if
- you want to fill a 10 m high fixed bed reactor (industry)
- you want to run a liquid phase reaction or operate a fluidized bed reactor (attrition)



Diffusion and mass transfer problems
Secondary reactions

- Slows down the reaction
- A and B see different concentrations of reactants and products; can modify the metal particle and/or its catalytic activity
- In case consecutive reactions are possible, will affect the selectivity of the reaction.



What is the right porosity / the right material?


UOP

Choosing a support is all about making compromises.

Many parameters are linked, which makes the choice even more difficult (cf. pore volume - specific surface area – mechanical stability)

Do not forget:

- A support is not an inert material. It may react with the active phase or with the reactants/products under reaction conditions. (Can be desired: bifunctional catalysts)
- It may undergo transformations (dissolution, phase transition, change in pore size distribution) depending on the pH, the temperature, the presence of steam, etc.

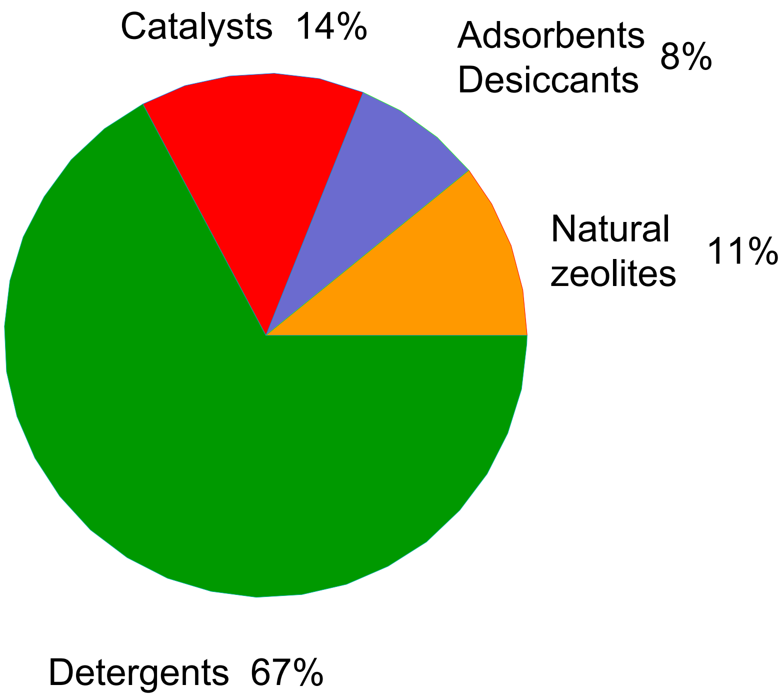
In fundamental research, the material aspects are the most important (dispersion, SMSI, modification of the active phase – chemical, structural, electronic).

At some point, you will have to take into account mass and heat transfers, particle morphology (packing in the reactor), deactivation/regeneration, recycling, costs for catalyst synthesis (problem for zeolites, SBA).

A typical example of catalyst design

Zeolites
Design at the atomic, micro, meso and macro levels

Importance of zeolites



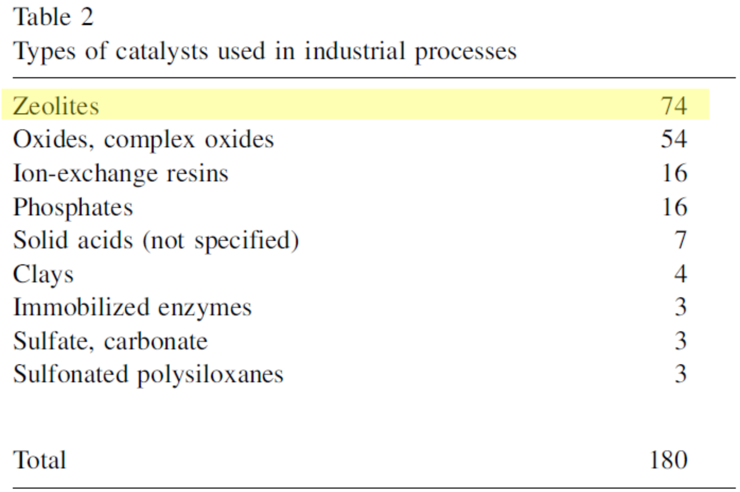


Table 2
Types of catalysts used in industrial processes

Zeolites	74
Oxides, complex oxides	54
Ion-exchange resins	16
Phosphates	16
Solid acids (not specified)	7
Clays	4
Immobilized enzymes	3
Sulfate, carbonate	3
Sulfonated polysiloxanes	3
Total	180

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Importance of zeolites in acid-base catalysis

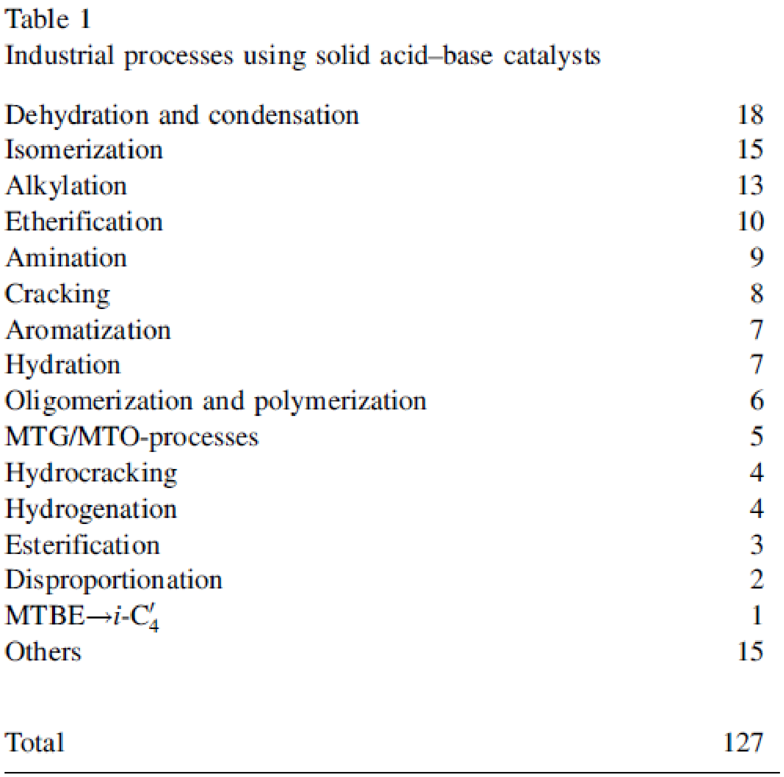

Table 1
Industrial processes using solid acid–base catalysts

Dehydration and condensation	18
Isomerization	15
Alkylation	13
Etherification	10
Amination	9
Cracking	8
Aromatization	7
Hydration	7
Oligomerization and polymerization	6
MTG/MTO-processes	5
Hydrocracking	4
Hydrogenation	4
Esterification	3
Disproportionation	2
$\text{MTBE}\rightarrow i\text{-C}_4'$	1
Others	15
Total	127

On 127 industrial processes listed in 1999, ca. 40% were catalyzed by zeolites.

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Example 1: EB synthesis

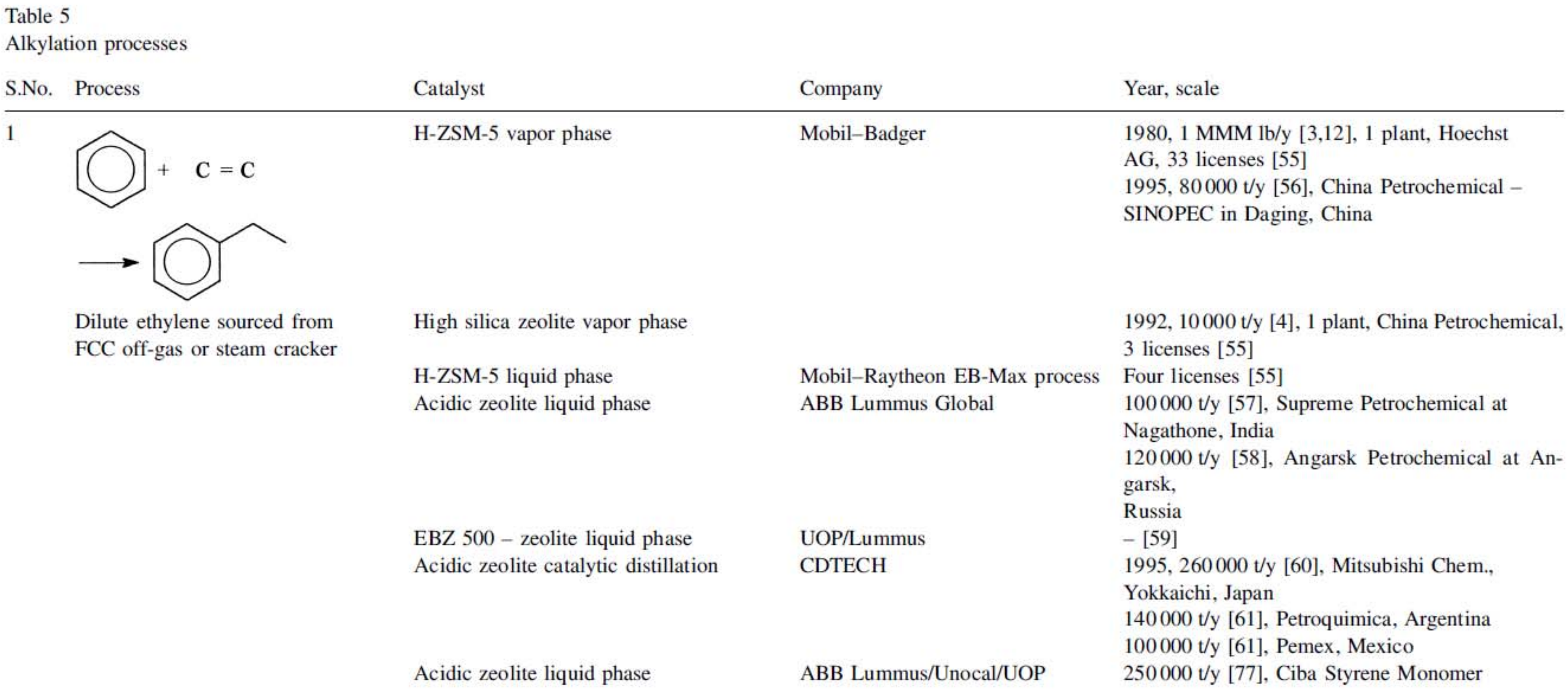

Table 5
Alkylation processes

S.No.	Process	Catalyst	Company	Year, scale
1	+ C = C	H-ZSM-5 vapor phase	Mobil–Badger	1980, 1 MMM lb/y [3,12], 1 plant, Hoechst AG, 33 licenses [55] 1995, 80000 t/y [56], China Petrochemical – SINOPEC in Daqing, China
	Dilute ethylene sourced from FCC off-gas or steam cracker	High silica zeolite vapor phase		1992, 10000 t/y [4], 1 plant, China Petrochemical, 3 licenses [55]
		H-ZSM-5 liquid phase	Mobil–Raytheon EB-Max process	Four licenses [55]
		Acidic zeolite liquid phase	ABB Lummus Global	100000 t/y [57], Supreme Petrochemical at Nagathone, India 120000 t/y [58], Angarsk Petrochemical at Angarsk, Russia
		EBZ 500 – zeolite liquid phase	UOP/Lummus	– [59]
		Acidic zeolite catalytic distillation	CDTECH	1995, 260000 t/y [60], Mitsubishi Chem., Yokkaichi, Japan 140000 t/y [61], Petroquimica, Argentina 100000 t/y [61], Pemex, Mexico
		Acidic zeolite liquid phase	ABB Lummus/Unocal/UOP	250000 t/y [77], Ciba Styrene Monomer

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Example 2: Xylene isomerization

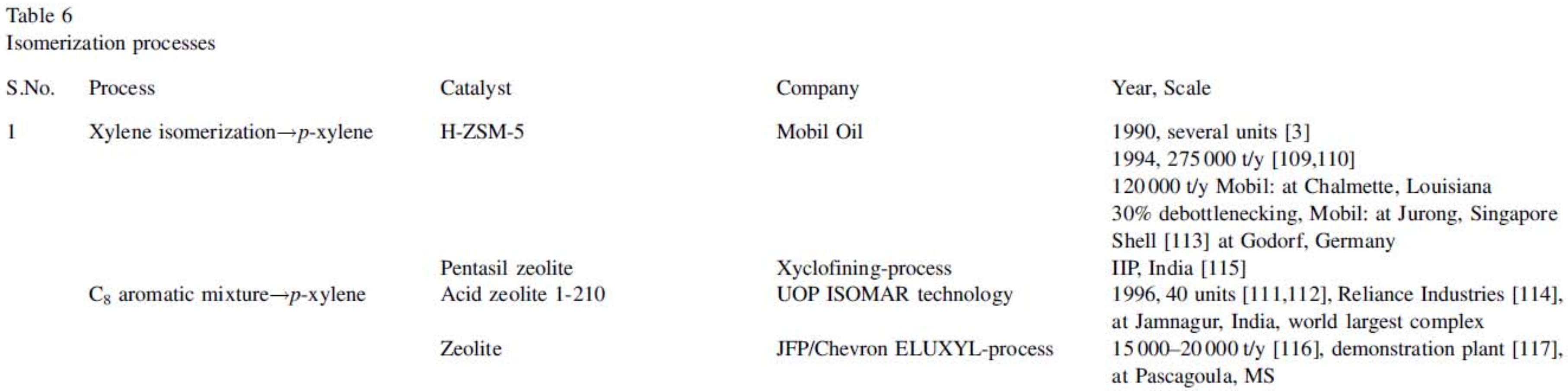

Table 6
Isomerization processes

S.No.	Process	Catalyst	Company	Year, Scale
1	Xylene isomerization→*p*-xylene	H-ZSM-5	Mobil Oil	1990, several units [3] 1994, 275 000 t/y [109,110] 120 000 t/y Mobil: at Chalmette, Louisiana 30% debottlenecking, Mobil: at Jurong, Singapore Shell [113] at Godorf, Germany
		Pentasil zeolite	Xyclofining-process	IIP, India [115]
	C_8 aromatic mixture→*p*-xylene	Acid zeolite 1-210	UOP ISOMAR technology	1996, 40 units [111,112], Reliance Industries [114], at Jamnagur, India, world largest complex
		Zeolite	JFP/Chevron ELUXYL-process	15 000–20 000 t/y [116], demonstration plant [117], at Pascagoula, MS

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Example 3: Fluid Catalytic Cracking (FCC)

