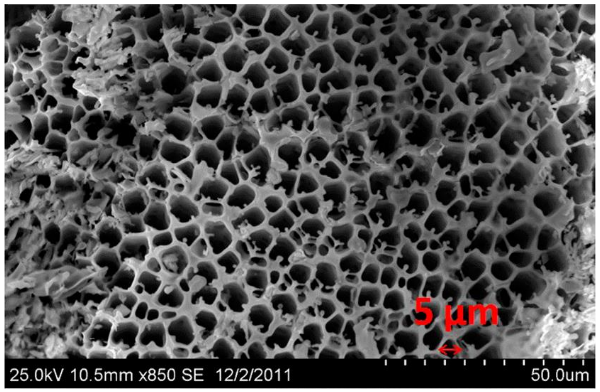
Zeolites and Metal-Organic Frameworks

Porous Materials

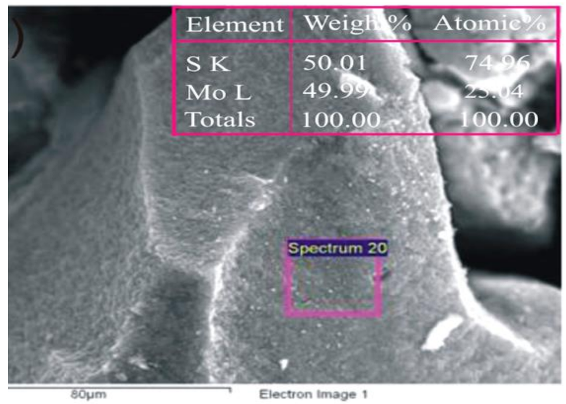
- Classically Inorganic Molecules; A large number of Inorganic Porous Materials have been developed, metal, oxides, chalcogenides etc
- Ordered or irregular arrangement of pores
- Porous materials: Materials with different pore sizes (from nanometer to millimeter)
  - Microporous, smaller than 2 nm
  - Mesoporous, between 2 and 50 nm
  - Macroporous, larger than 50 nm

Porous Chalcogenides



$ASnSb_2S_6$
Fard, Islam, Kanatzidis,
Chem. Mater., **2015**, *27*, 6189

Water Purification



MoS_x: Gels
Islam, et al. *Chem. Mater.*, **2014**, *26,* 5151

Catalysis

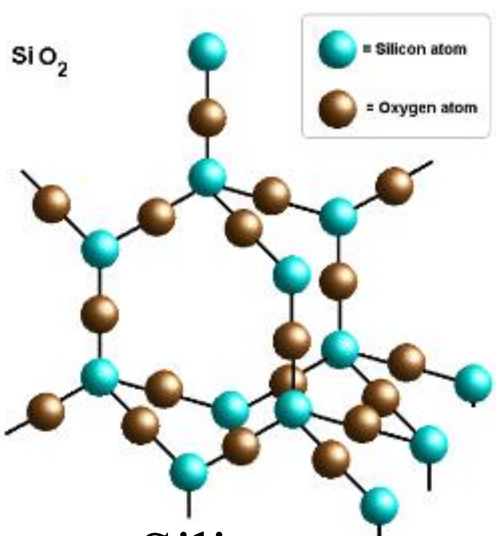
Gas separation
Ion exchange
Gas absorber
Catalysis

Zeolites

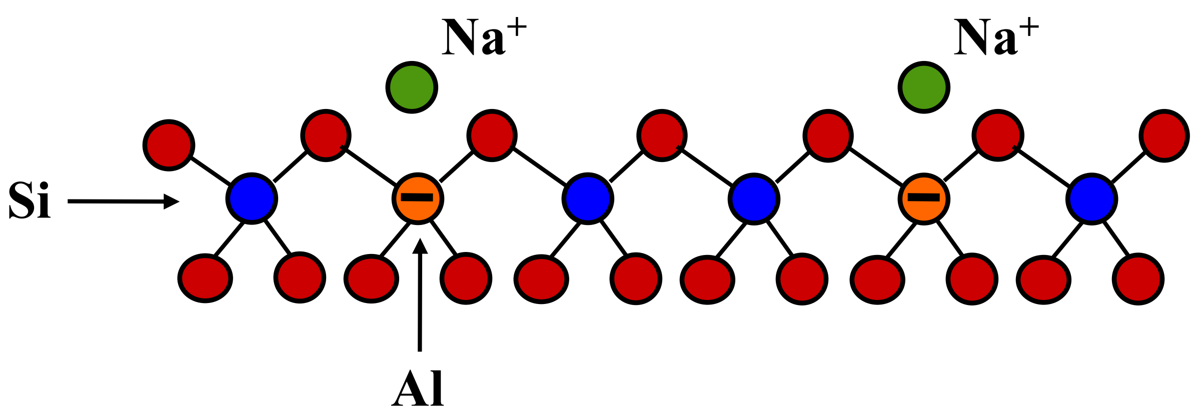
- 1756 - Boiling (zeo) stones (lithos)
- Crystalline 3D porous solids containing cavities and channels ranging 4-20 Å in size
  - Note: some have only 1D or 2D channels

Zeolite Chemistry

- General formula: $M_{x/n}[(AlO_2)_x(SiO_2)_y] \cdot mH_2O$
- SiO_2 tetrahedra are electrically neutral (e.g., quartz)
- What affect will substitution with Al have?
  - Substitution of Si(IV) by Al(III) creates an electrical imbalance
  - Neutrality provided by an exchangeable cation – $M^{1+ \text{ or } 2+}$



Silica



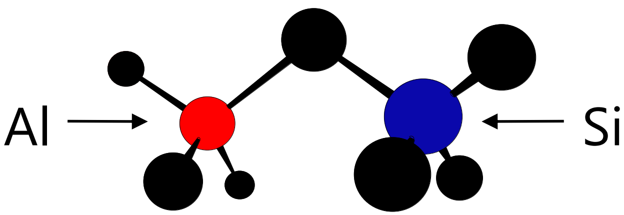
Zeolite

What type of solid are Zeolites?

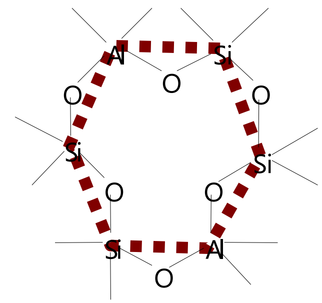
- Zeolites are ionic frameworks, and can be considered an inorganic polymer
- Zeolites are special because of their:
    1) Porosity / Channels
        - Size limitation for molecular sieves
    2) Acidity / Basicity
        - Catalysts
    3) Electronic Fields
        - Adsorption
- All of these factors vary with zeolite framework and composition
    - Si/Al ratio controls the chemical and physical properties for a given framework

Zeolite 3D Structure

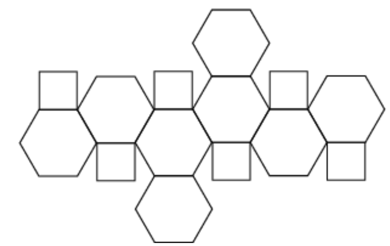
- Primary building blocks are $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra linked by corner sharing oxygen atoms.



Linked tetrahedra

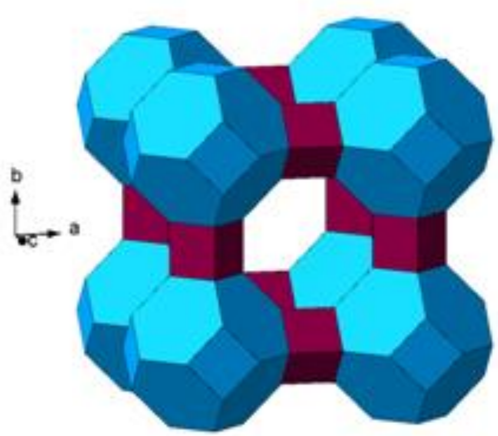


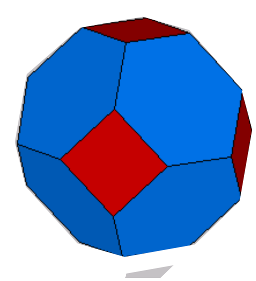
Rings



Supercages

Channels
Accommodate
$M^{1+,2+}$ & H_2O

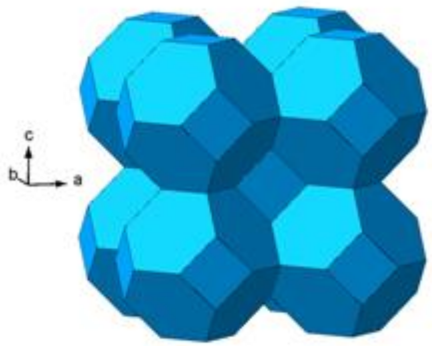
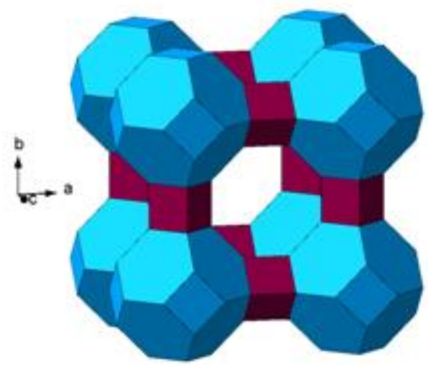
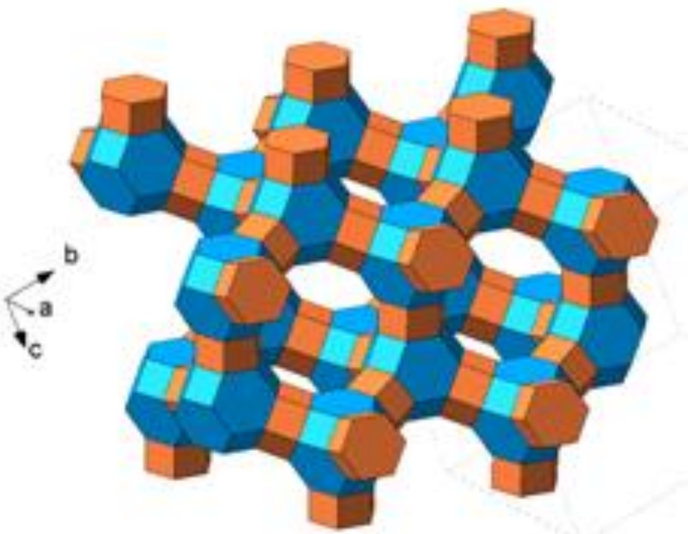
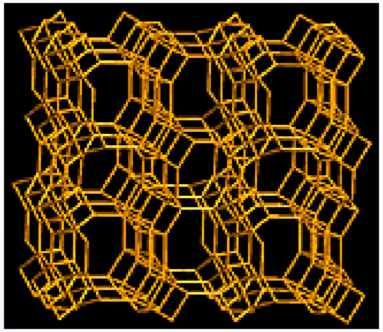
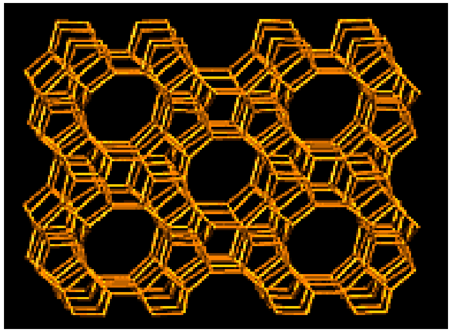
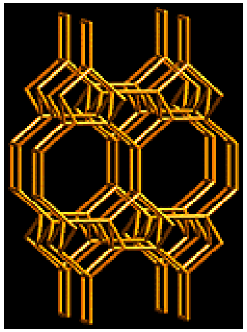
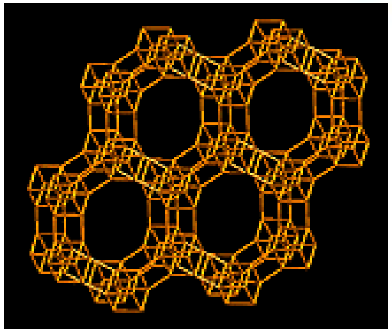
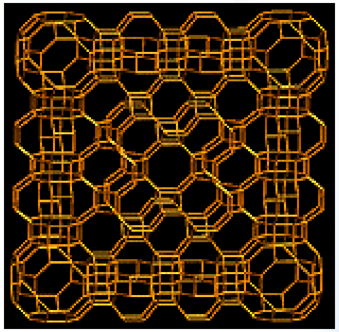




