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Development of Nanocrystalline Zeolite Materials as Environmental Catalysts

Vicki Grassian and Sarah Larsen

Department of Chemistry, University of Iowa

- *Postdoctoral Associate*
  - Dr. Weiguo Song
- *Graduate Students*
  - Gonghu Li
  - Conrad Jones
  - Ramasubraman Kanthasamy
  - Lanell Rupert
- *Undergraduates*
  - Rachelle Justice

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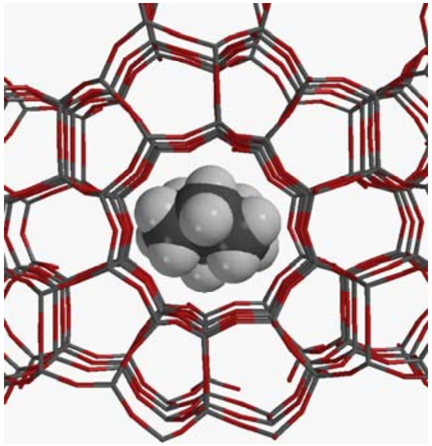
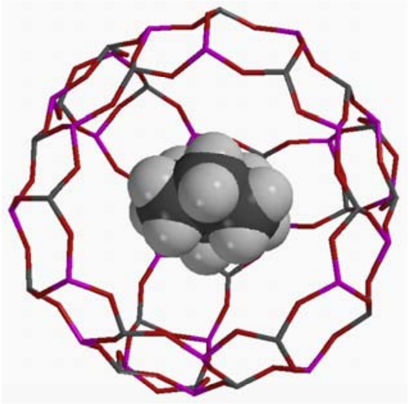
Zeolites

- Zeolites are aluminosilicates with well-defined openings of molecular dimensions (0.4 - 10 nm).

- Currently a large number of applications in:
  - Adsorption
    - Drying, purification, separation
    - Removal of volatile organics from air streams
  - Catalysis
    - Shape selective, acid catalysts, environmental catalysts
  - Ion exchange
    - Water-softeners in powdered laundry detergents