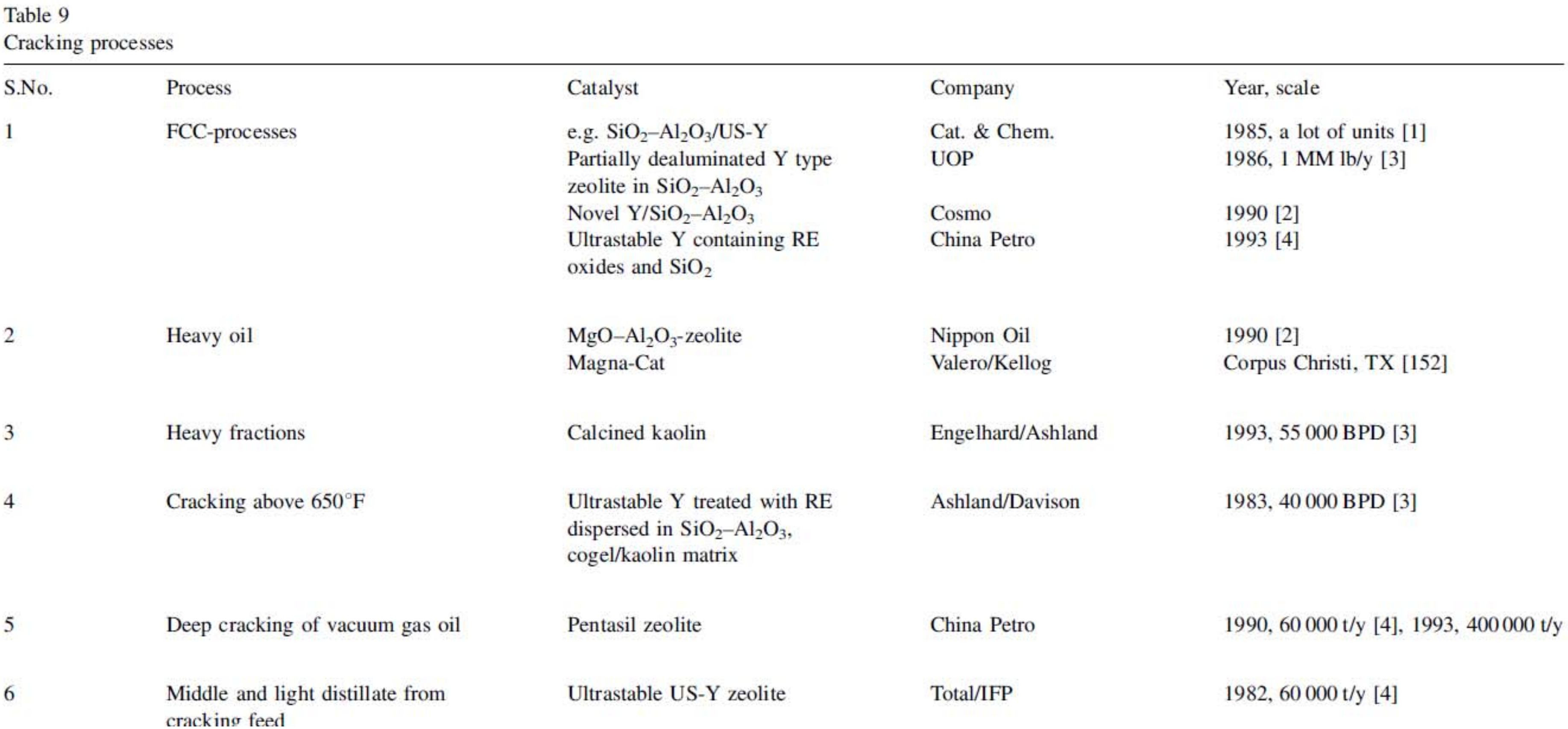

Table 9
Cracking processes

S.No.	Process	Catalyst	Company	Year, scale
1	FCC-processes	e.g. SiO_2–Al_2O_3/US-Y Partially dealuminated Y type zeolite in SiO_2–Al_2O_3 Novel Y/SiO_2–Al_2O_3 Ultrastable Y containing RE oxides and SiO_2	Cat. & Chem. UOP Cosmo China Petro	1985, a lot of units [1] 1986, 1 MM lb/y [3] 1990 [2] 1993 [4]
2	Heavy oil	MgO–Al_2O_3-zeolite Magna-Cat	Nippon Oil Valero/Kellog	1990 [2] Corpus Christi, TX [152]
3	Heavy fractions	Calcined kaolin	Engelhard/Ashland	1993, 55 000 BPD [3]
4	Cracking above 650°F	Ultrastable Y treated with RE dispersed in SiO_2–Al_2O_3, cogel/kaolin matrix	Ashland/Davison	1983, 40 000 BPD [3]
5	Deep cracking of vacuum gas oil	Pentasil zeolite	China Petro	1990, 60 000 t/y [4], 1993, 400 000 t/y
6	Middle and light distillate from cracking feed	Ultrastable US-Y zeolite	Total/IFP	1982, 60 000 t/y [4]

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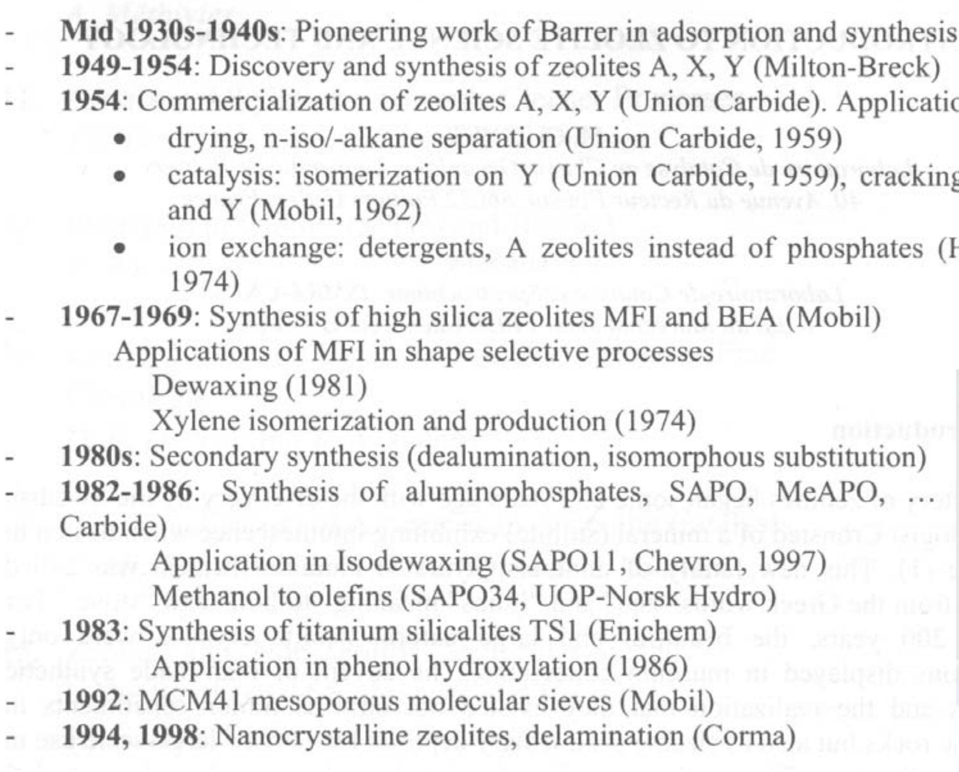
Milestones in zeolite synthesis

- **1756:** Crönsted discovers that when heating stilbite, large amounts of steam are produced. He calls this family of minerals “zeolite”, from Greek “zeo” (to boil) and “lithos” (stone).

Zeolites stay in museums for 200 years.



- **Mid 1930s-1940s**: Pioneering work of Barrer in adsorption and synthesis
- **1949-1954**: Discovery and synthesis of zeolites A, X, Y (Milton-Breck)
- **1954**: Commercialization of zeolites A, X, Y (Union Carbide). Applications in
  - drying, n-iso/-alkane separation (Union Carbide, 1959)
  - catalysis: isomerization on Y (Union Carbide, 1959), cracking on X and Y (Mobil, 1962)
  - ion exchange: detergents, A zeolites instead of phosphates (Henkel, 1974)
- **1967-1969**: Synthesis of high silica zeolites MFI and BEA (Mobil)
  Applications of MFI in shape selective processes
  Dewaxing (1981)
  Xylene isomerization and production (1974)
- **1980s**: Secondary synthesis (dealumination, isomorphous substitution)
- **1982-1986**: Synthesis of aluminophosphates, SAPO, MeAPO, … Carbide)
  Application in Isodewaxing (SAPO11, Chevron, 1997)
  Methanol to olefins (SAPO34, UOP-Norsk Hydro)
- **1983**: Synthesis of titanium silicalites TS1 (Enichem)
  Application in phenol hydroxylation (1986)
- **1992**: MCM41 mesoporous molecular sieves (Mobil)
- **1994, 1998**: Nanocrystalline zeolites, delamination (Corma)

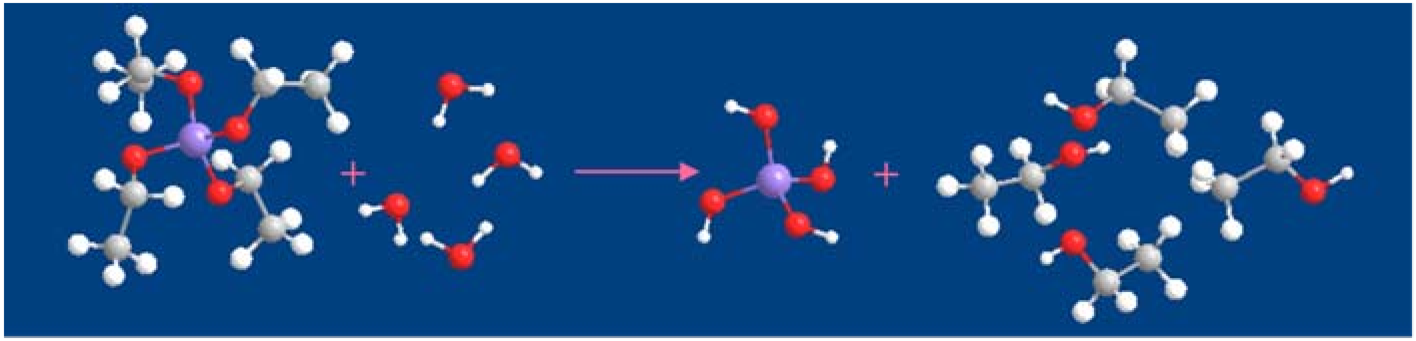
Chabasite-Ce, Sr
Coll. Z. Gabelica © R. Warin

Yugawaralite - Nasik

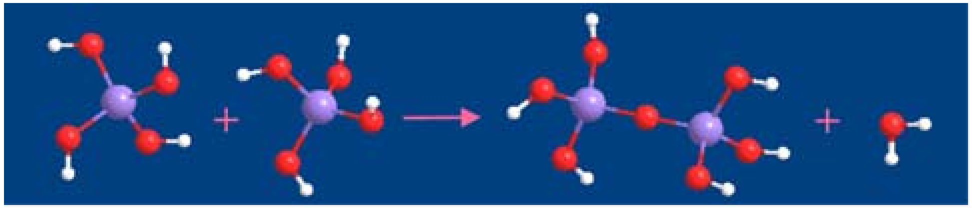
Silicate synthesis

Typically: sol-gel synthesis, using tetraethoxysilane ($Si(OC_2H_5)_4$, TEOS)

1st step: TEOS hydrolysis $\longrightarrow$ $Si(OH)_4 + 4\ C_2H_5OH$



2nd step: Silanol condensation



Structured silicate synthesis

TEOS hydrolysis and condensation is catalyzed at both low pH and high pH (slowest at pH 7).

Low pH (<1)

Hydrolysis wins over condensation. Formation of small particles, followed by progressive aggregation. If an organic template is present, such as a surfactant, the particles will aggregate around the micelles.

SBA-15: P-123 triblock copolymer. Forms cylindrical micelles.

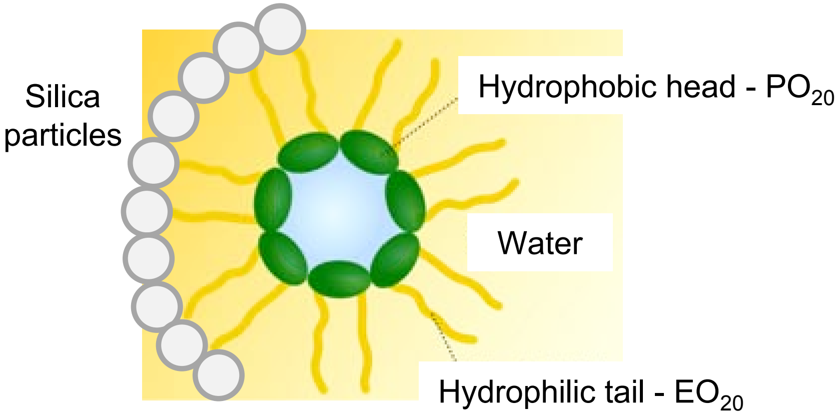
$HO(CH_2CH_2O)_{20} - (CH_2CH(CH_3)O)_{70} - (CH_2CH_2O)_{20}H$

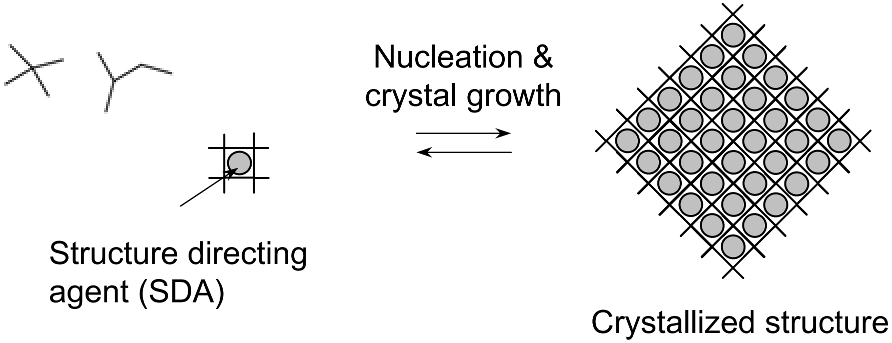
Poly(Oxyethylene) - Poly(Oxypropylene) - Poly(Oxyethylene)

High pH (>10)

Condensation reaction faster than hydrolysis. Formation of nuclei, growth by addition/condensation of monomers. Particles are negatively charged, which prevents the formation of aggregates.

Zeolites: Condensation occurs around a SDA, typically an inorganic (Na^+) or organic cation (Tetrapropylammonium, TPA^+).