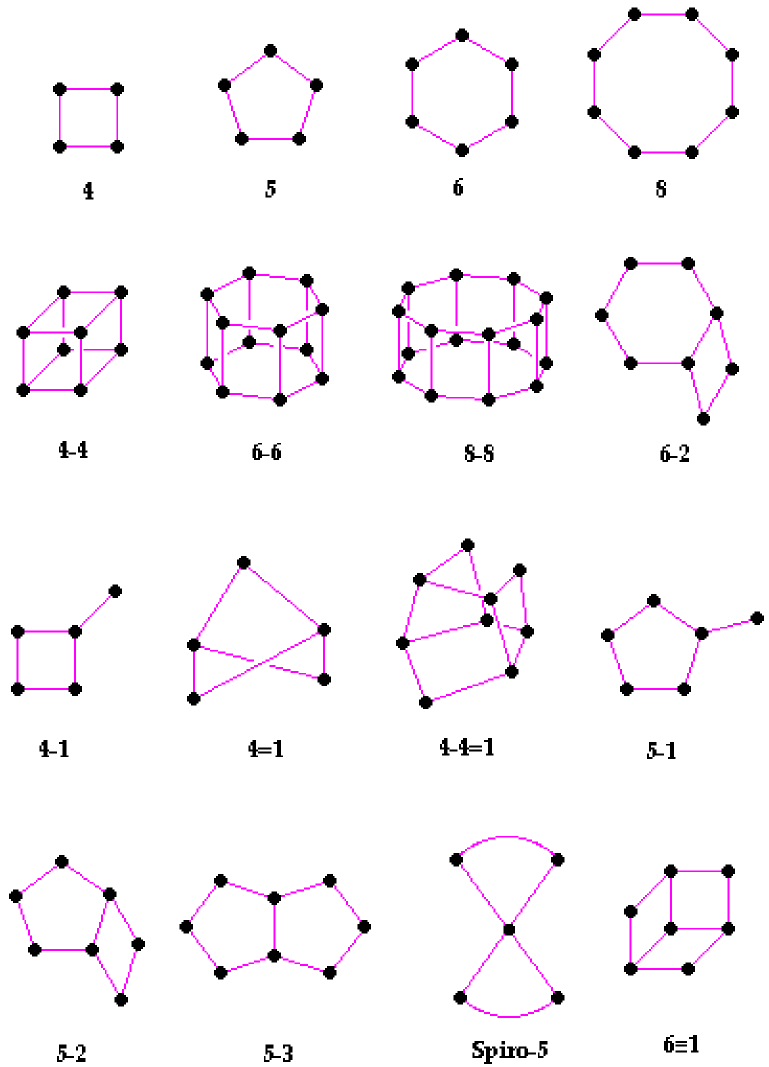
$M_{24}O_{36}$ Cages (M = Si, Al)

Zeolite 3D Structure

- Enormous variety in chemical composition and structure
  - ~ 48 naturally occurring zeolites characterized
  - Over 150 synthesized

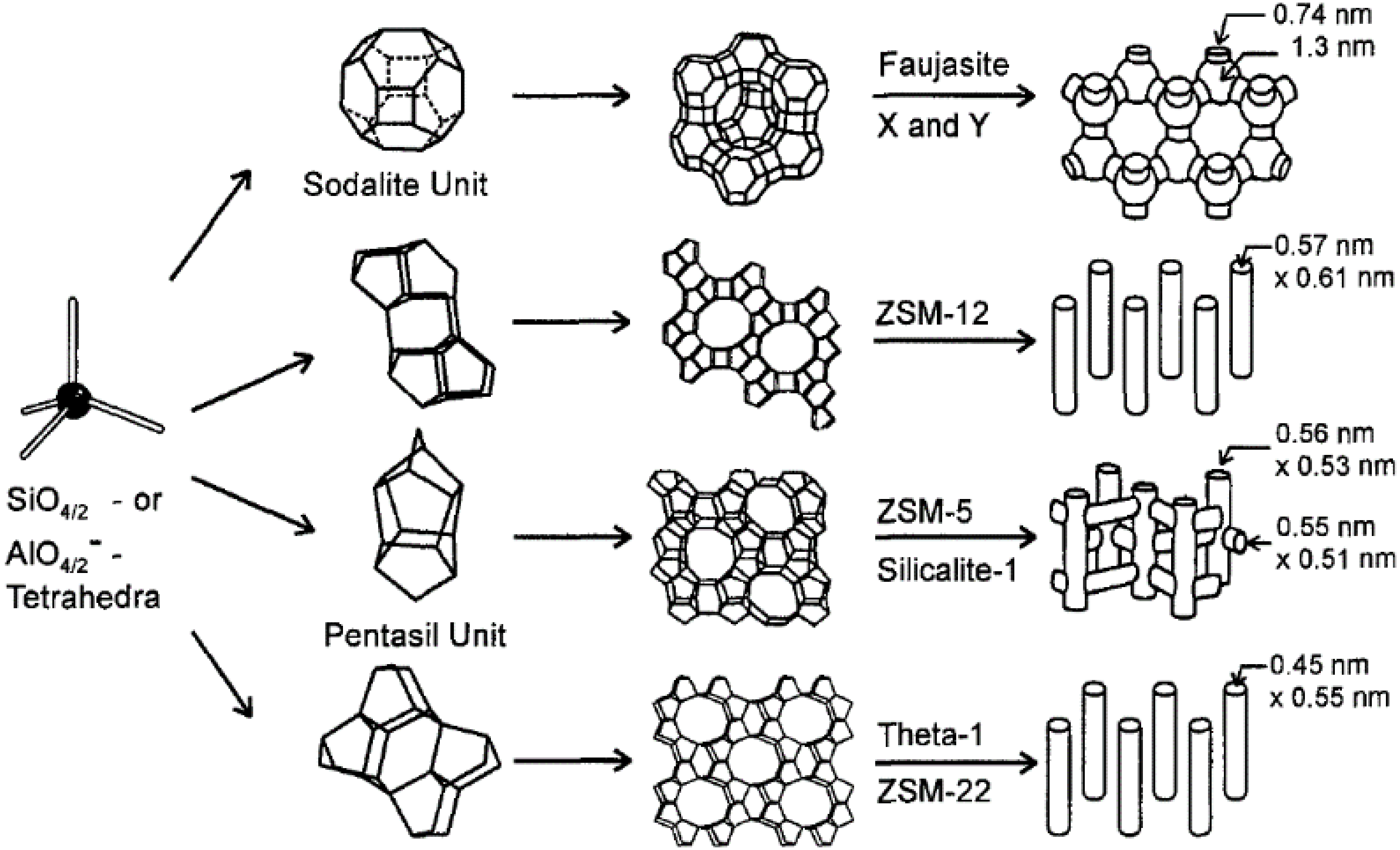









Structural building block of zeolite



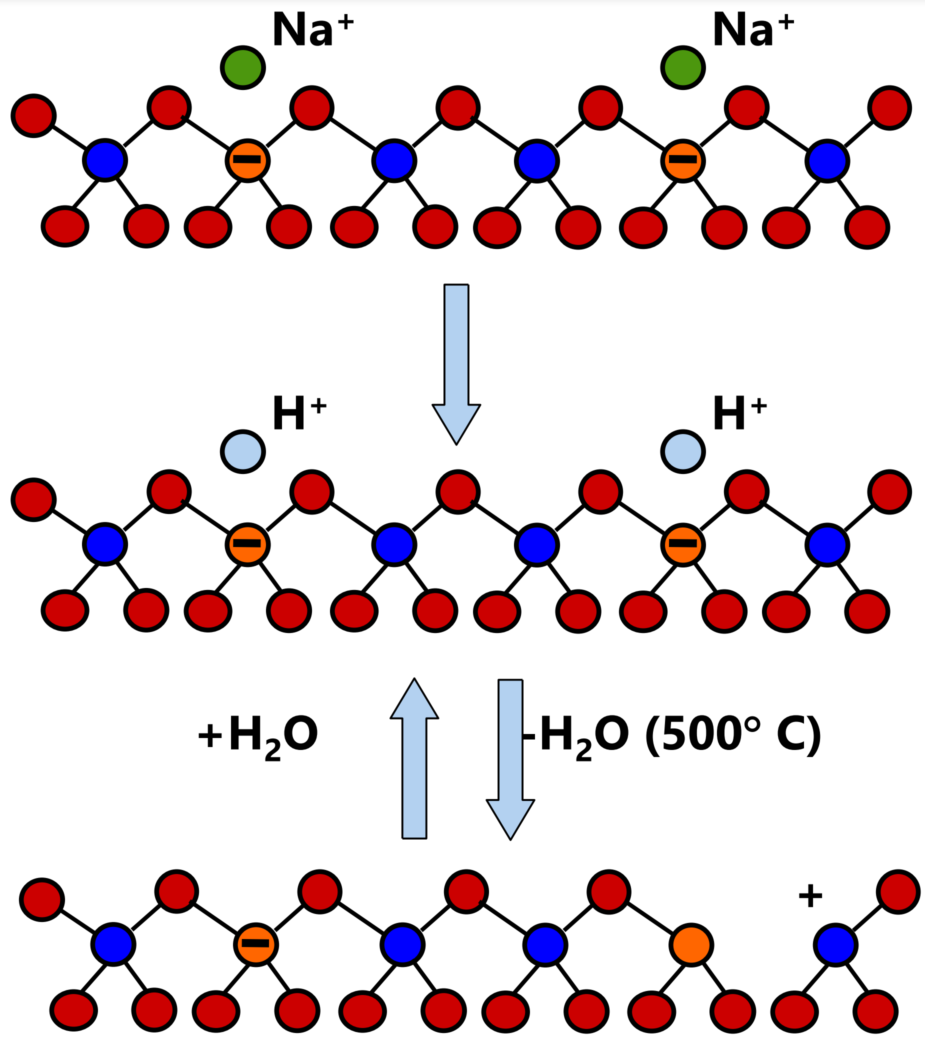
http://www.ch.ic.ac.uk/vchemlib/course/
zeolite/structure.html