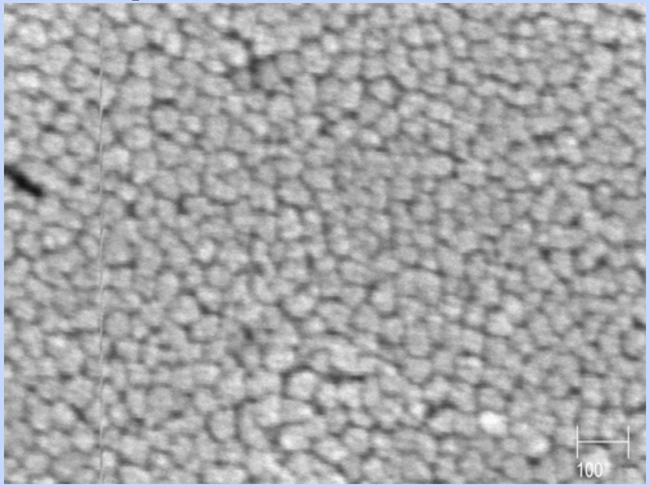


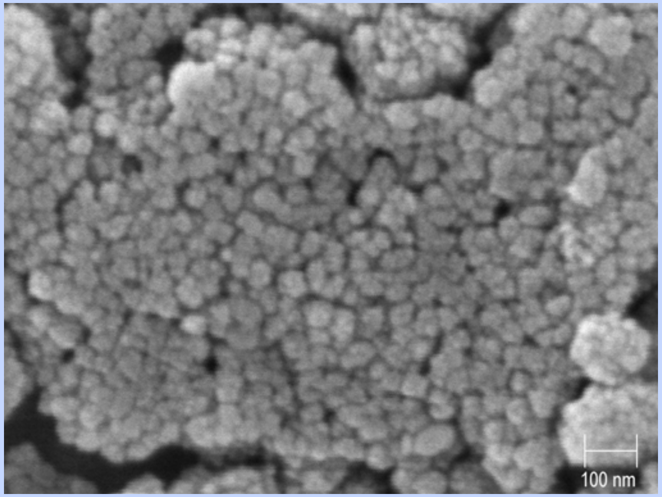
ZSM-5, 0.55 nm

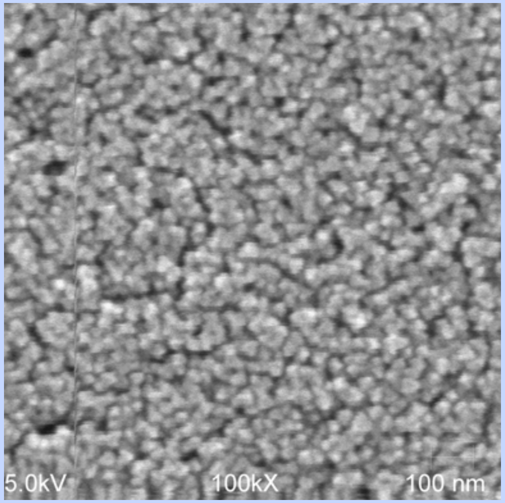


Y, 0.75 nm

Synthesis of Nanocrystalline Zeolites





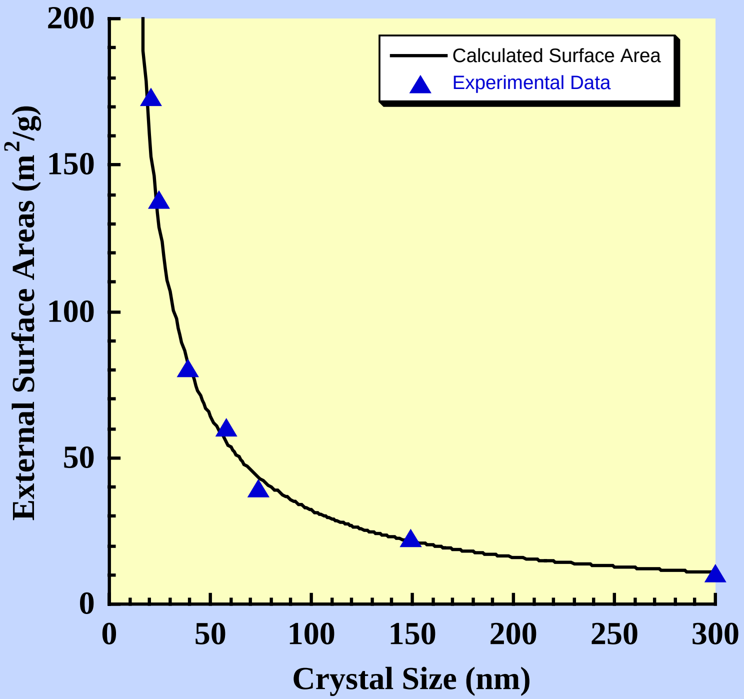


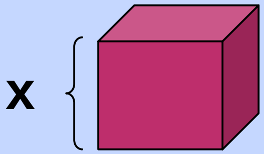
Silicalite	ZSM-5	Y
20 nm	15 nm	23 nm
174 (506) m^2/g	198 (492) m^2/g	173 (576) m^2/g

References: Song, Justice, Jones, Grassian and Larsen, a) Langmuir, **2004**, *20*, 4696-4702, b) Langmuir, **2004**, in press

Characterization

- **Powder X-ray Diffraction (XRD)**
  - Crystallinity and particle size (line width analysis)
- **Scanning Electron Microscopy(SEM)**
  - Particle size and morphology
- **Spectroscopic Characterization**
  - Solid State NMR Studies (Al, Si)
  - FTIR Studies (hydroxyl group region to determine more about the acidic properties of the zeolite)
  - Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)
- **Physical Characterization**
  - BET Analysis (external and internal surface area measurements)