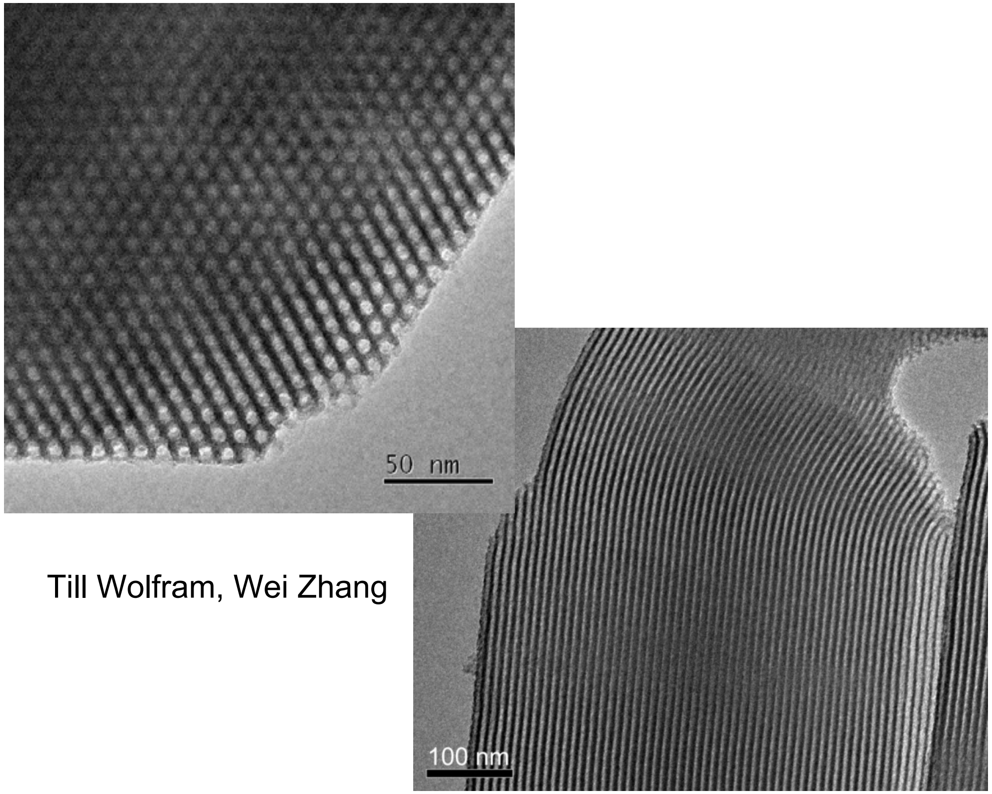


Difference between both routes

Low pH (<1)

Amorphous silica particles aggregate around the cylindrical micelles (template).

The result is an ordered mesoporous material, but which remains amorphous.

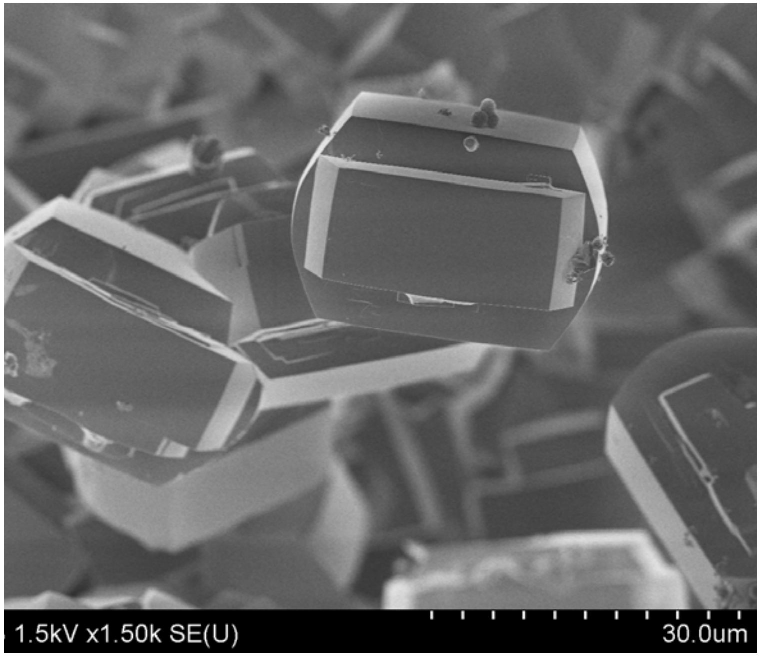


Till Wolfram, Wei Zhang

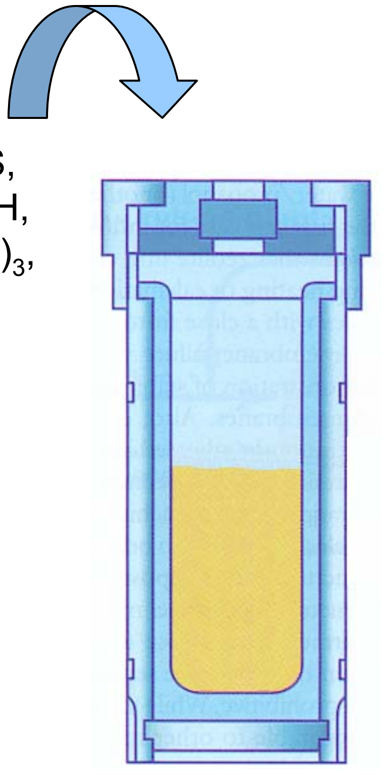
High pH (>10)

Condensation occurs around an atomic/molecular template.

Hydrothermal synthesis at 150-275°C for several days. Progressive reconstruction of the material until forming a crystalline structure. Zeolites are microporous materials.

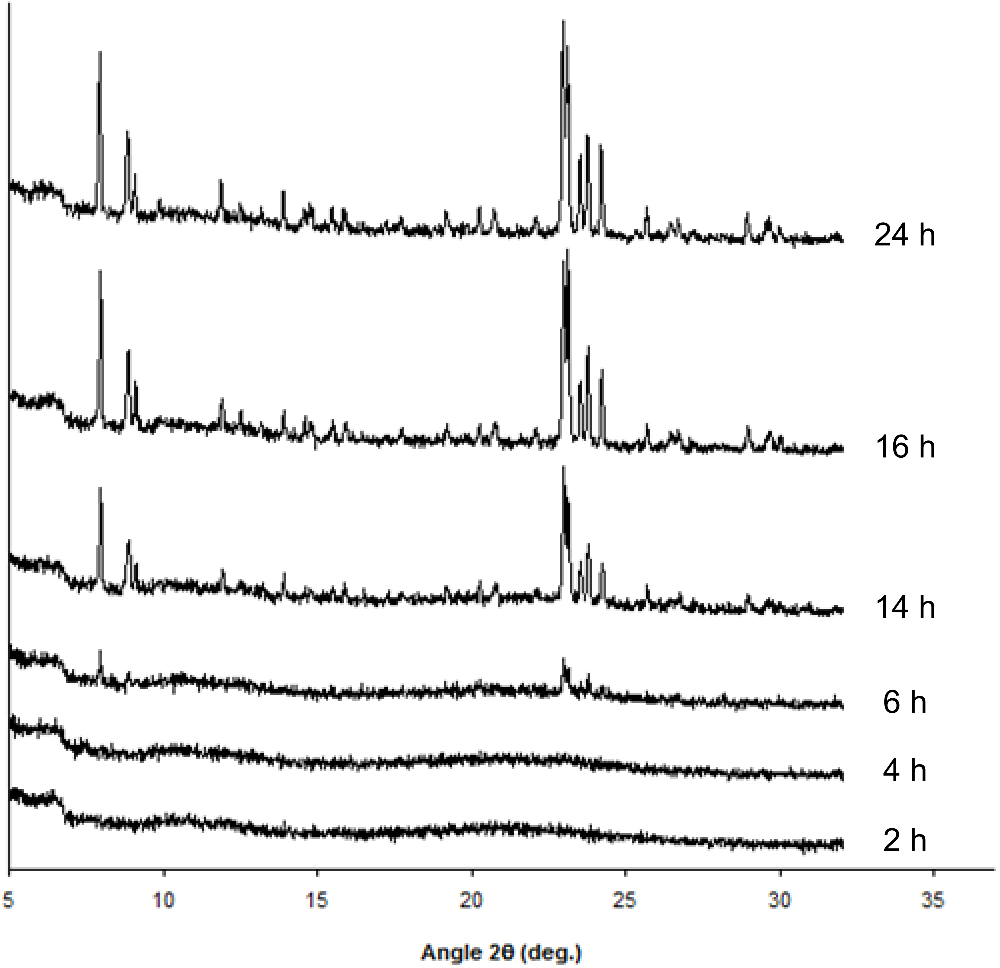


Example: ZSM-5 zeolite



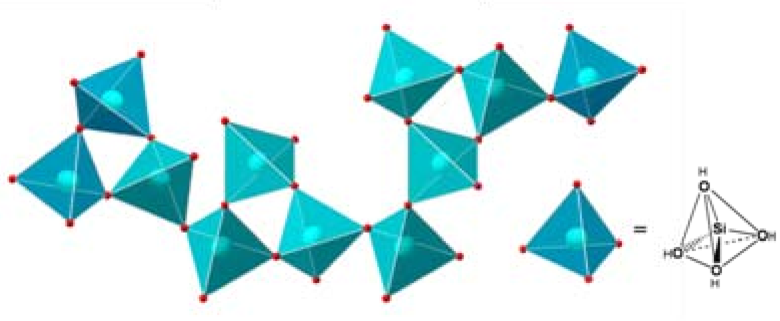
TEOS,
TPAOH,
$Al(NO_3)_3$,
H_2O

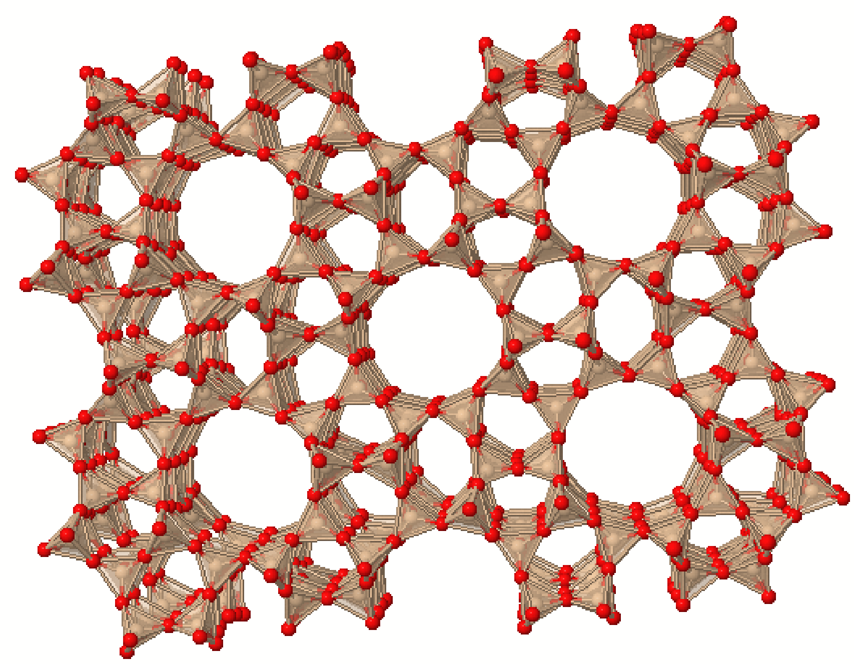
Placed in the oven, 150°C



Zeolite structure

Connecting SiO_4 tetrahedra in such a way that a crystalline, porous structure is formed.



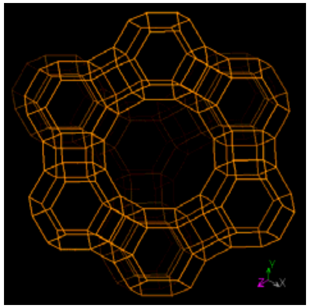


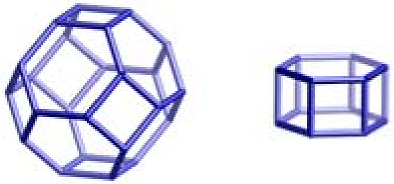
There are 48 natural zeolite structures.
There are 194 known structures in total (18 new framework types since 2008).

http://www.iza-structure.org/
http://mrsec.wisc.edu/Edetc/pmk/pages/ZSM5.html

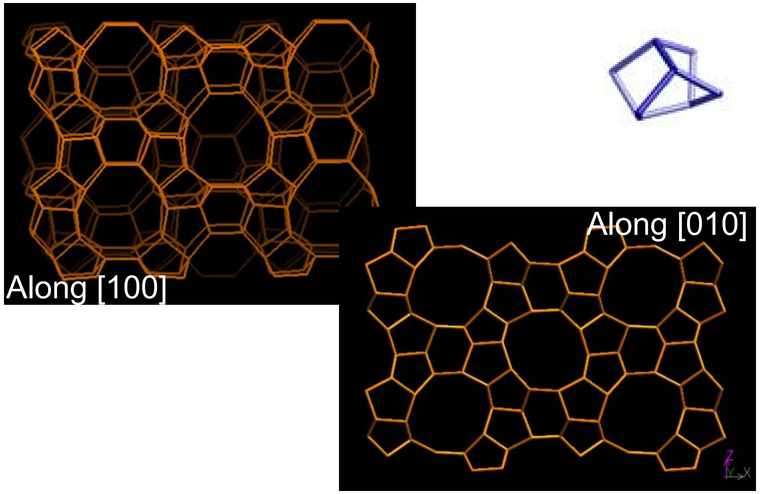
Famous zeolite structures

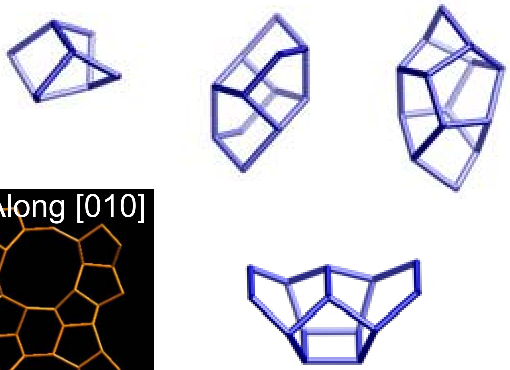
Structure	Building blocks	Name & information



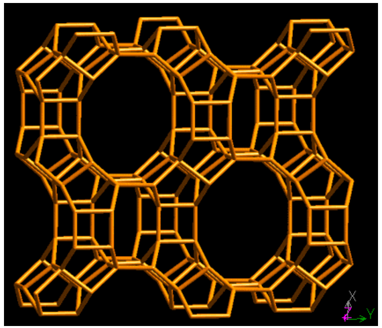


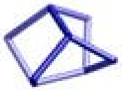
Framework type: FAU
Zeolite names: Y, USY
12 T atoms
3-D pore system
Pore diameter: 7.4 Å + super-cage 13 Å
Application: cracking





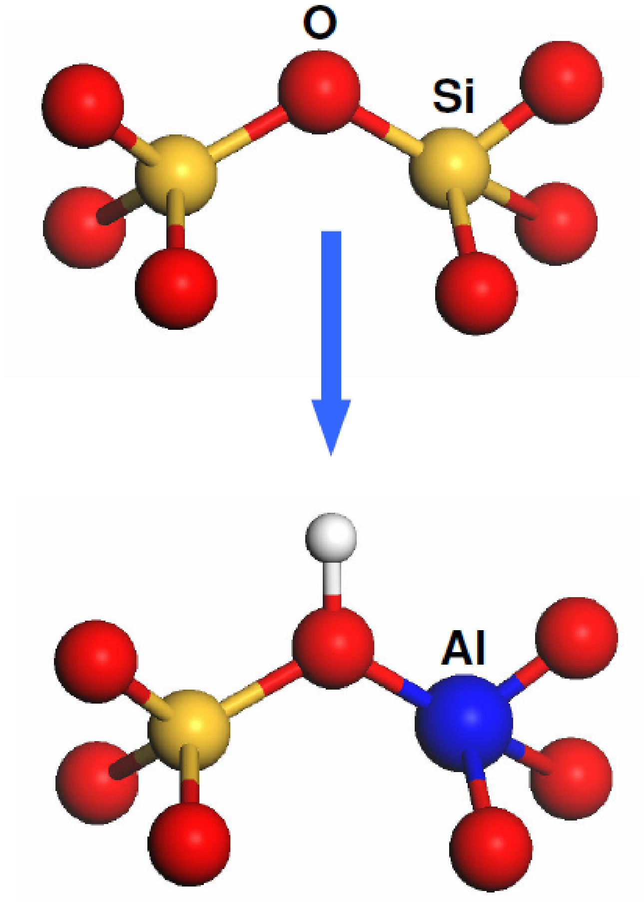
Framework type: MFI
Zeolite names: ZSM-5, Silicalite
10 T atoms
3-D pore system
Pore diameter: 5.1 x 5.5 Å, 5.3 x 5.6 Å
Application: isomerization, alkylation
aromatization





Framework type: MOR
Zeolite names: Mordenite
12 T atoms
1-D pore system
Pore diameter: 6.5 x 7.0 Å
Application: isomerization, alkylation

Introduction of an active site



No framework charge

One negative excess charge per Al

Compensating cations to ensure overall neutrality

Protons give zeolites Brönsted acidic properties

Introduction of an active site

- Most zeolites are crystalline aluminosilicates.