Zeolite Structural Diversity



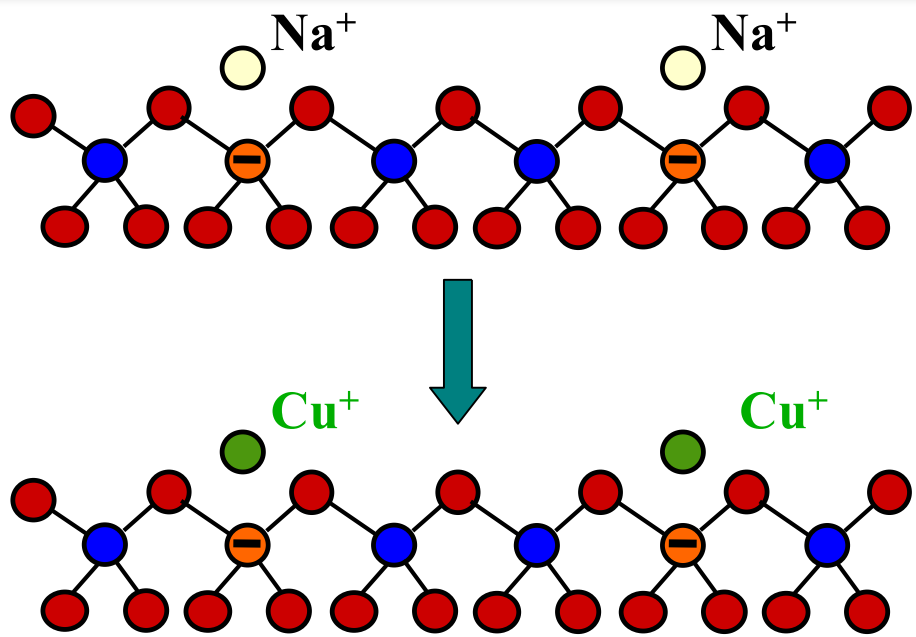
Acid/Base Chemistry

- Zeolite as synthesized
- Bronsted acid form
- Lewis acid form



Ion Exchange

- Zeolite as synthesized
- Ion exchanged

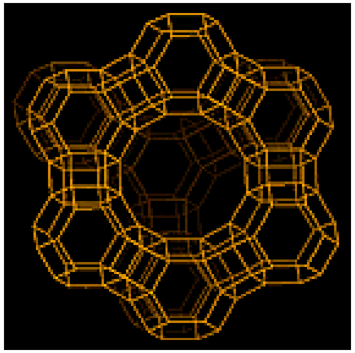


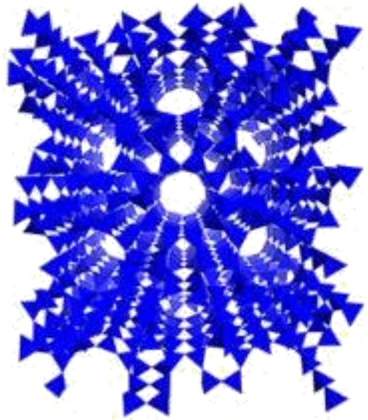
Or any toxic ions such as Hg^{2+}, Pb^{2+} etc.

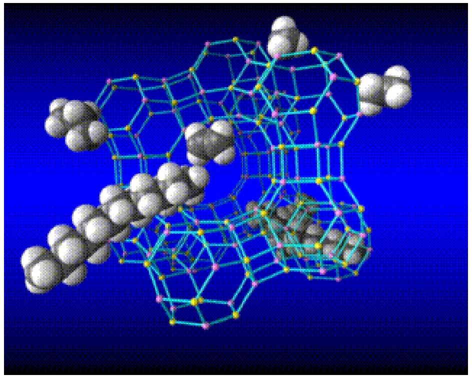
Ion Exchange is one way to alter the properties of zeolites. This can be used to change channel size (typically with anions) and create catalytic sites (typically Transition Metal cations).

Zeolite Applications

- Tremendous Industrial Applications:
  - Ion Exchangers
  - Molecular Sieves & Sorbents
  - Catalysts



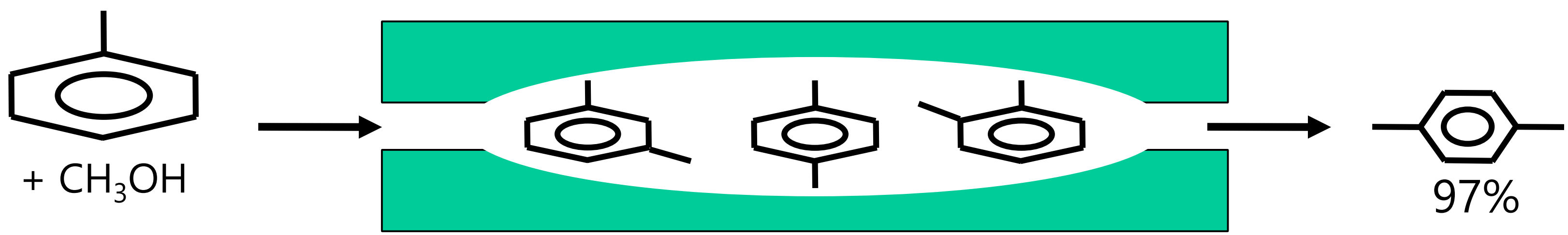




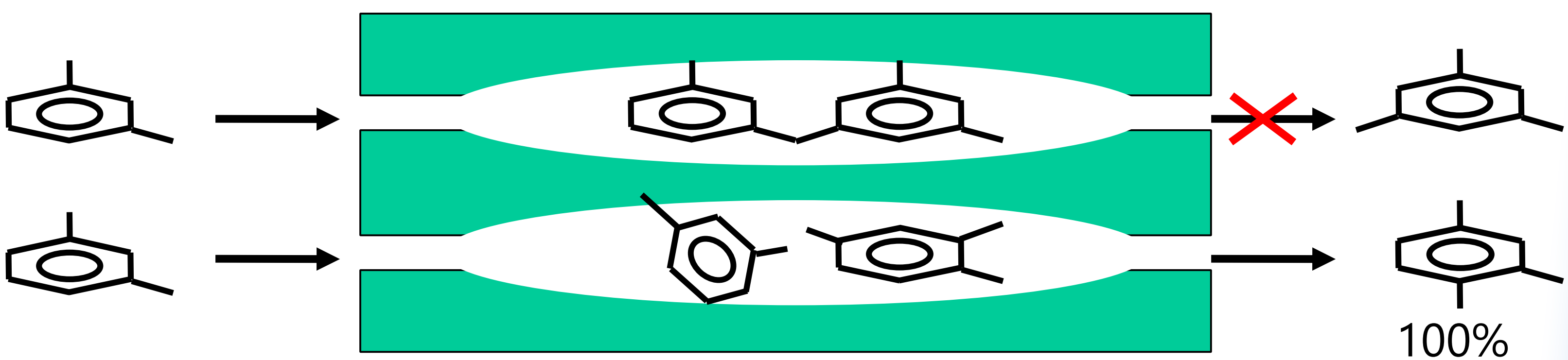
Size and Shape Selectivity

Reactant Selectivity

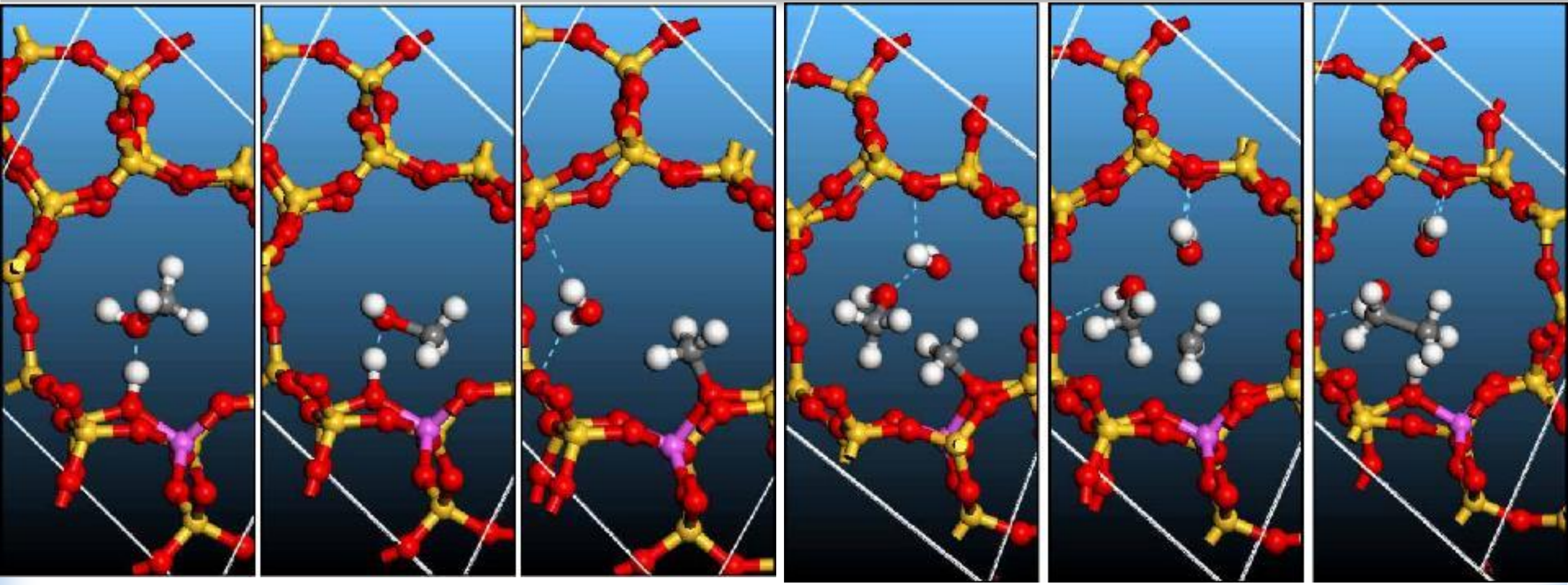
Product Selectivity



Transition State Selectivity



Methanol To Gasoline (MTG)

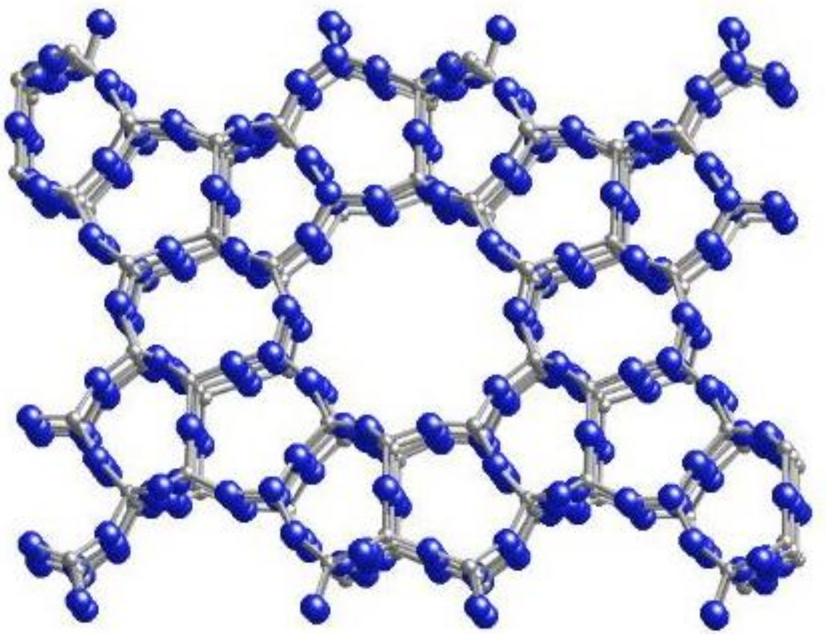


- Zeolites can be used to build up large alcohols and hydrocarbons from small ones, or to break apart (crack) large hydrocarbons

ZSM-5

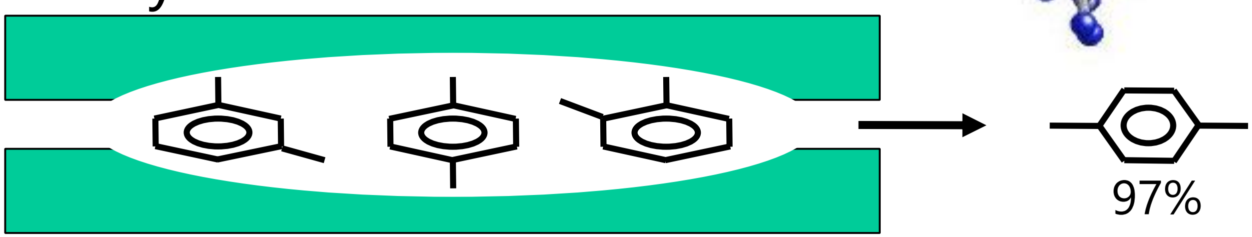
Formula: $Na_nAl_nSi_{96-n}O_{192} \cdot 16H_2O$

N < 27, typically around 3



Contains 10-member rings

Xylenes isomerization



- Synthesis of ethylbenzene
  - Needed for styrene

Zeolite X: Na-X

Typical Formula: $Na_nSi_{24-n}Al_nO_{48}$, $n = 9.6\text{-}12$

Si:Al ratio ~ 1

High Al content – how will chemistry be affected?