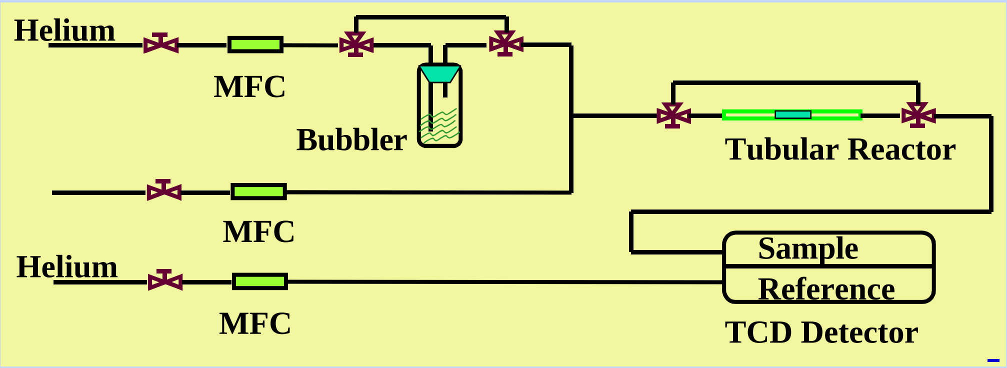


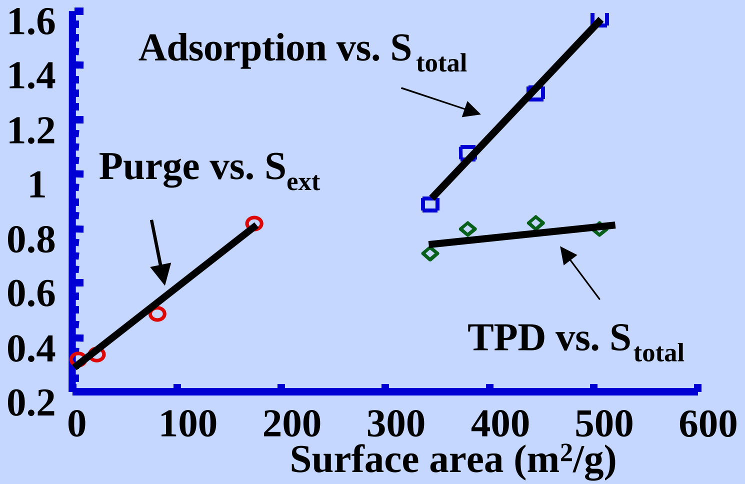


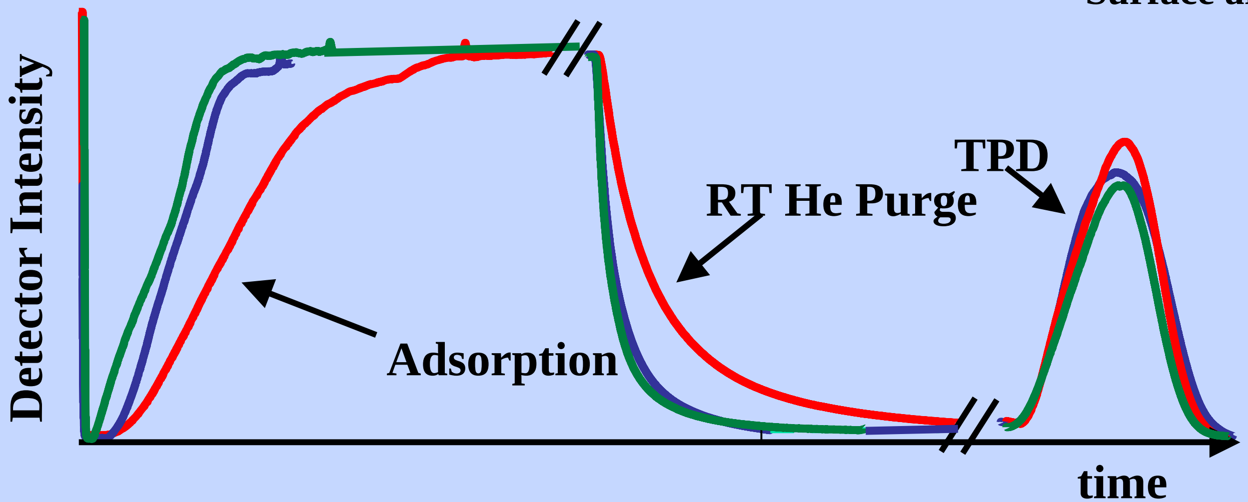
External surface area of cubic crystal:

$$\frac{3214}{x} \; m^2/g$$

Adsorption of VOC's on Nanocrystalline Zeolites

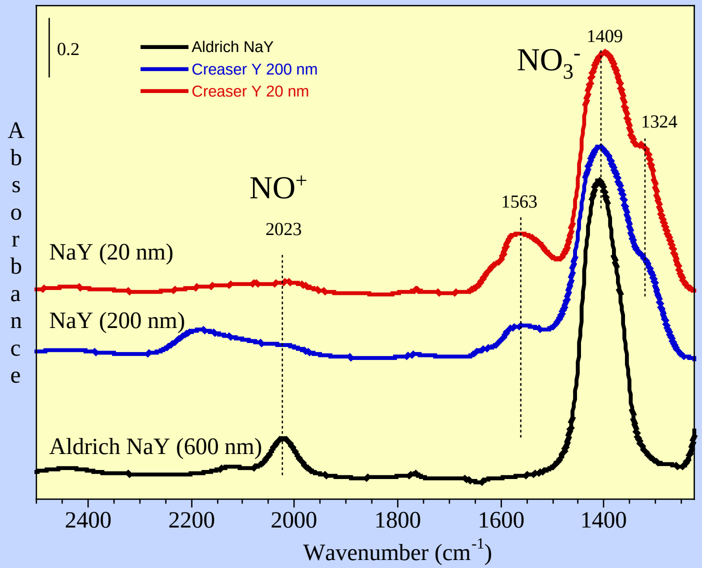






Selective Catalytic Reduction of NO_2 with Propylene

NO_2 Adsorption

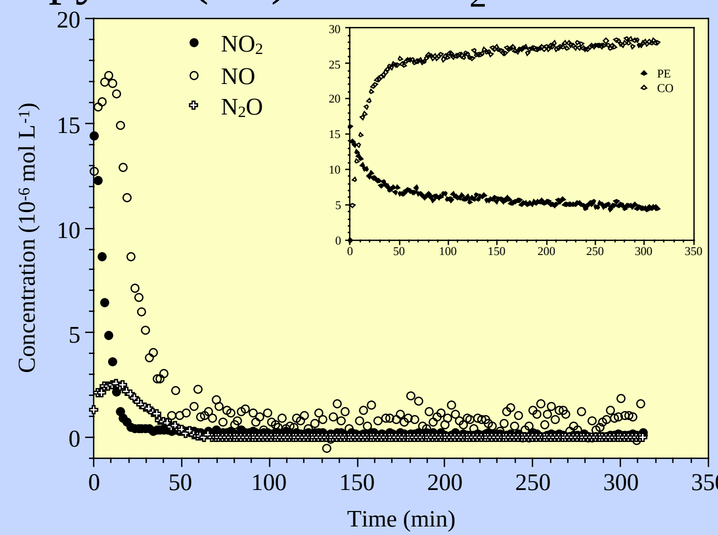


$$2NO_2 \text{ --> } NO_3^- + NO^+$$

NO_2 is stored on NaY as nitrate and nitrite species. NO_2 and propylene on NaY react completely at 473 K to form N_2 and O_2.