- General formula: $M_{x/n}(AlO_2)_x(SiO2)_y$

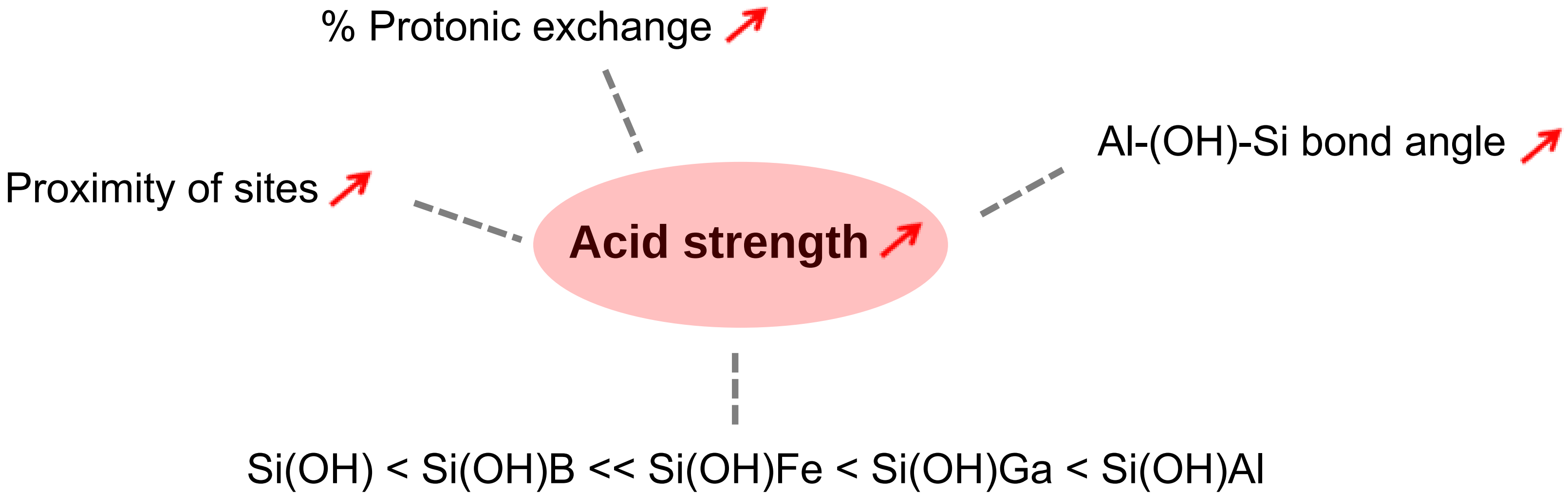
  M is a cation of valence n, x+y is the total number of tetrahedra per unit cell

- x/y corresponds to the atomic Si/Al ratio. The lowest Si/Al ratio is 1 (Lowenstein’s rule).

- The highest number of protonic sites is the number of framework Al atoms (for Si/Al = 1, $[H^+] = 8.3$ mmol g^{-1}). In general it is slightly lower because of ion exchange, dehydroxylation, etc.

Tuning the acid sites' density and strength

- Density: Number of acid sites ≈ number of Al atoms. In general, 100% of Al in the gel is introduced in the zeolite framework.
- Strength:



% Protonic exchange ↗

Proximity of sites ↗

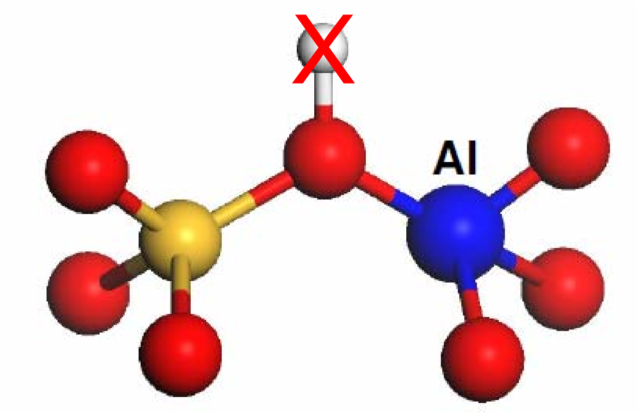
Acid strength ↗

Al-(OH)-Si bond angle ↗

Si(OH) < Si(OH)B << Si(OH)Fe < Si(OH)Ga < Si(OH)Al

Example:
Acid sites in HMOR (143-180°) are stronger than in HFAU (138-147°), which explains why HMOR isomerizes n-C_4 and n-C_6 at 200-250°C while HFAU cannot.

Other use of acid sites – anchoring metals



Replace H^+ by another cation
using ion exchange (totally or partially).

If partial exchange → bifunctional catalyst

Fe-ZSM-5: $C_6H_6 + N_2O \rightarrow$ phenol

Cu-ZSM-5: deNO$_x$

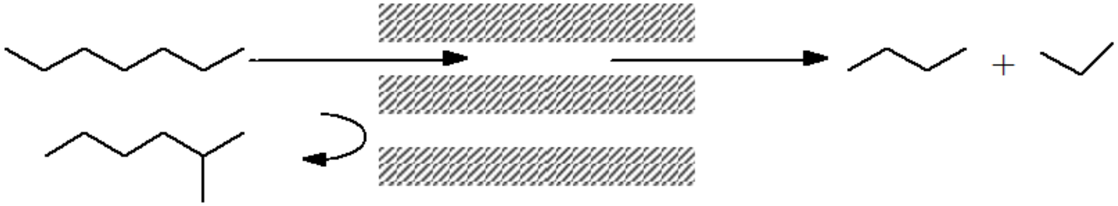
Ga-ZSM-5: propane aromatization

Mo-ZSM-5: methane aromatization

Importance of the pore size

Shape selectivity!

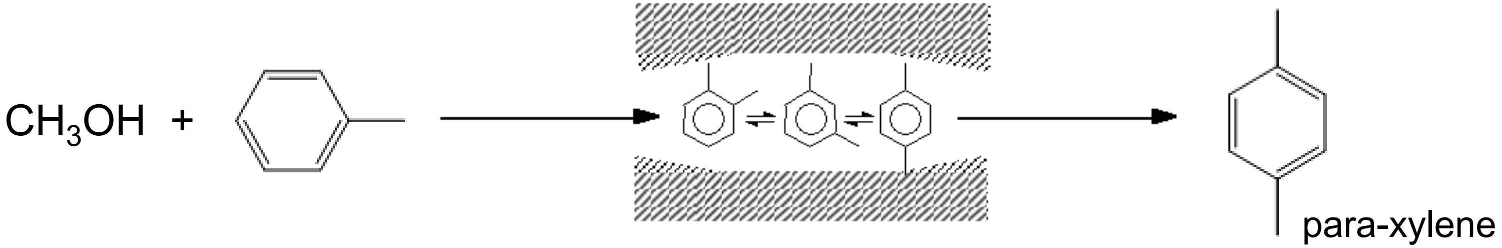
1. Reactant selectivity



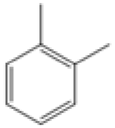
Molecular sieving effect. Only molecules which can diffuse into the crystal will be transformed. Application: separation of n-C_4/i-C_4, cracking of n-C_6.

Shape selectivity by tuning the pore size

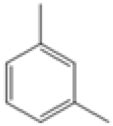
2. Product selectivity



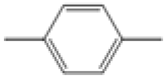
Thermodynamic equilibrium at 400 °C:



ortho, 27%
Phthalic anhydride



meta, 50%
Isophtalic acid used as co-polymer for PET

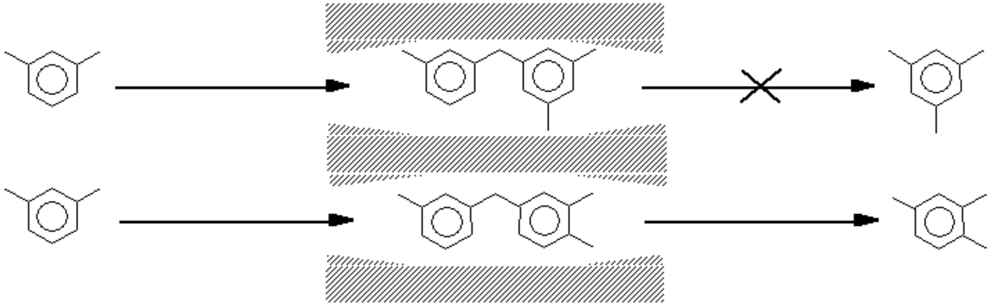


para, 23%
Terephthalic acid, polyester

Para-xylene is the main product because of its faster diffusion.
Ortho- and meta-xylene are isomerized to para-xylene while diffusing.

Shape selectivity by tuning the pore size

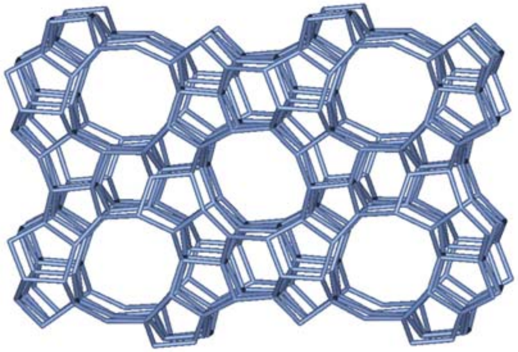
3. Restricted transition-state selectivity



The formation of 1,3,5-trimethylbenzene is prevented because the intermediate A is too bulky to accomodate the pore.

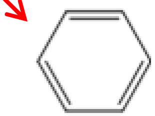
Example of shape selectivity: the MDA reaction

$CH_4 \xrightarrow{700\ °C}$

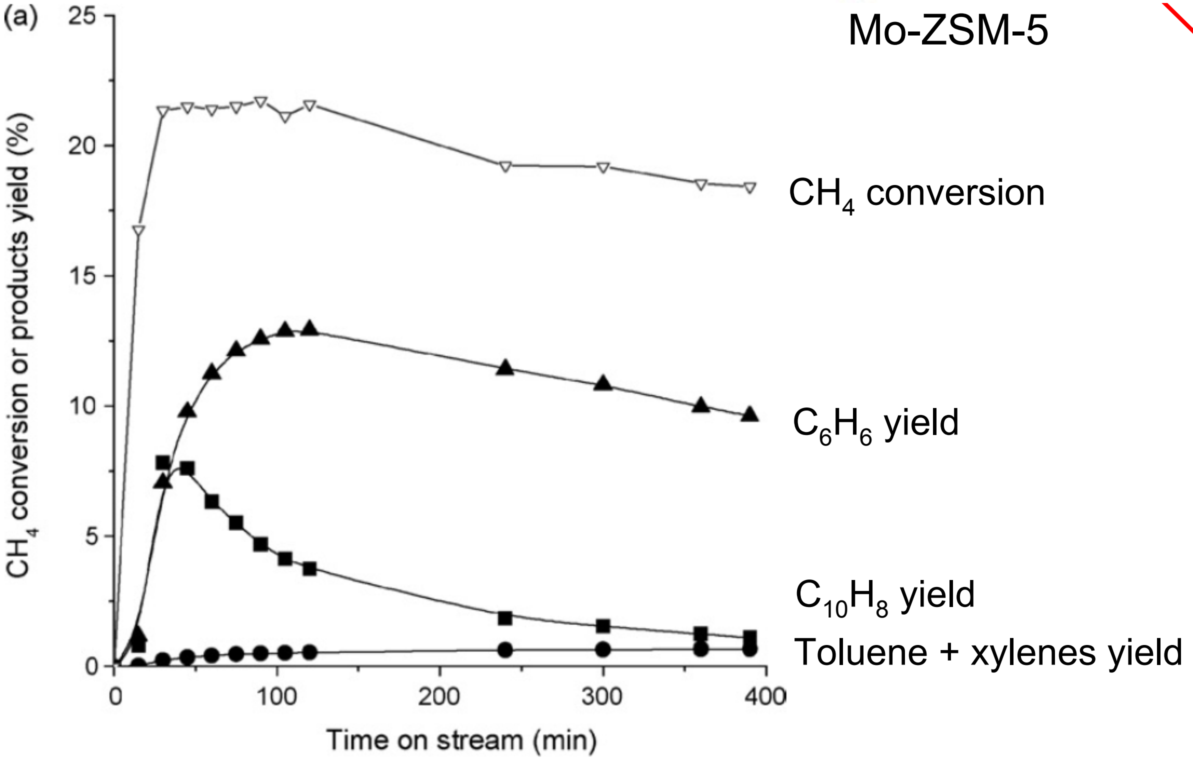


$\longrightarrow$ Benzene
Naphthalene

Mo-ZSM-5



Pore diameter: 5.1 x 5.5 Å, 5.3 x 5.6 Å
=
Dynamic diameter of C_6H_6: 5.5 Å



Critical parameters for shape selectivity

Reactant or transition state shape selectivity

↓

diameter of the cage

Product shape selectivity

↓

diameter and length of the pore

How to improve shape selectivity?