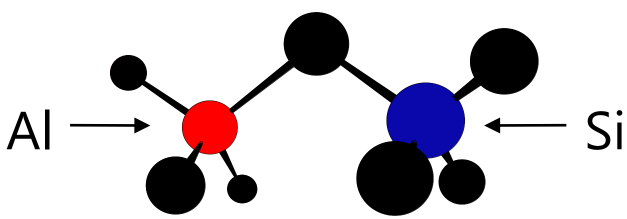
Large number of cations required to charge balance
How will this affect applications?

Increased cation exchange capacities
Many charged sites – effective absorbers for water, polar, and polarizable molecules

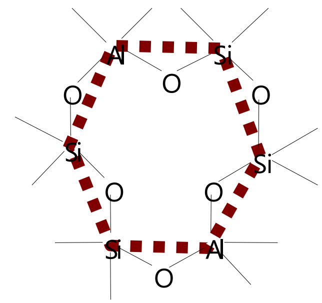
Synthesized on industrial scale for cracking heavy petroleum distillates – increased yields of gasoline

Zeolite 3D Structure

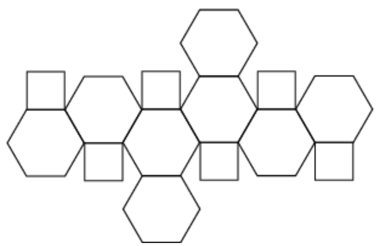
- Primary building blocks are $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra linked by corner sharing oxygen atoms.

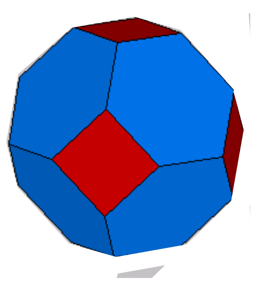


Linked tetrahedra

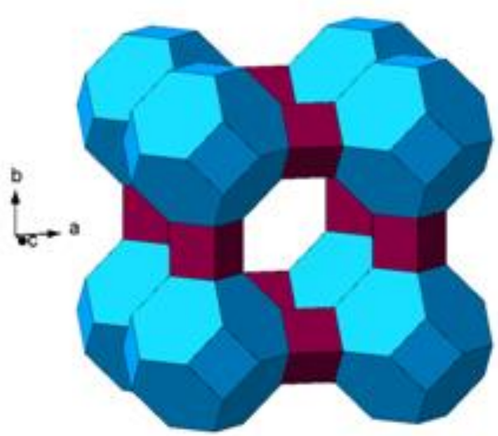


Rings





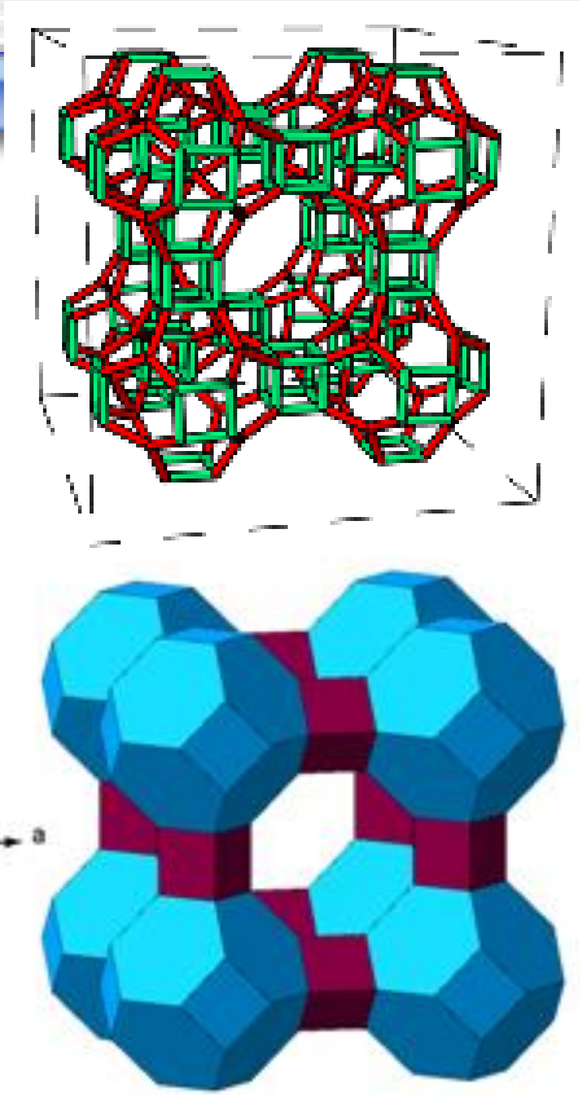
$M_{24}O_{36}$ Cages (M = Si, Al)



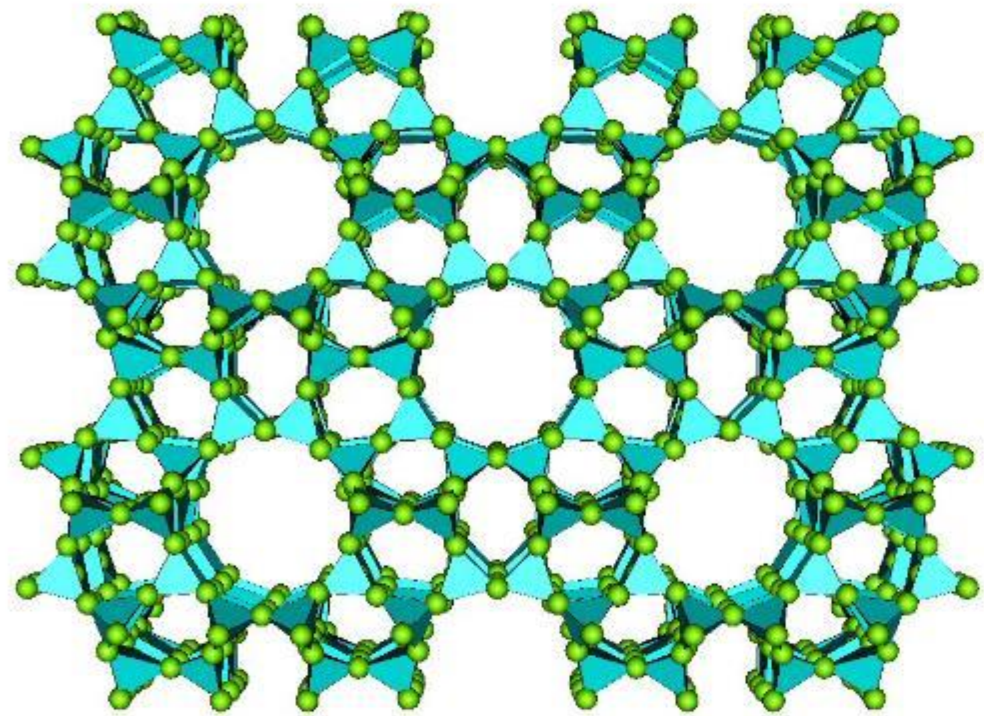
Supercages

Channels Accommodate $M^{1+,2+}$ & H_2O

Zeolite 3D Structure



Zeolite A



ZSM-5

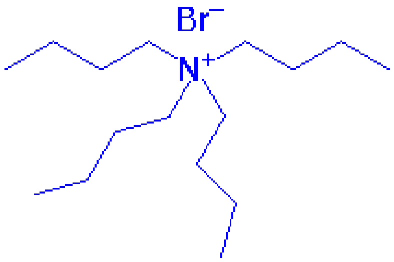
Synthesis of Zeolites

- In general: heat silica, alumina, and a hydroxide salt in water

$$SiO_2 + Al_2O_3 + AOH \xrightarrow{\Delta} zeolite$$

- Other sources of aluminum and silicon may be used
  - *E.g.* sodium silicate or sodium aluminate

- Cavities and channels formed directly around $[A(H_2O)]^+$ species or by using an organic templating molecule (e.g. TPA)

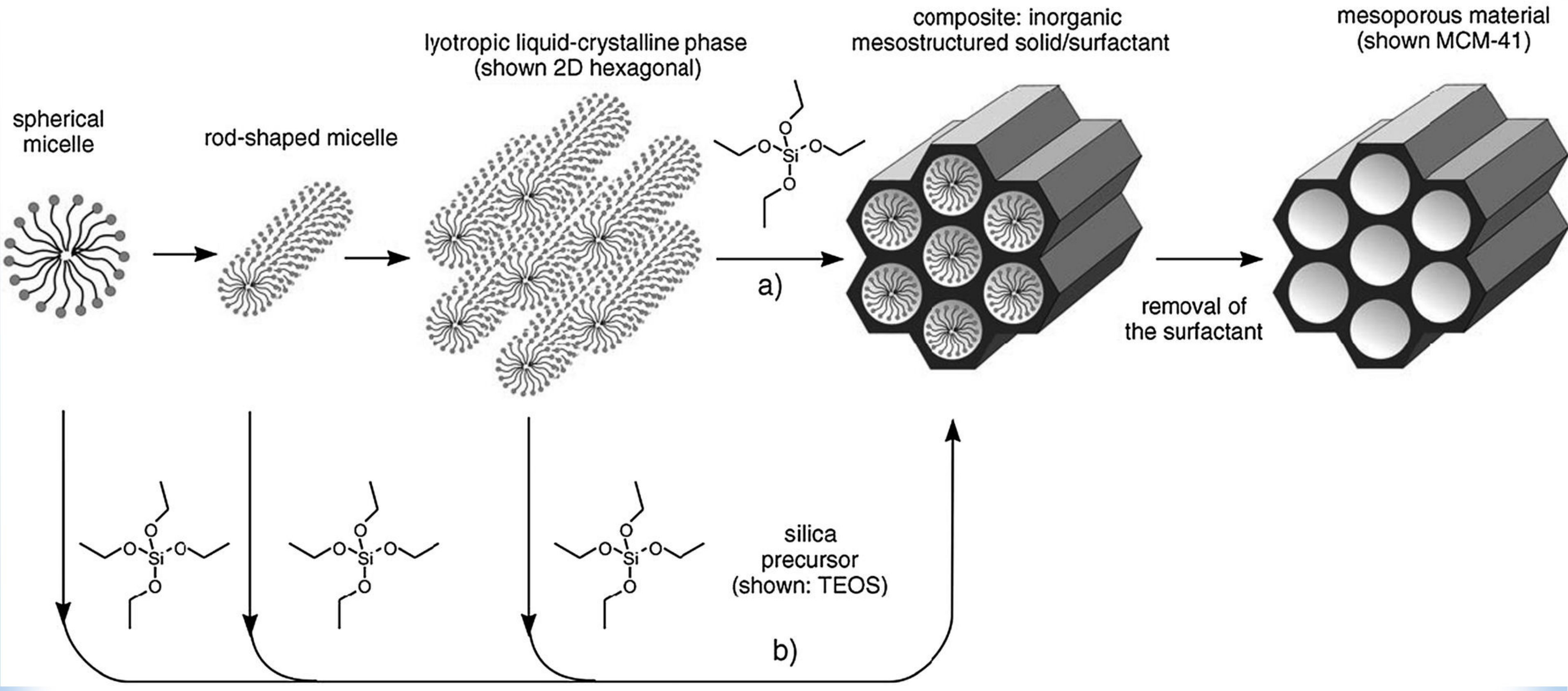


TBAB

- What problem(s) might one face when synthesizing zeolites?
- Different zeolites formed by varying ratios of reactants, order of reactions, temperature, pH, etc.