Other framework type

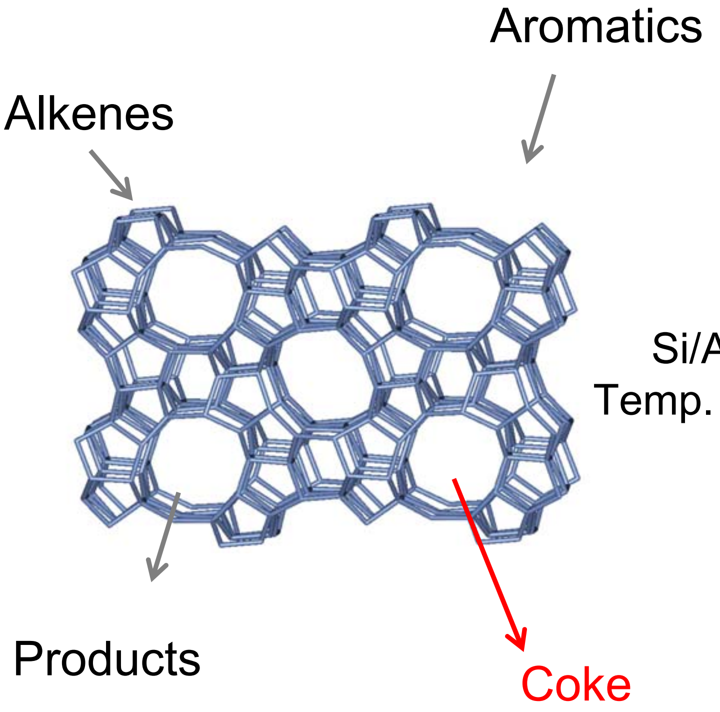
Silylation or coking to reduce the pore size

~~Other framework type~~

Silylation or coking to reduce the pore size

Change the size or aspect ratio of the crystals

Expected problems with zeolite catalysts



Aromatics

Alkenes

Si/Al = 15-80
Temp. = 50-800 °C

Products

Coke

- Kills the atom economy (waste of carbon atoms).
- Deactivation of the catalyst by encapsulation of the active sites and/or blocking of the pores.
- Change in the selectivity of the reaction because of the narrowing of the pores.

Possible solutions

Standard solution: burn-off the coke to regenerate the catalyst

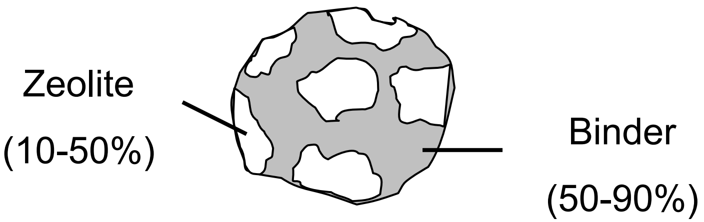
Drawback: waste of atoms and of energy, produces CO_2

Clever solution: avoid its formation!

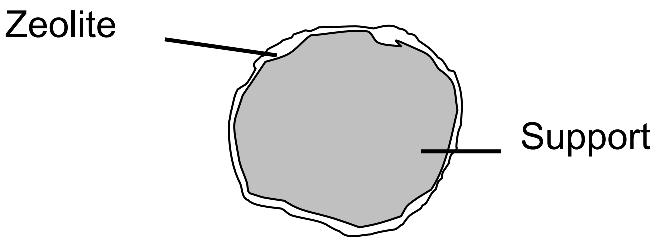
Drawback: not easy!

Possible solutions: supported zeolites, nanocrystals, post-treatments,
hard templating (exo, endo), soft templating (exo, endo)

(I) Supported zeolites



Cross section of a grain
or extrudate



Cross section – zeolite
grown on a support

Hypothesis:

- Diffusion problems to the core of the grain/extrudate
- Part of the zeolite does not see the reactants
- Long diffusion path for the products back to the reaction medium (gas or liquid)
- Binder can block the pores

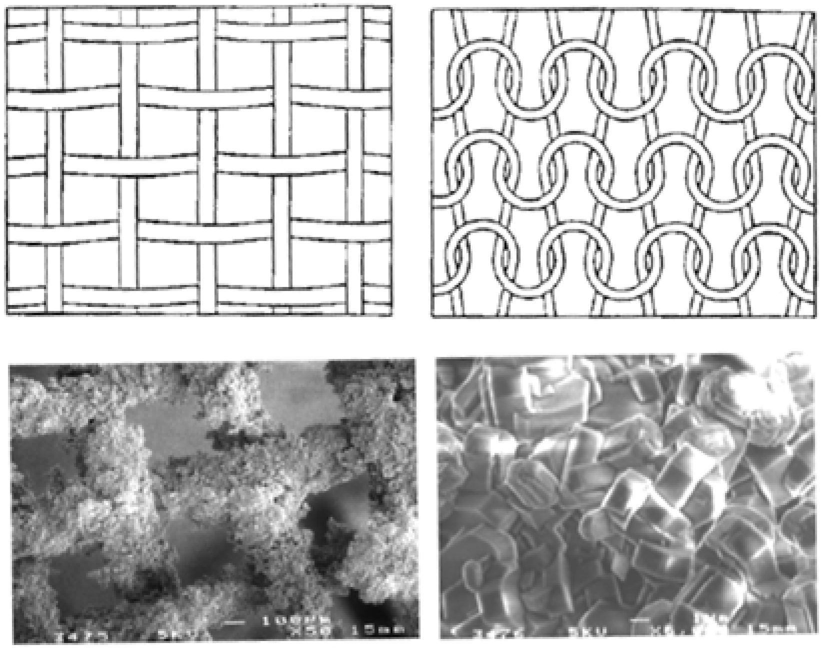
Proposed solution:

- Grow a thin layer of zeolite on the surface of a support. Shape of the catalyst = shape of the support.
- By controlling the thickness of the zeolite layer, it is possible to reduce diffusion and mass transfer problems.

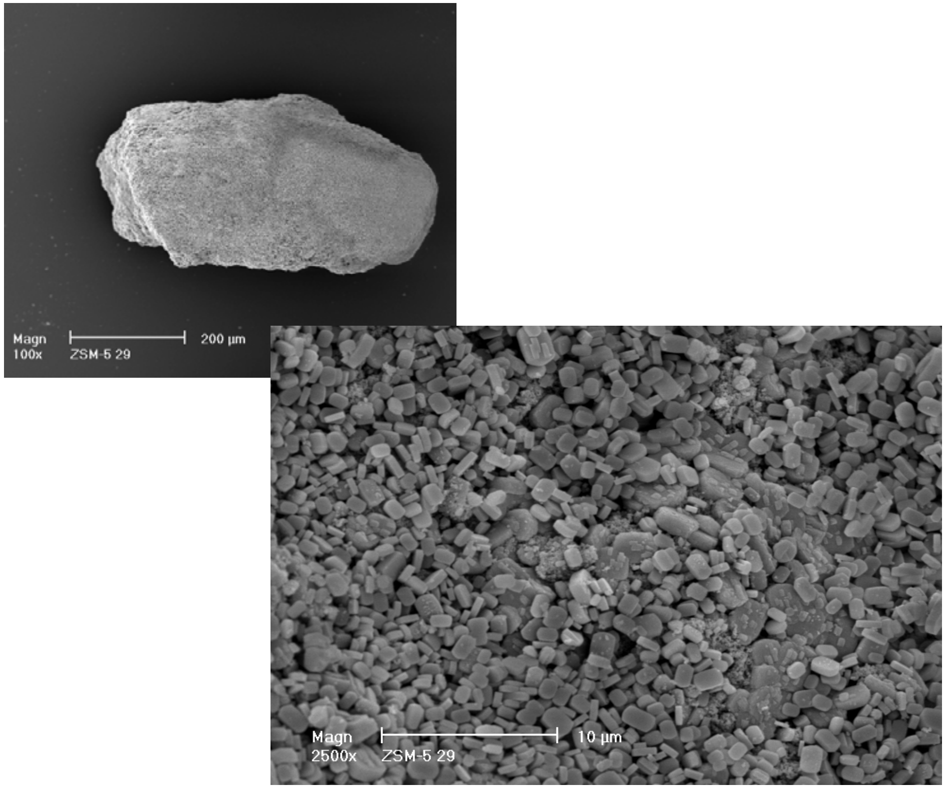
Drawback:

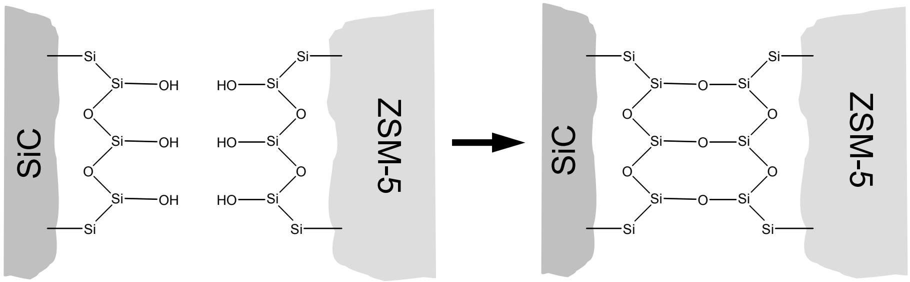
- Difficult to find a suitable support. gamma-Al_2O_3 is (partially) dissolved during synthesis. Same for silica. Alters the chemical composition of the gel.

(I) Exemples of supported zeolites

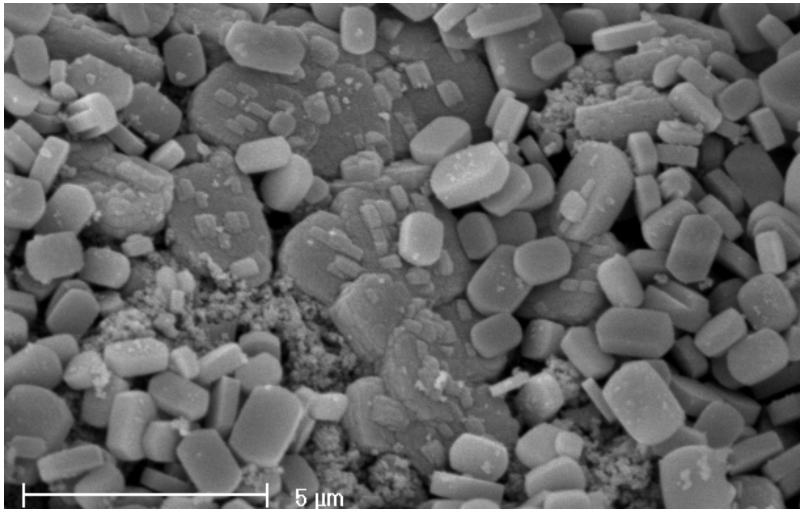


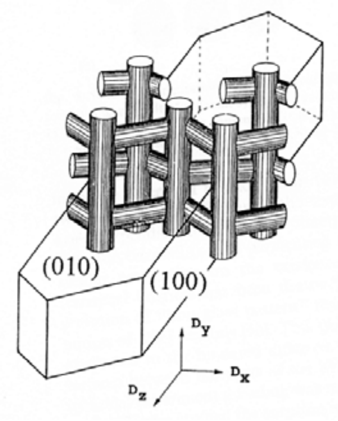
ZSM-5 on a stainless steel grid
B. Louis, A. Renken, EPFL





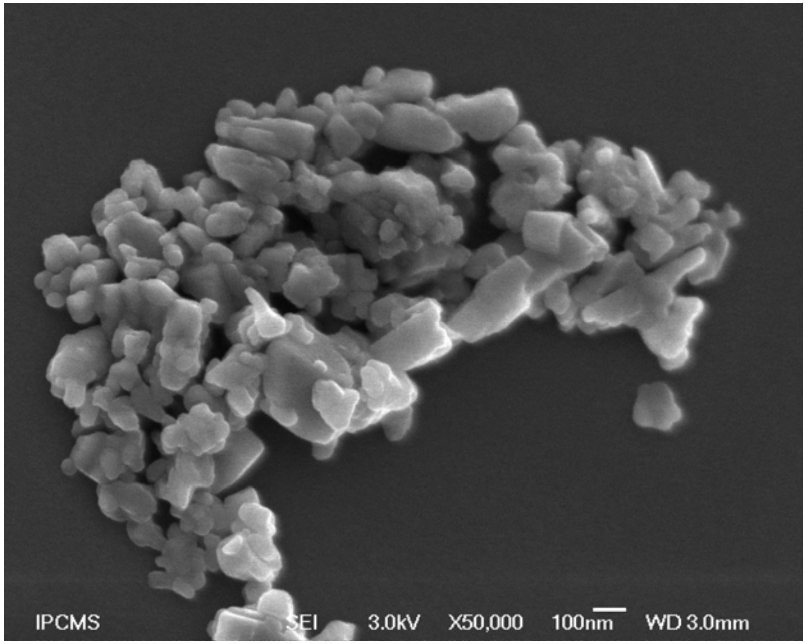
(II) Nanocrystals





ZSM-5: coffin like shape
Crystals are 1-10 µm long

Diffusing through the crystal for a 5 Å molecule, is like walking 10 km for a man.

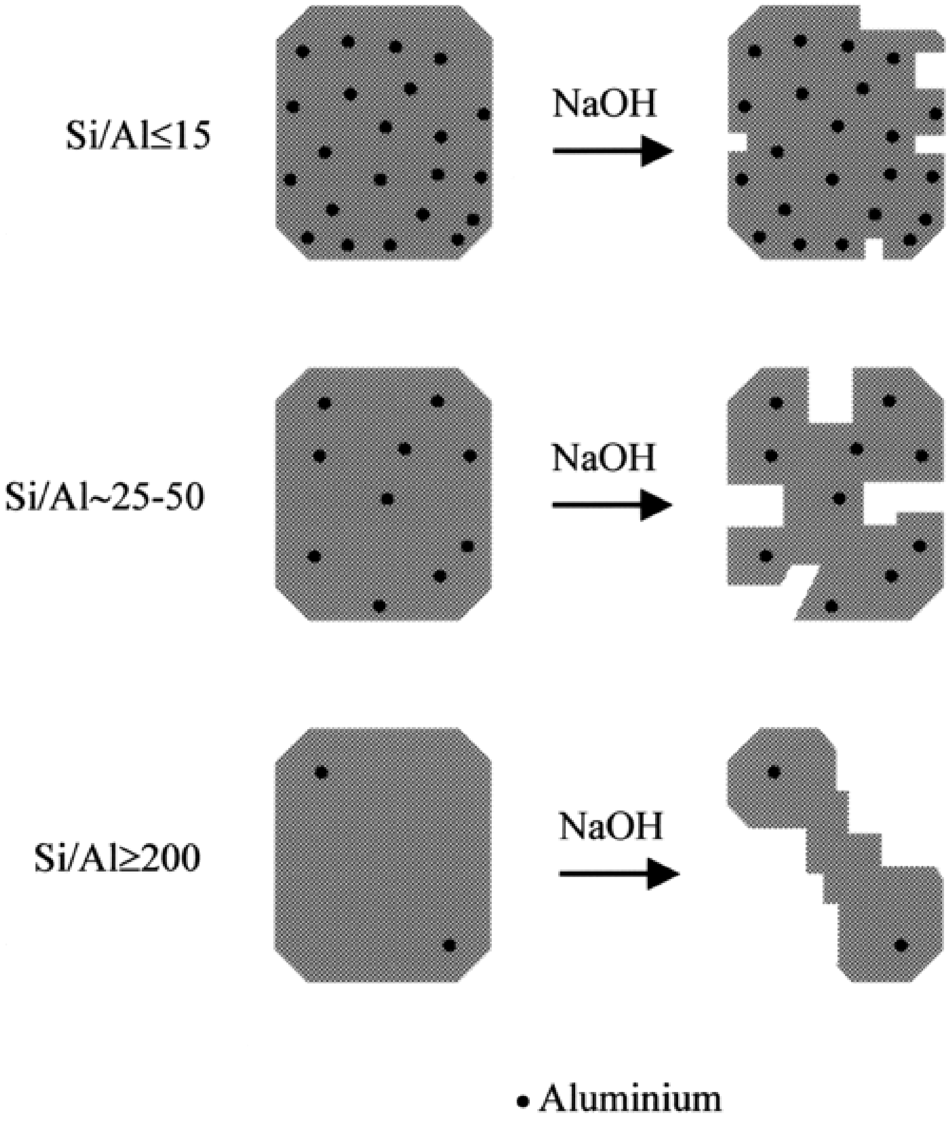


By playing with the gel concentration and the temperature, it is possible to favor nucleation over growth. Formation of nanocrystals with sizes of 50-100 nm. But poor crystallinity.

Strategy often followed by industry to also shorten the synthesis time.

Here ZSM-5 with Si/Al=15 (Zeolyst).

(III) Post-treatments: partial dissolution

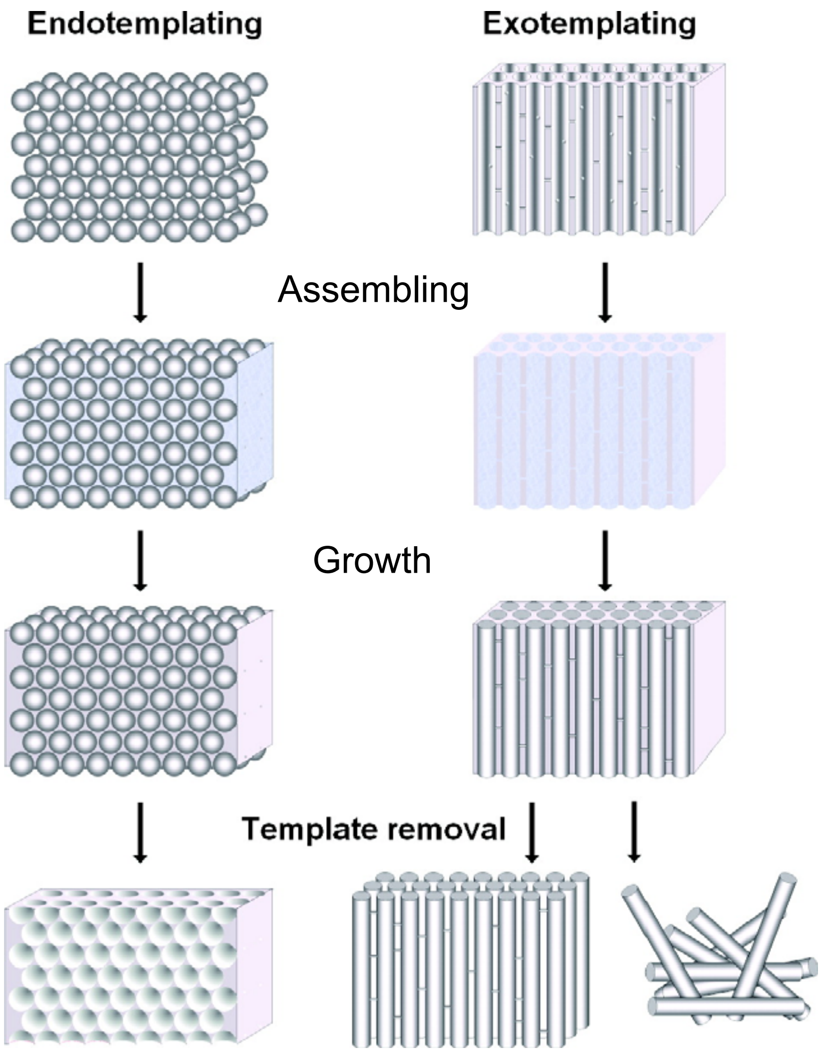


Partial dissolution of zeolite crystals with NaOH.

Stability depends on Si/Al

Chem. Rev. 106 (2006) 896-910

(IV) Hard templating

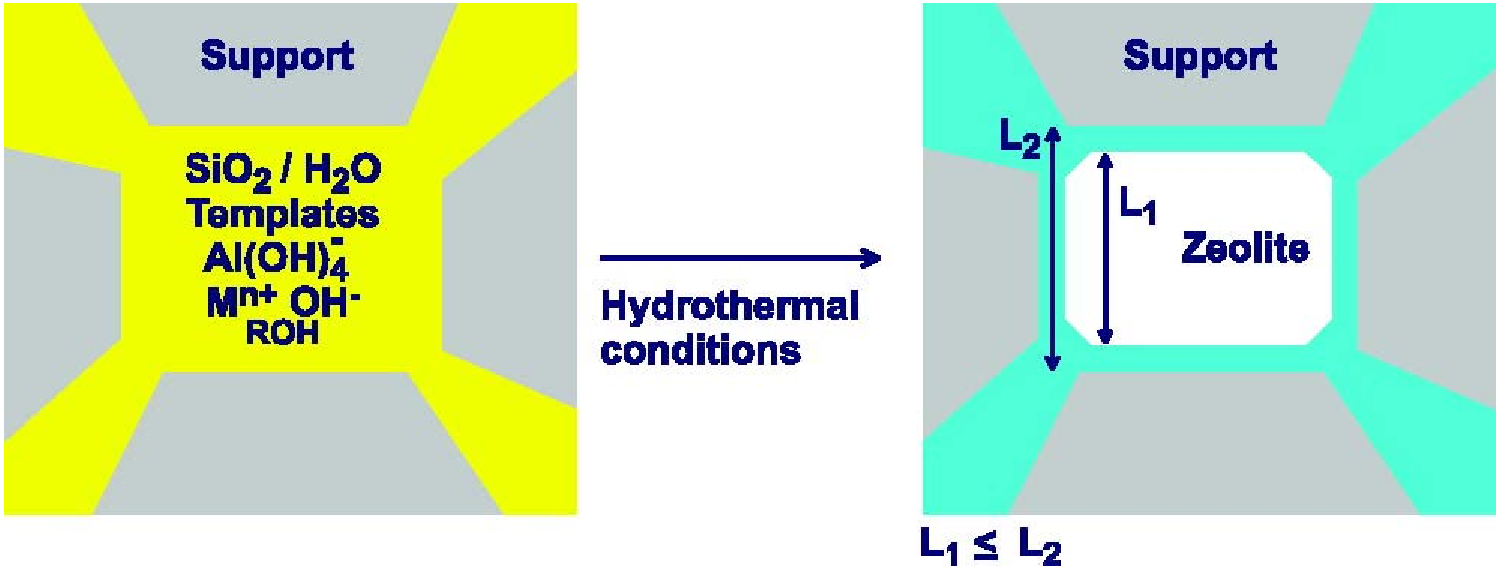


Endo templating: assembling and growth around/outside the template.

Exo templating: assembling and growth inside the template.

Chem. Rev. 20 (2008) 738-755

(IV) Hard templating - exo

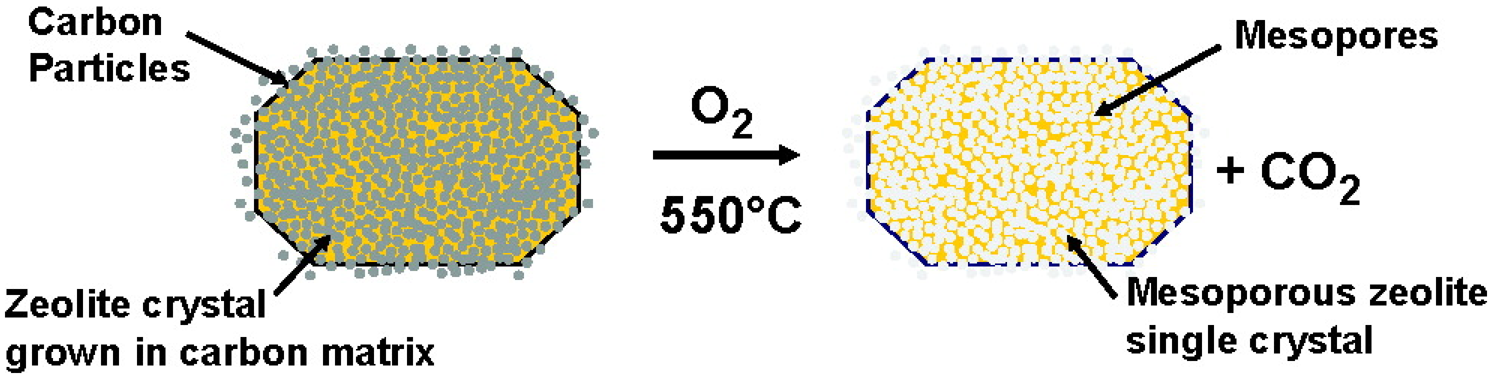


Zeolite crystal synthesis inside the pores of the template.
Crystal size defined by the pore size.

Example: ZSM-5 inside activated carbon.