Beyond Zeolites

MCM-41: Mesoporous Silicates



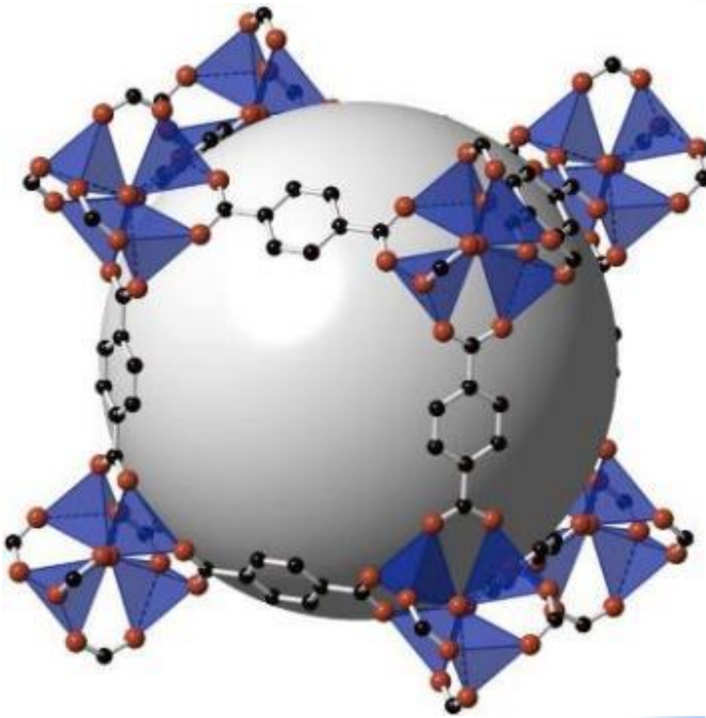
Zeolite Database

- Structural information for all known zeolites
- Generate simulated powder diffraction patterns
- 213 different framework structures – 3 letter codes
  - FAU (Zeolite X)
  - MFI (ZSM 5)

http://www.iza-structure.org/databases/

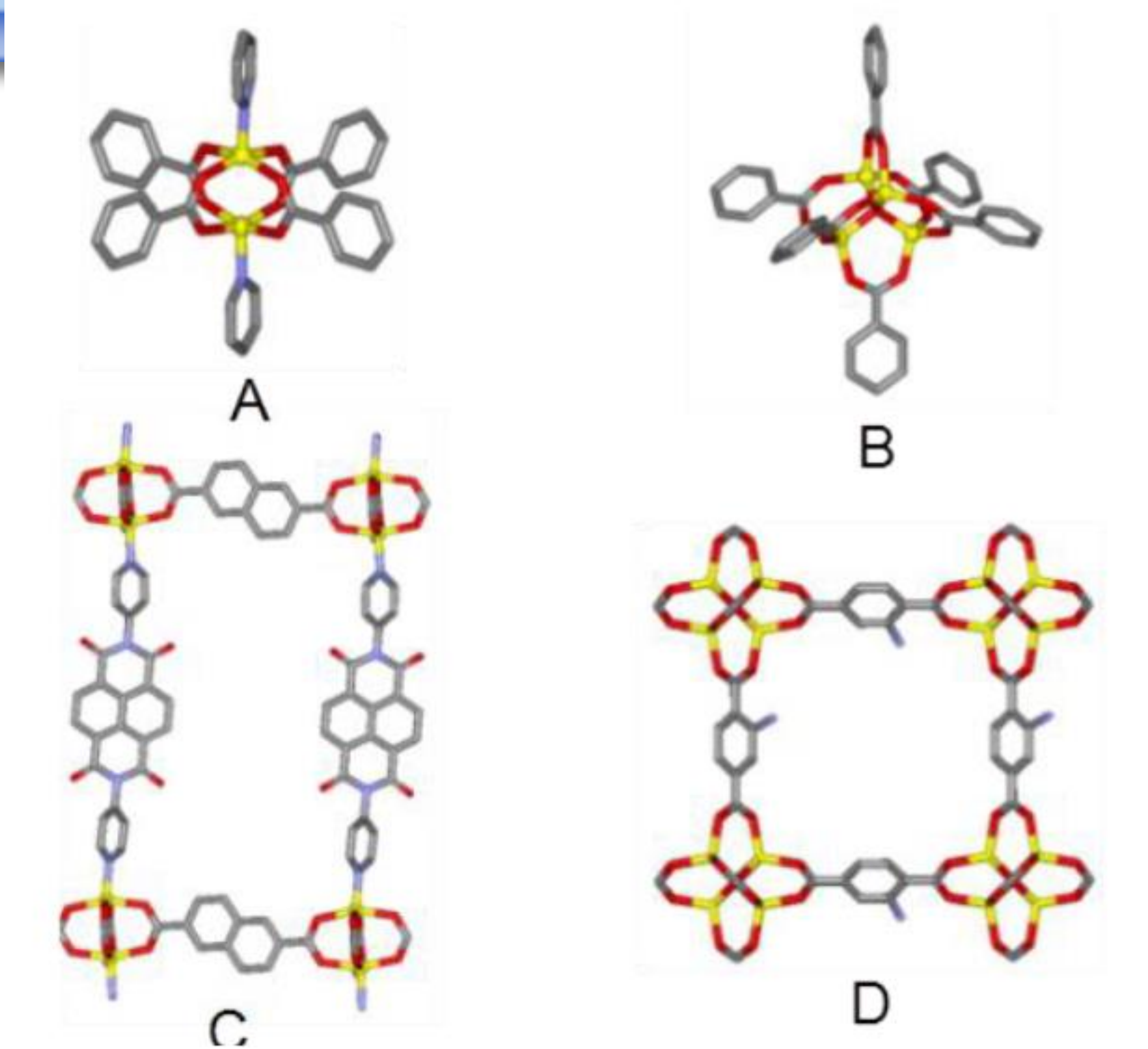
Metal-Organic frameworks

- Hybrid materials - inorganic and organic components
- Metal oxide clusters linked by organic molecules
- High surface areas – 1000 m^2/gram
- Functionalize components
- Gas storage, gas separation, catalysis



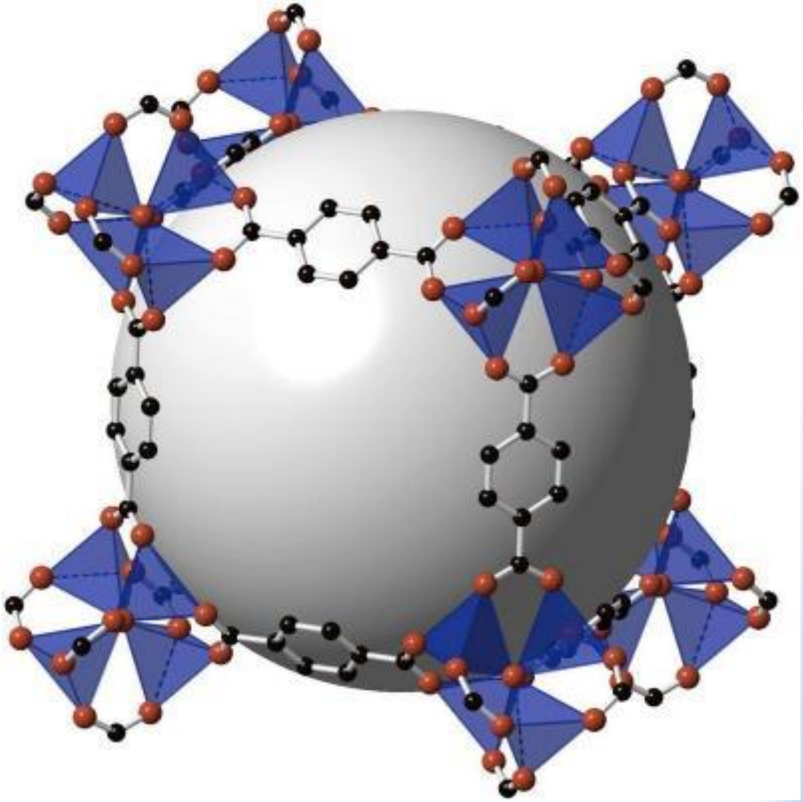
Yaghi, O.M. and Li, Hailian. *J. Am. Chem. Soc.* **1995**, *117*, 10401.
Noro, S.-I. *et al. J. Am. Chem. Soc.* **2002**, *124*, 2568.
Song, P. *et al. Microporous Mesoporous Mater.* **2011**, *142*, 208.
Bao, Z. *et al. J. Colloid Interface Sci.* **2011**, *357*, 504.
Ranocchiari, M. and van Bokhoven, J.A. *Phys. Chem. Chem. Phys.* **2011**, *13*, 6388.

Structure connectivity in MOFS



Metal-Organic Frameworks

- Hybrid materials - inorganic and organic components
- Metal oxide clusters linked by organic molecules
- Functionalize components
- High Surface Area



MOF-5

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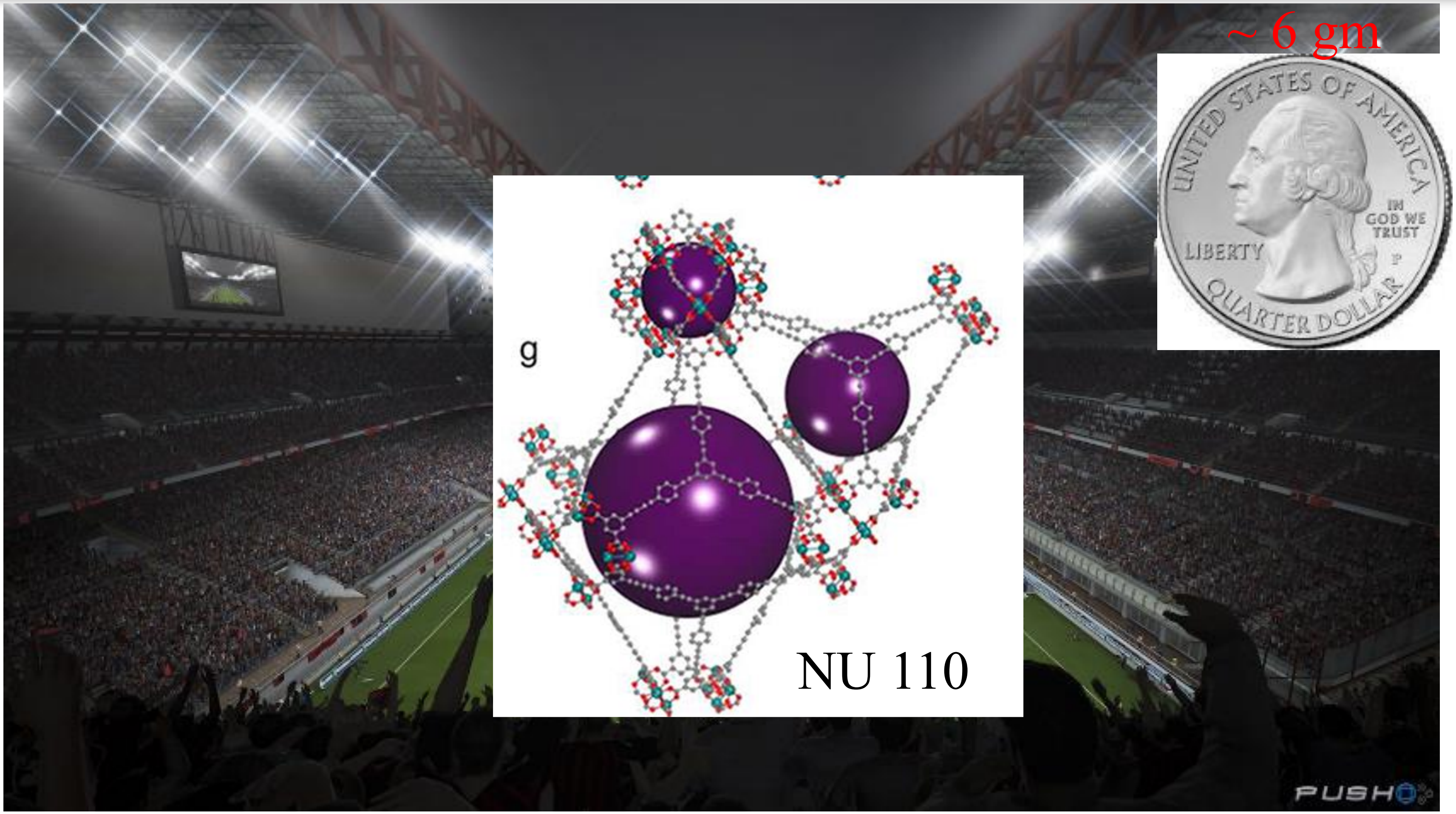
Farha, O.K. *et al. J. Am. Chem. Soc.* **2012**, *134*, 15016

MOFs



7140 m^2/gram: Farha, O.K. *et al. J. Am. Chem. Soc.* **2012**, *134*, 15016

MOF Applications

- Gas storage
  - H_2 fuel
- Gas separation
  - CO_2 and N_2

- Catalysis
- Drug delivery
- Sensors

Gas Storage

- Limited fuel supply and global warming warrant new energy solutions
- Hydrogen would be ideal solution
  - Hydrogen abundance
  - Burns cleanly
- Three big issues:
  - Hydrogen generation (from H_2O)
  - Efficient fuel cells
  - Storage

Gas Storage

Figure 1 Volume of 4 kg of hydrogen compacted in different ways, with size relative to the size of a car. (Image of car courtesy of Toyota press information, 33rd Tokyo Motor Show, 1999.)

Hydrides – too high temperatures and/or too low weight %
Liquid – cryogenics temperatures
Pressurized – too large/heavy tank

Schlapbach, L; Züttel, A. *Nature* **2001**. *114,* 353-358

Gas Storage

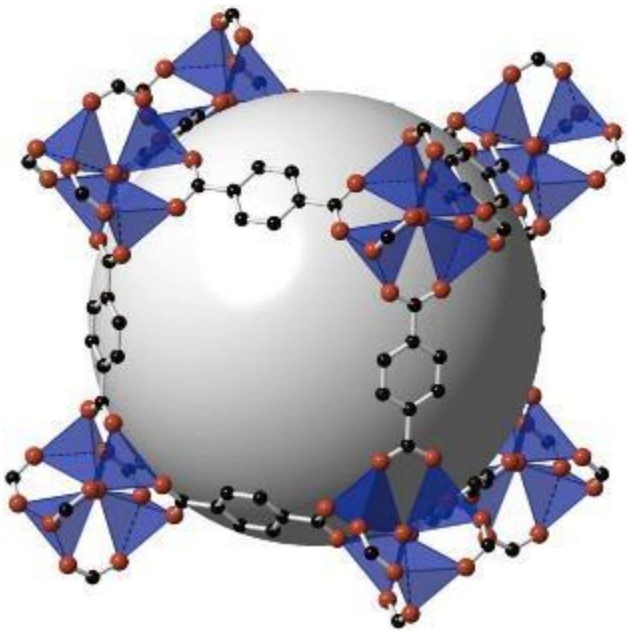
- MOFs – highly porous, can adsorb H_2 with high wt. %
- Physisorption
  - no strong hydride bonds
- Problems?
  - H_2 is bound too weakly (Van der Waals)
  - High pressure, low temperature needed to keep H_2 adsorbed

Gas Separation

- CO_2 – greenhouse gas produced from burning fuels
- Intense research for separating and storing CO_2 from products
- Porous structures in MOFs offer a potential solution

Gas Separation

- What challenges might MOFs have in separating CO_2 from a gaseous mixture?
  - Weak binding forces
  - Selectivity - how to selectively adsorb CO_2 over N_2
- Ideas?
  - CO_2 is more polarizable
  - larger quadrupole moment
- Functionalization
  - Open metal sites
  - Lewis base sites

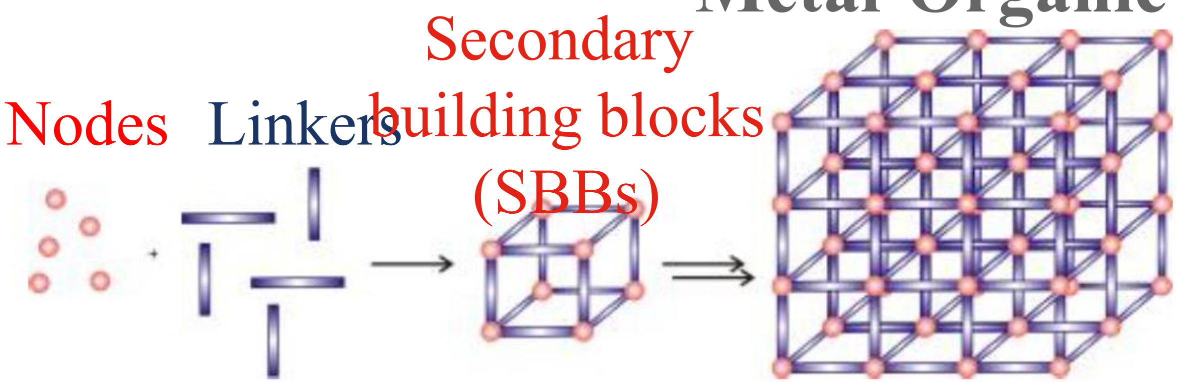


Synthesis

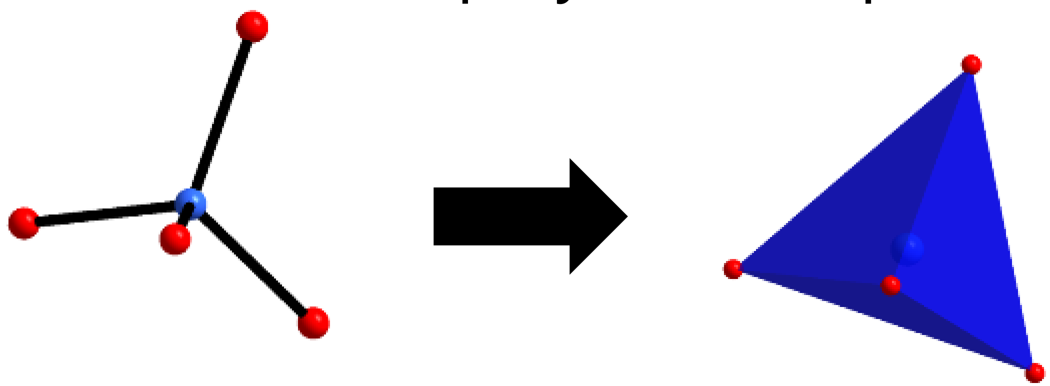
- Ligands and metal salts in solvent
- Room temperature – solvent evaporation
- Solvothermal Synthesis
  - Heating at elevated temperatures and pressures
- What other crystal growth techniques were discussed last lecture, and can they be used?

Structure

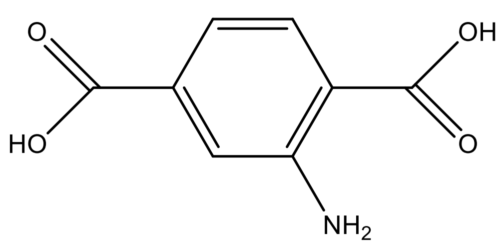
Metal-Organic Framework

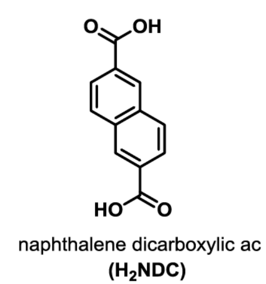


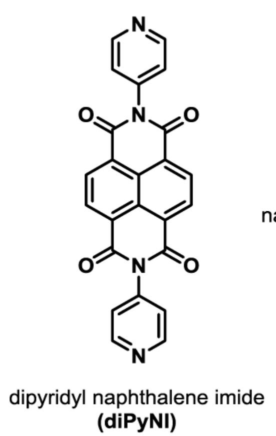
- Metal clusters - polyhedral representations