Chem. Mater. 20 (2008) 946-960

(IV) Hard templating - endo



Carbon Particles

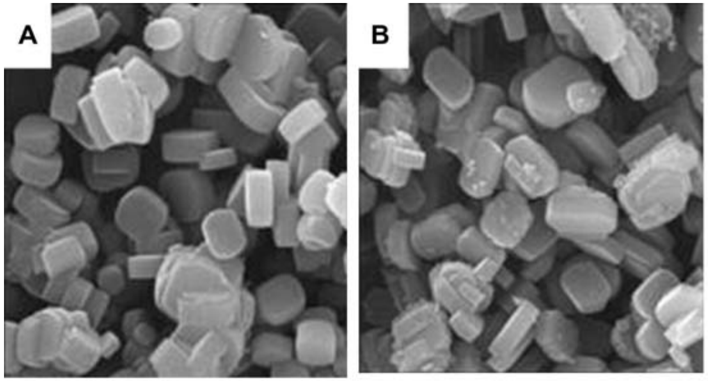
Zeolite crystal grown in carbon matrix

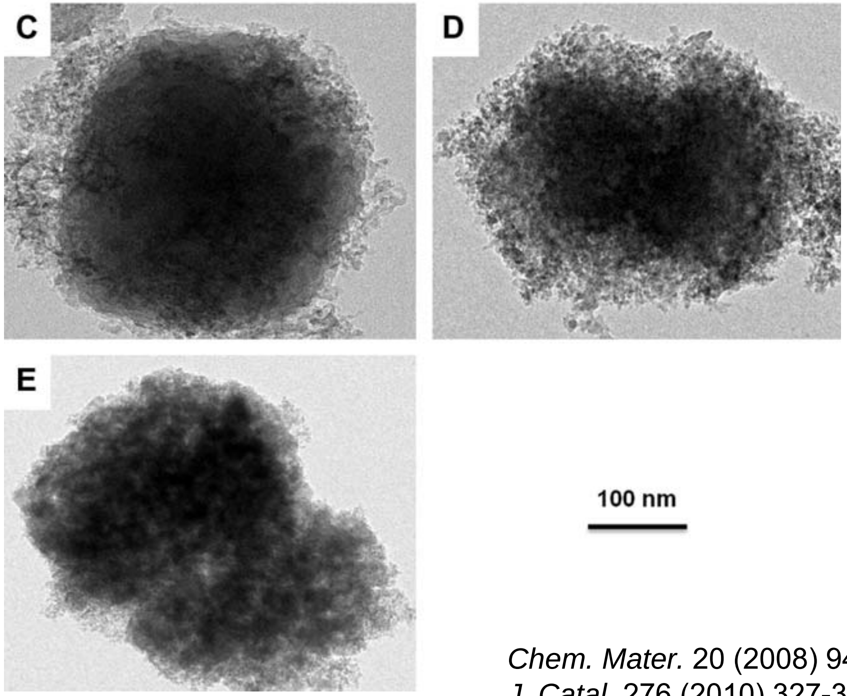
$\xrightarrow[550°C]{O_2}$

Mesopores

$+ CO_2$

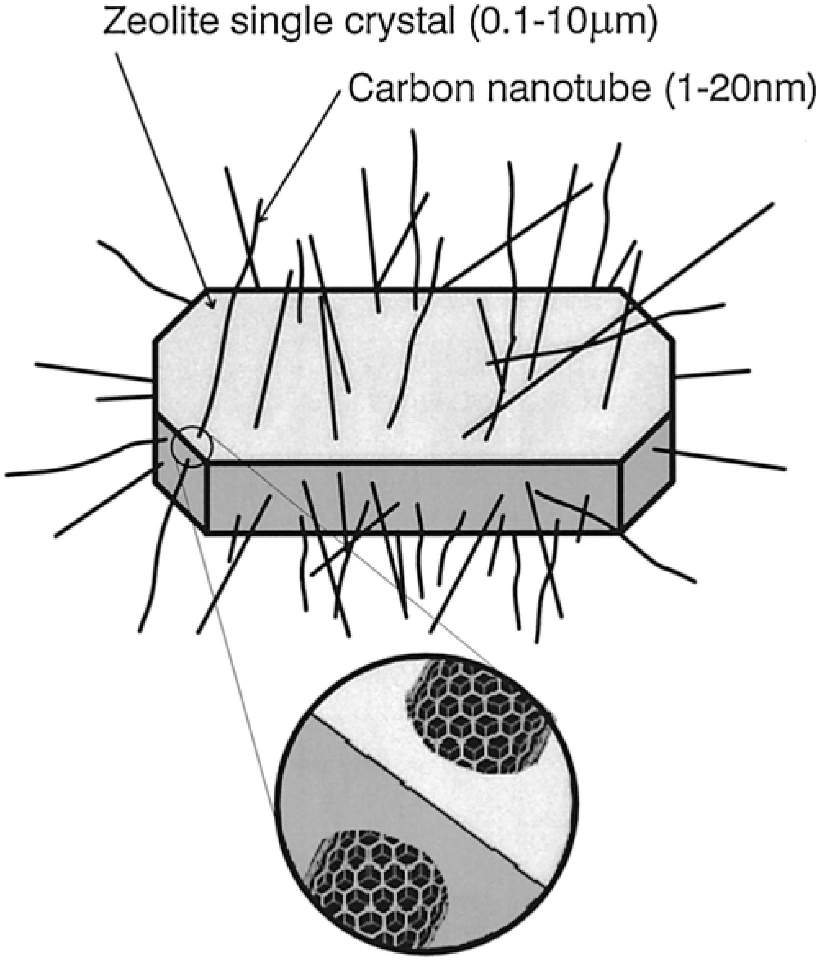
Mesoporous zeolite single crystal





Chem. Mater. 20 (2008) 946-960
J. Catal. 276 (2010) 327-334

(IV) Hard templating - endo

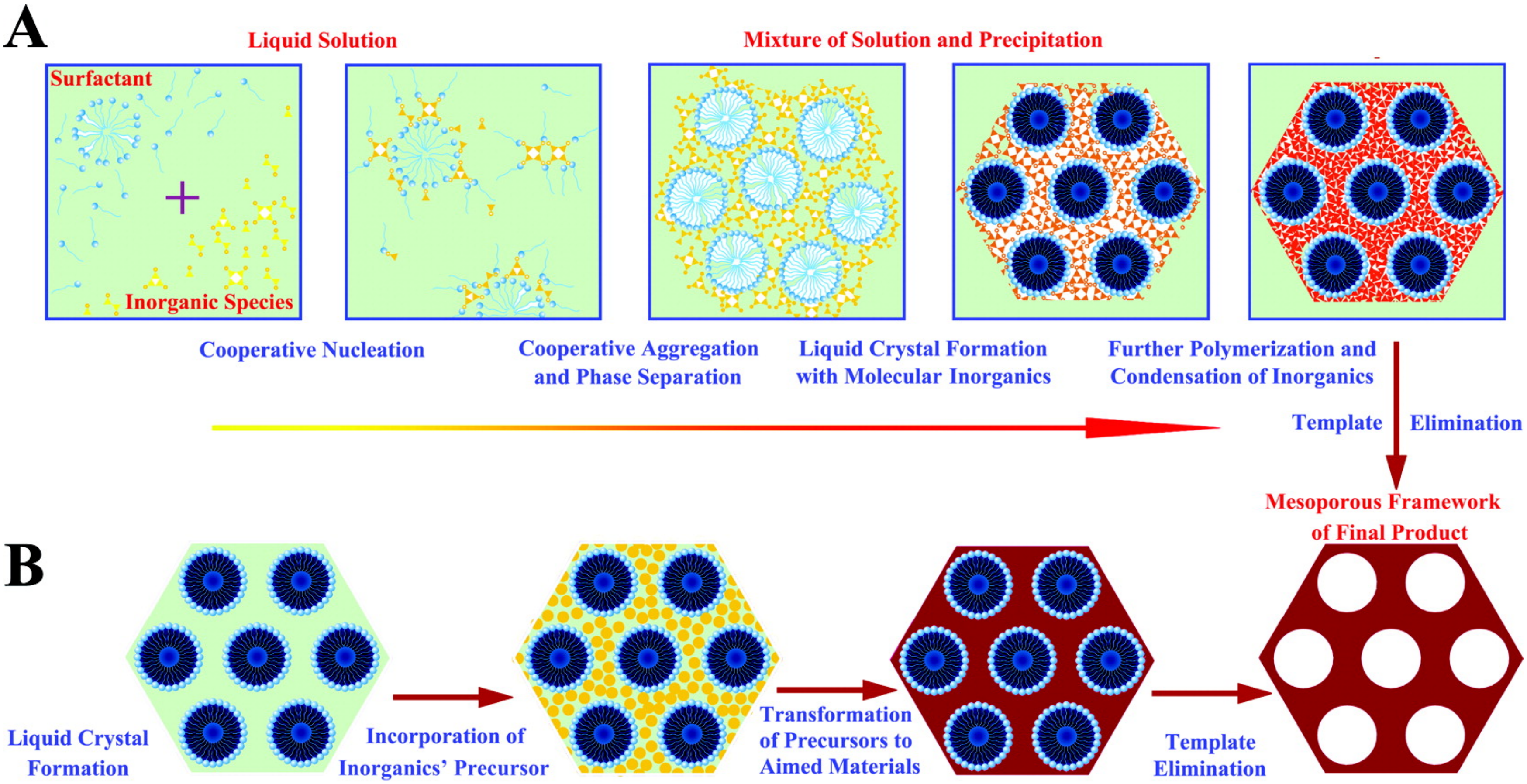


Carbon particles: isolated pores (cages)

Carbon nanotubes: channels

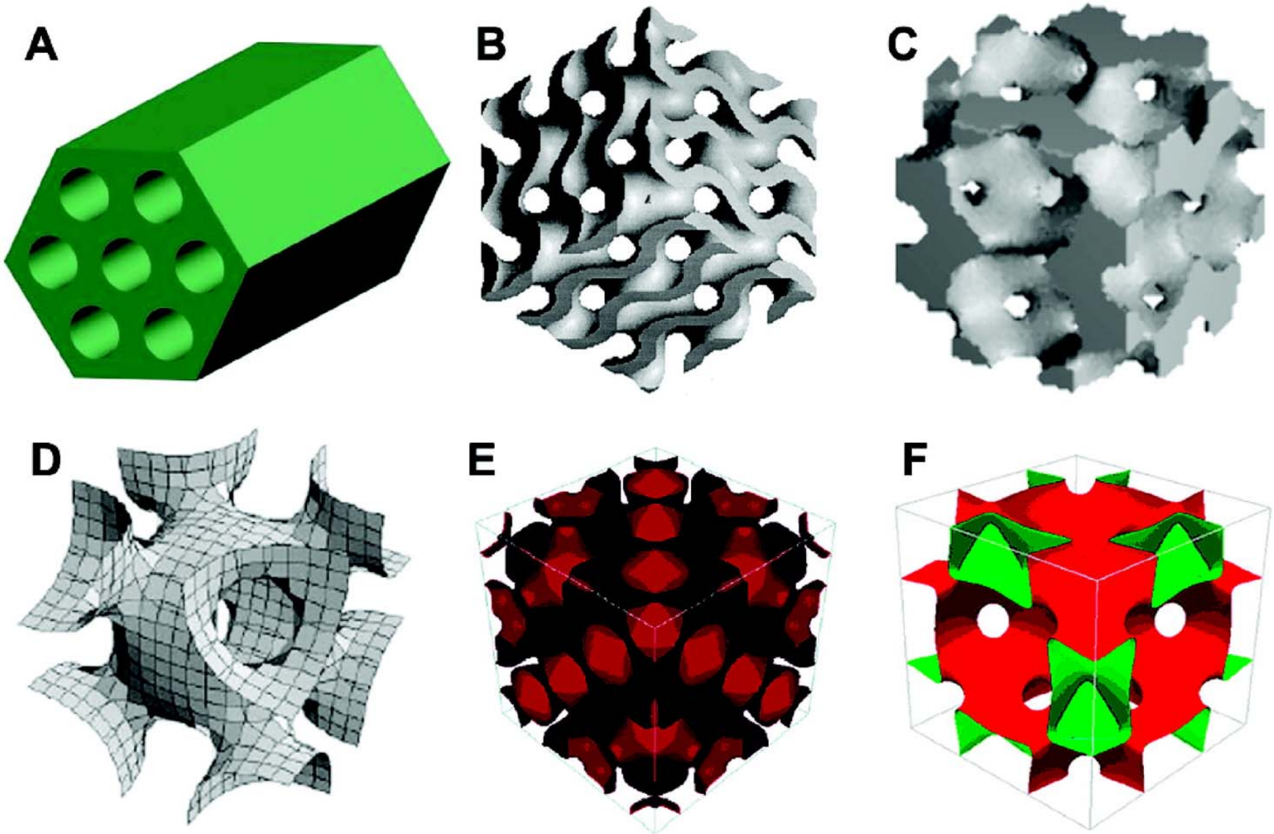
Chem. Mater. 20 (2008) 946-960

(IV) Soft templating - endo



Chem. Rev. 107 (2007) 2821–2860

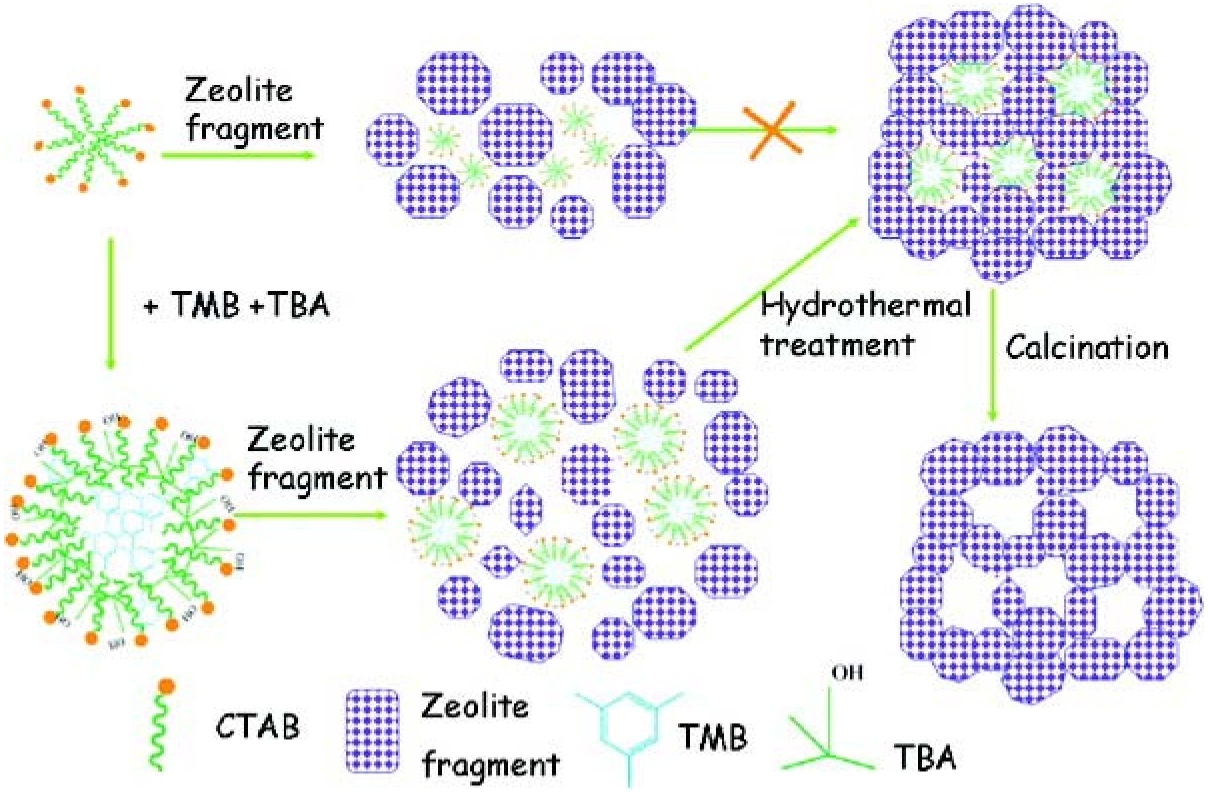
(IV) Soft templating - endo



The pore structure depends on the template.