- Organic ligands

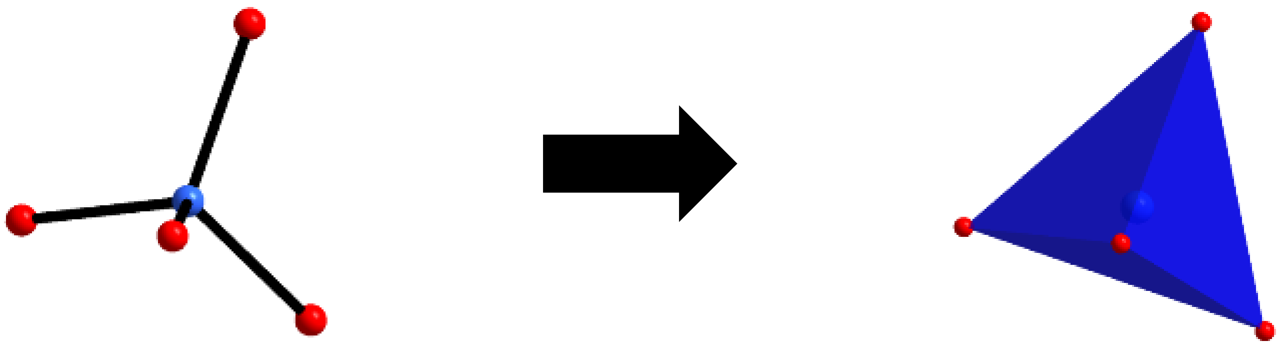




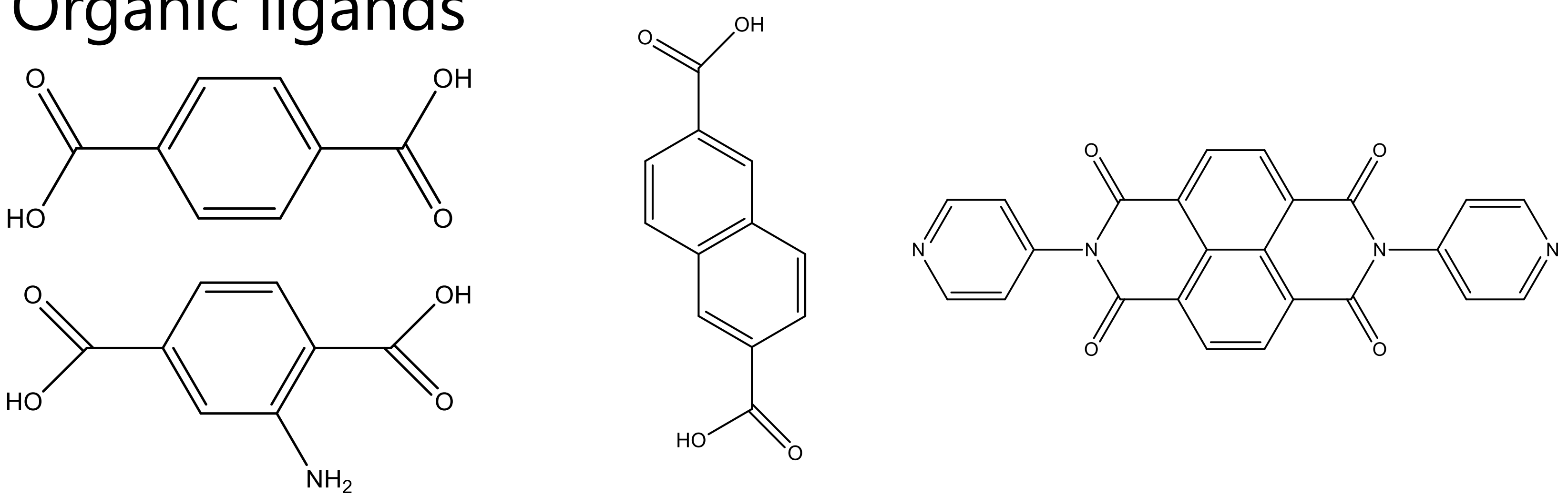


Structure

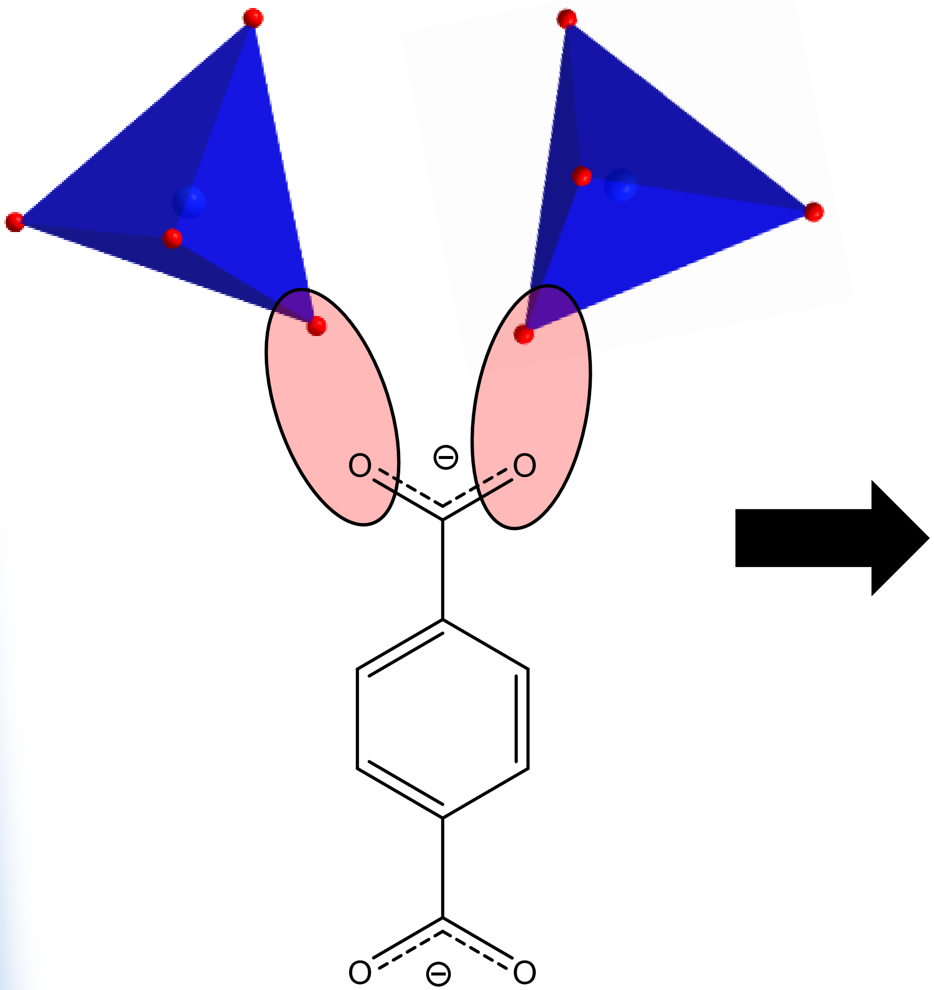
- Metal clusters - polyhedral representations

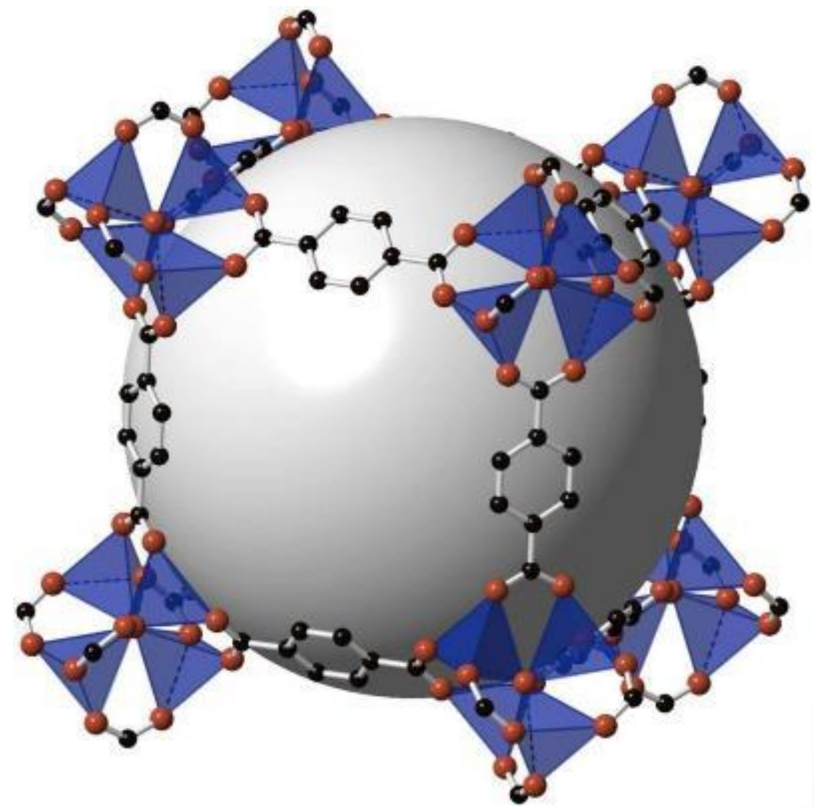


- Organic ligands



Structure

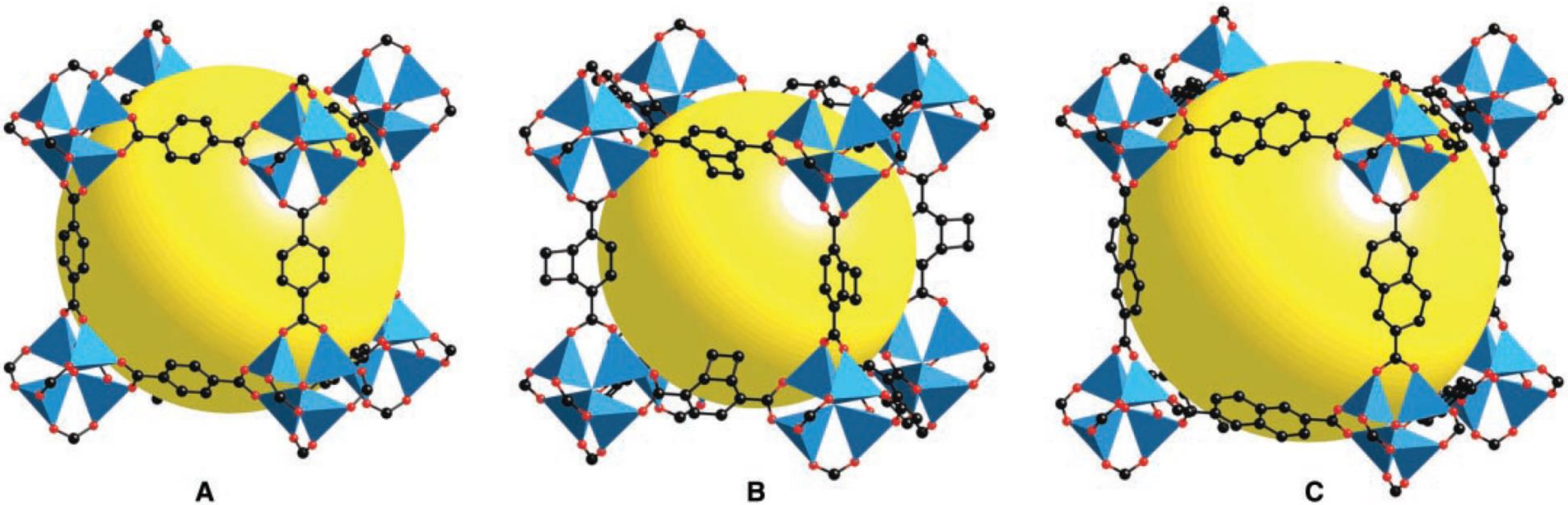




MOF-5

MOF Structural diversity

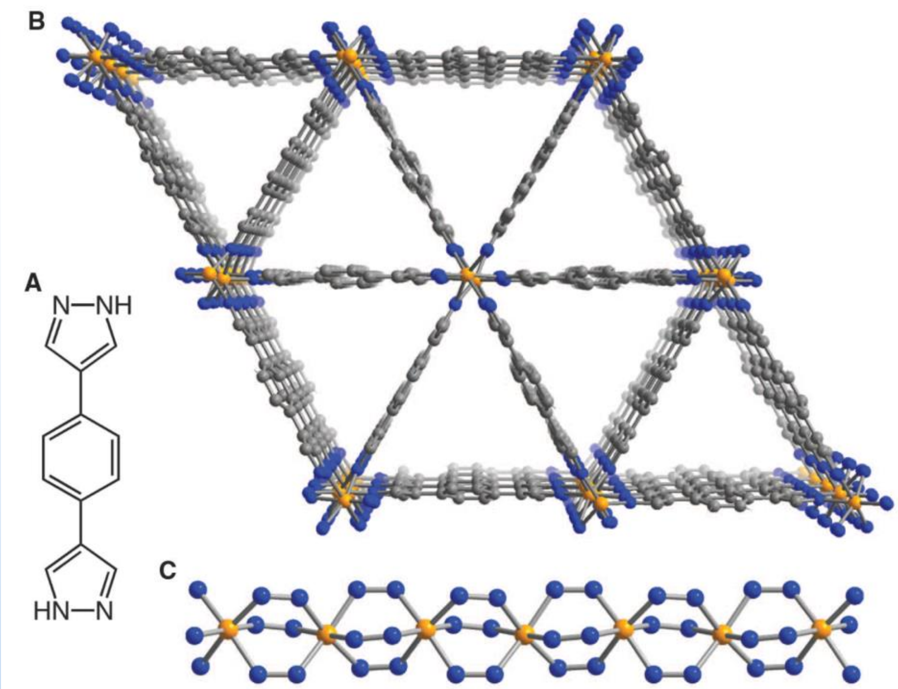
Reticular synthesis

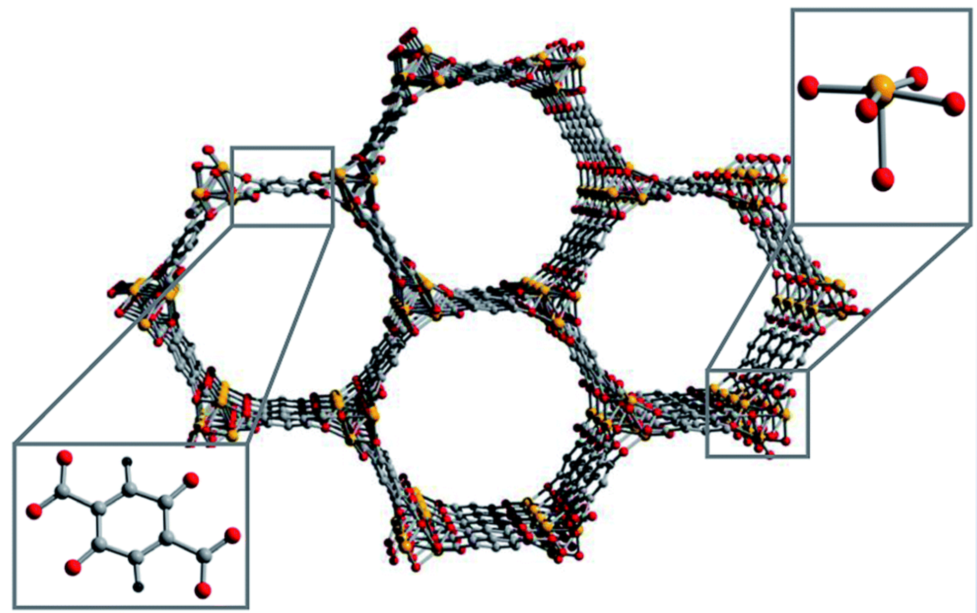


MOF Structural diversity

$Fe_2(BDC)_3$

$M_2(dobdc)$

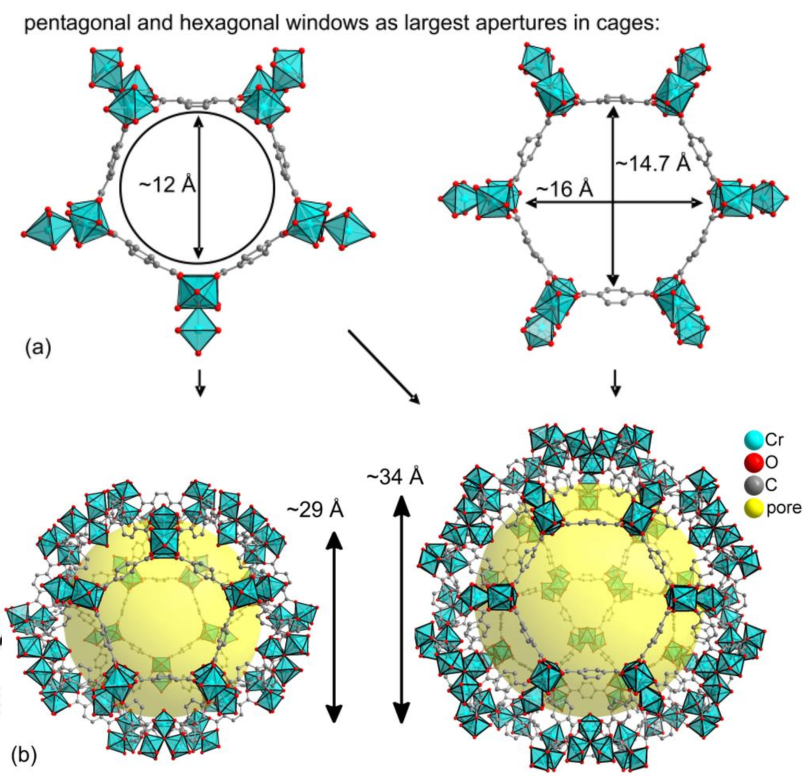


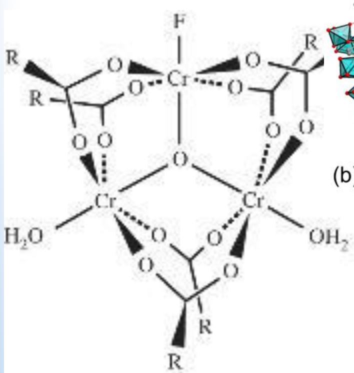


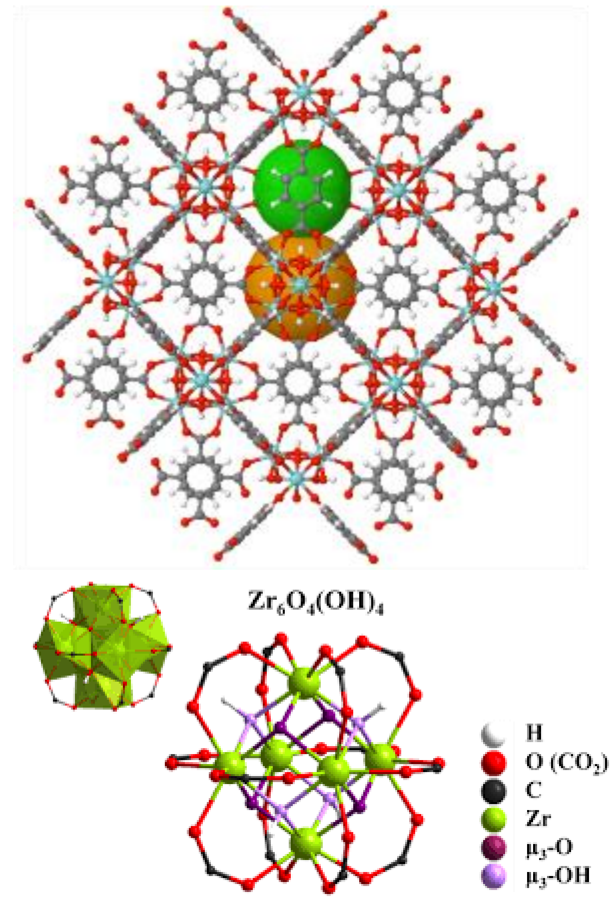
MOF Structural diversity

MIL-101

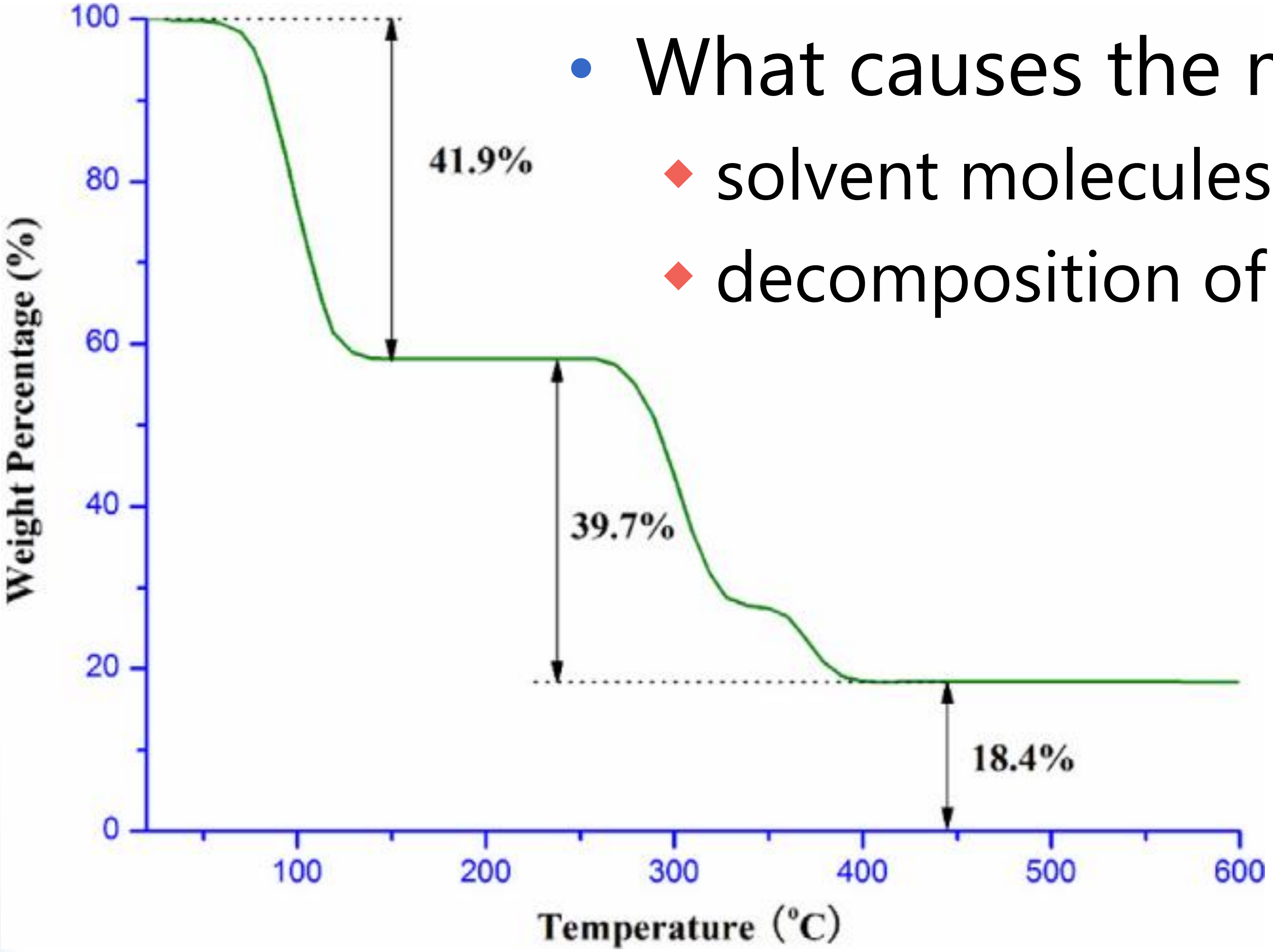
UiO-66







Thermogravitional analysis (TGA)



- What causes the mass loss?
  - solvent molecules in pores
  - decomposition of organic ligands