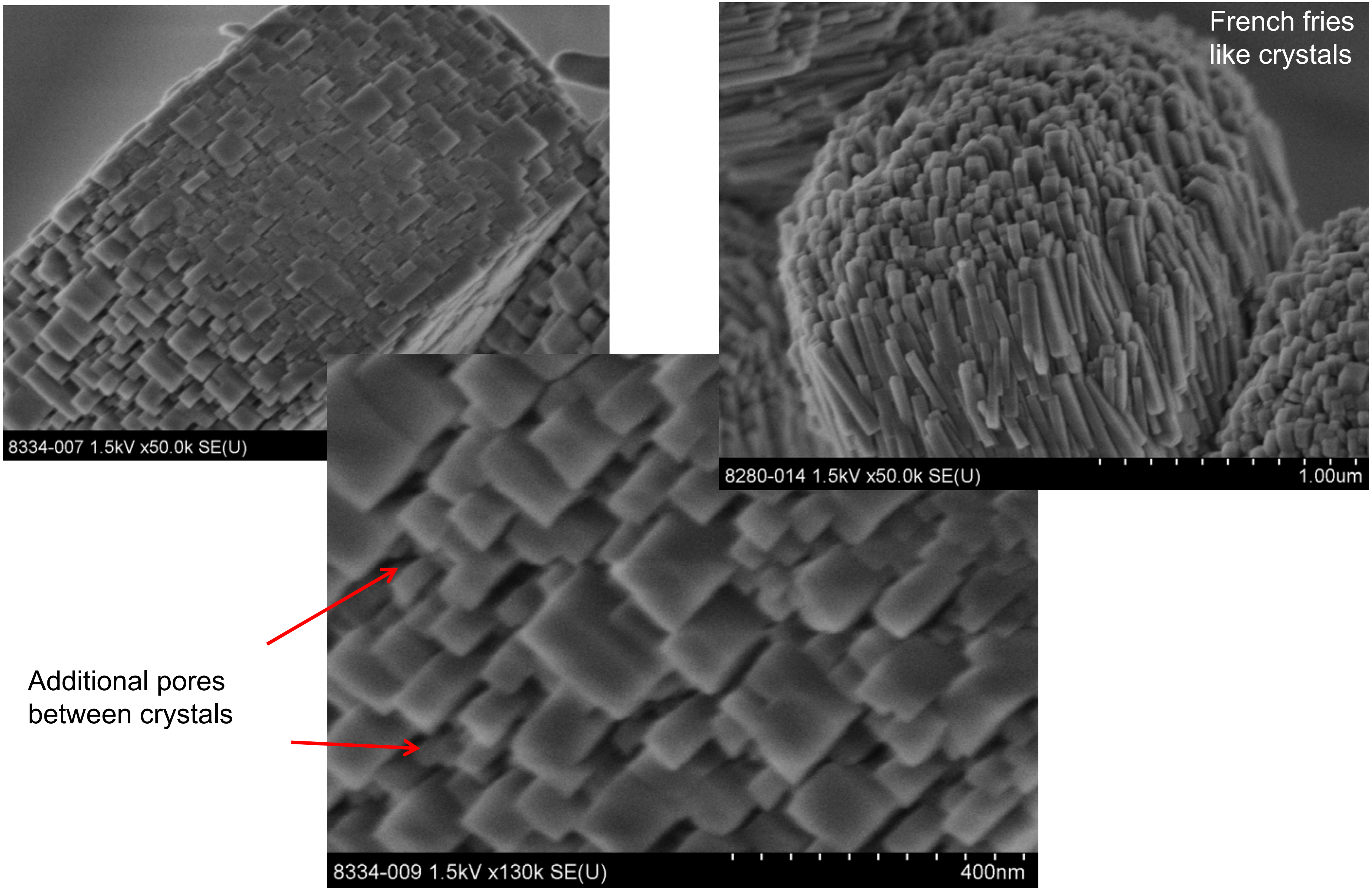
Chem. Rev. 107 (2007) 2821–2860

(IV) Soft templating - endo



Chem. Mater. 22 (2010) 2442–2445

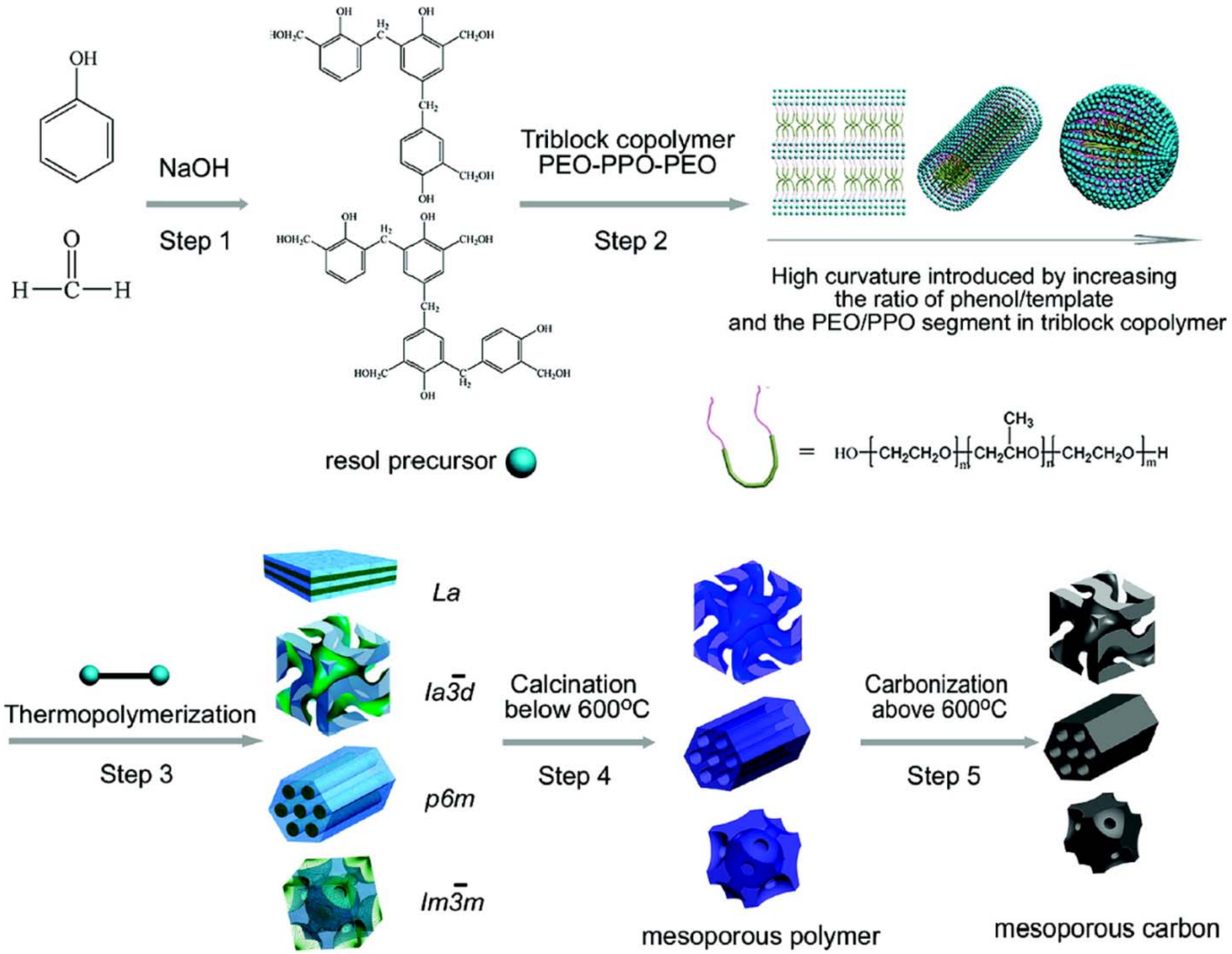
(IV) Soft templating - endo



French fries
like crystals

Additional pores
between crystals

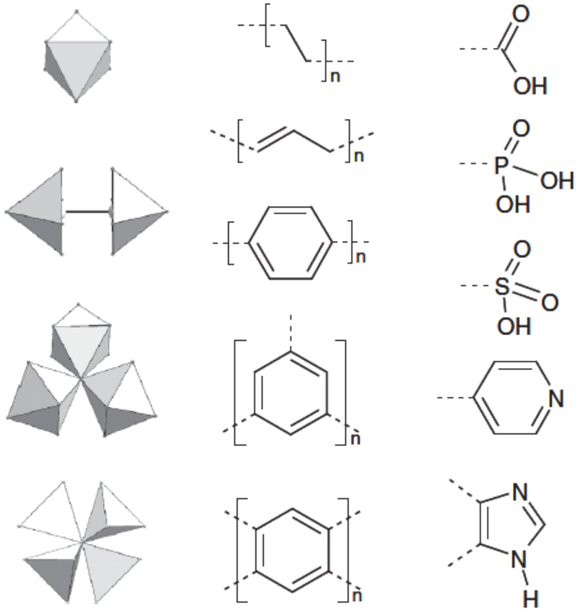
Other mesoporous materials



Strategies developed for zeolites and ordered mesoporous silicas can also be applied for other inorganic oxides and carbon.

Chem. Rev. 107 (2007) 2821–2860

MOFs



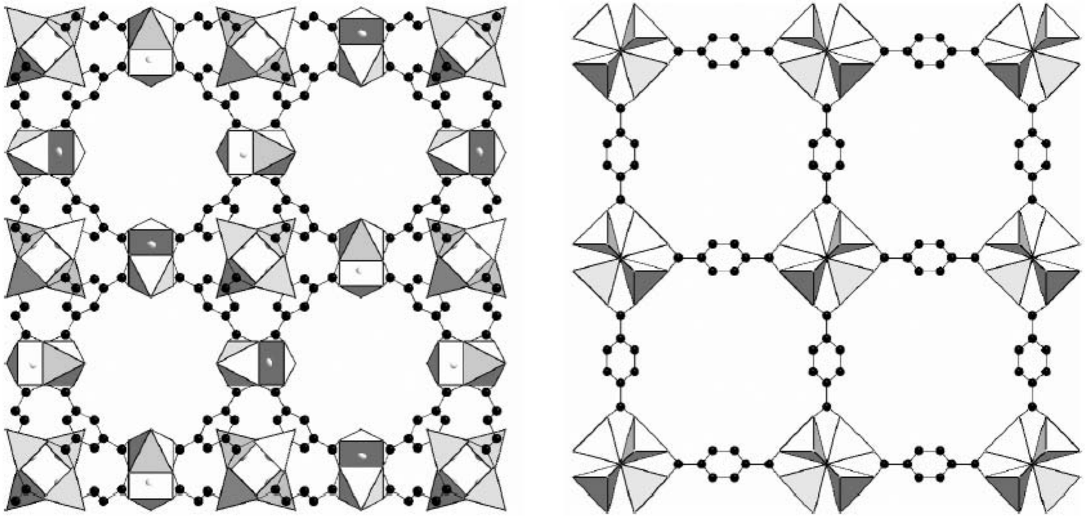
Typical inorganic sub-units, organic linkers and complexing functions

Inorganic building blocks interconnected with organic linkers.

Very high surface area: 1800-3000 $m^2\ g^{-1}$

Promising for applications such as adsorption, gas purification, H_2 storage.

Low stability at high temperature, limits the applications in catalysis to organic chemistry or similar (for the moment).



View of the structures of HKUST-1 and MOF-5.

MOFs

MOFs with a zeolitic structure. Same shape selectivity than zeolites but more flexibility in terms of chemical composition.

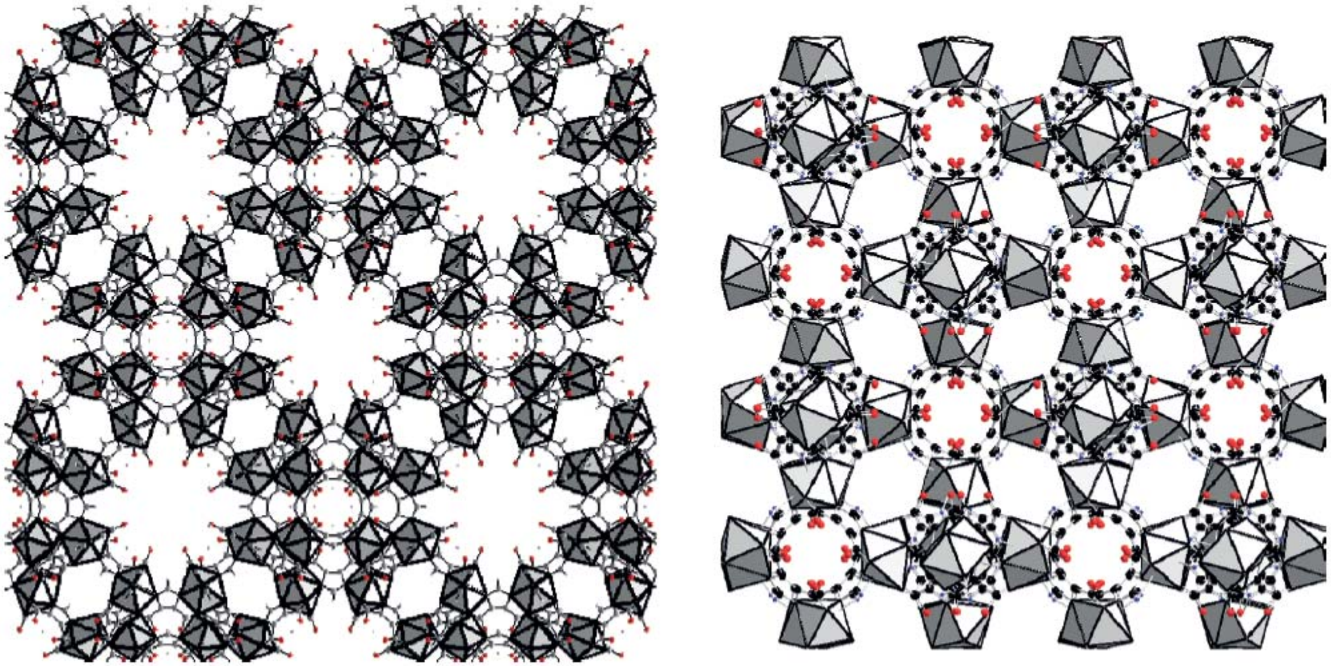
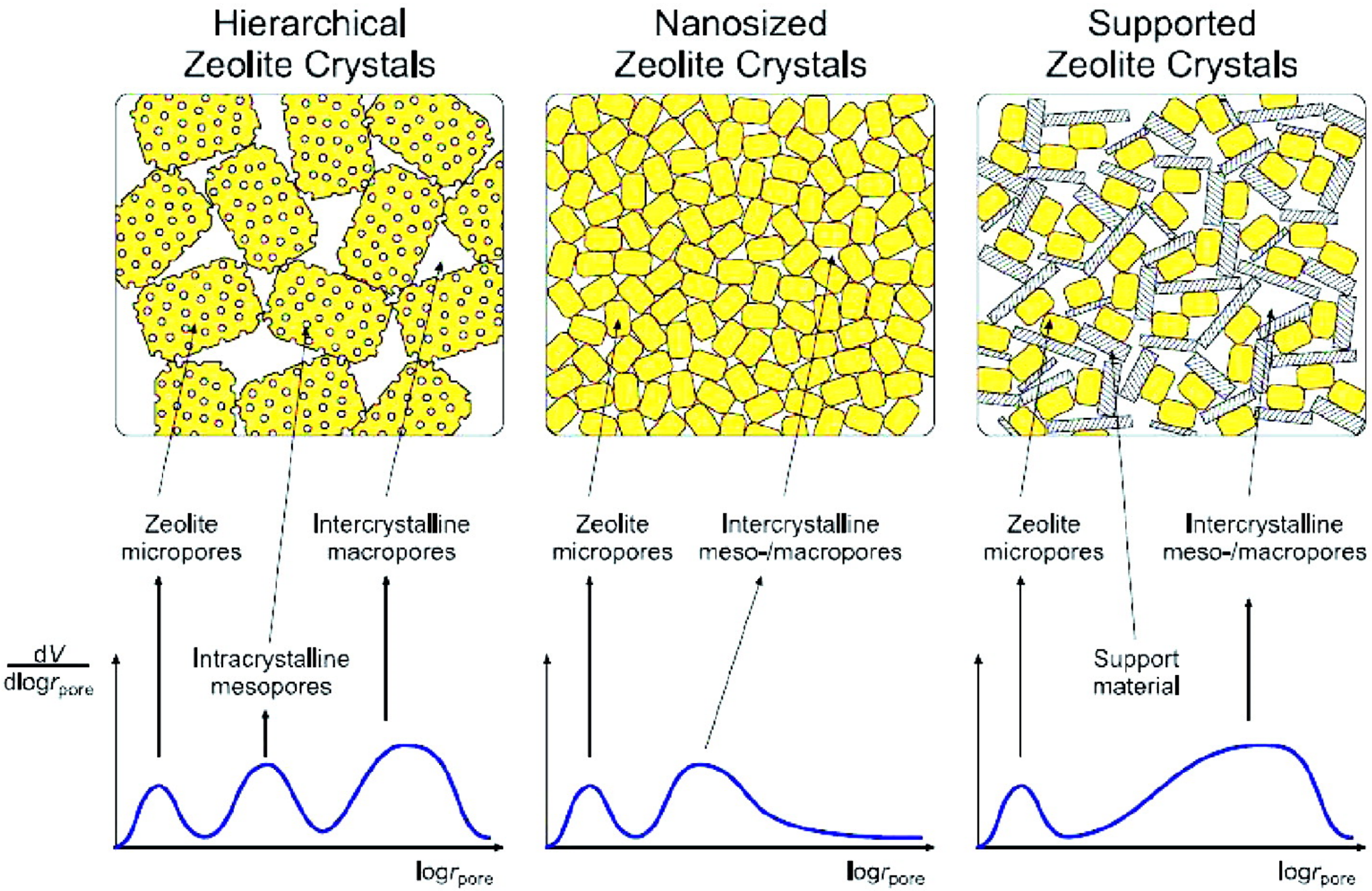


Figure 4.3 View of the structures of the ZMOFs with a sodalite and a zeolite-rho topology.

Conclusion



- Hierarchical materials allow an accurate control of the pore sizes at the micro, meso and macro levels.
- Improved diffusion of reactants and products while keeping the shape selectivity.
- Higher catalytic activity, lower deactivation.

Recommended literature

Zeolites for Cleaner Technologies
M. Guisnet, J.P. Gilson, Eds., Imperial College Press, 2002.

Catalysis and Zeolites: Fundamentals and Applications
J. Weitkamp, L. Puppe, Eds., Springer, 1999.

Ordered Porous Solids: Recent Advances and Prospects
V. Valtchev, S. Mintova, M. Tsapatsis, Eds., Elsevier, 2009.

K. Tanabe, W.F. Hölderich, *Appl. Cata. A: Gen.* 181 (1999) 399-434

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K. Egeblad, C.H. Christensen, M. Kustova, C.H. Christensen, *Chem. Mater.* 20 (2008) 946-960

Thank you for your attention!