Propylene(PE) and NO_2 on NaY

Gas phase

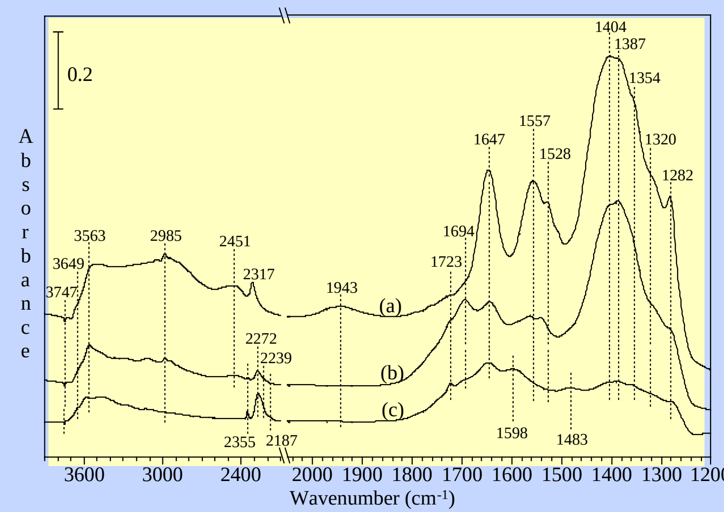


Surface species

298 K

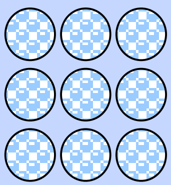
373 K

473K

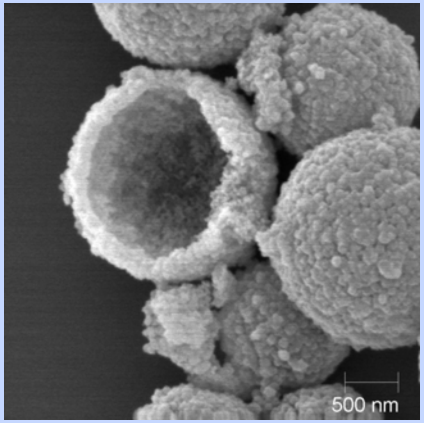


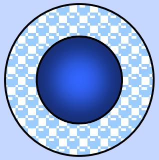
Hierarchical Assemblies of Nanocrystalline Zeolites

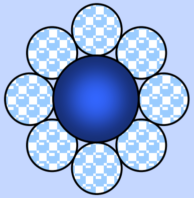
- A variety of nanoarchitectures can be constructed using nanocrystalline zeolites as building blocks.

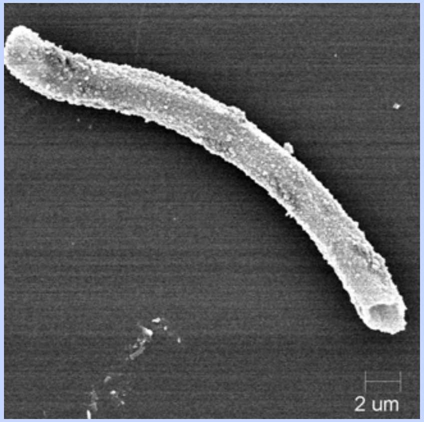


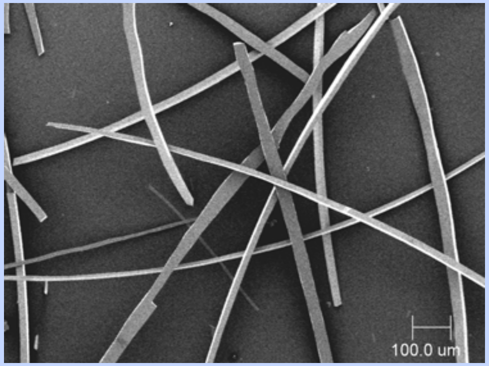
Hollow zeolite spheres or tubes







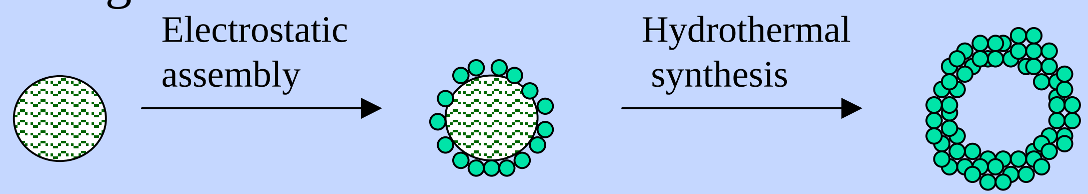




Self-assembled films and fibers

Preparation of Hollow Zeolite Structures

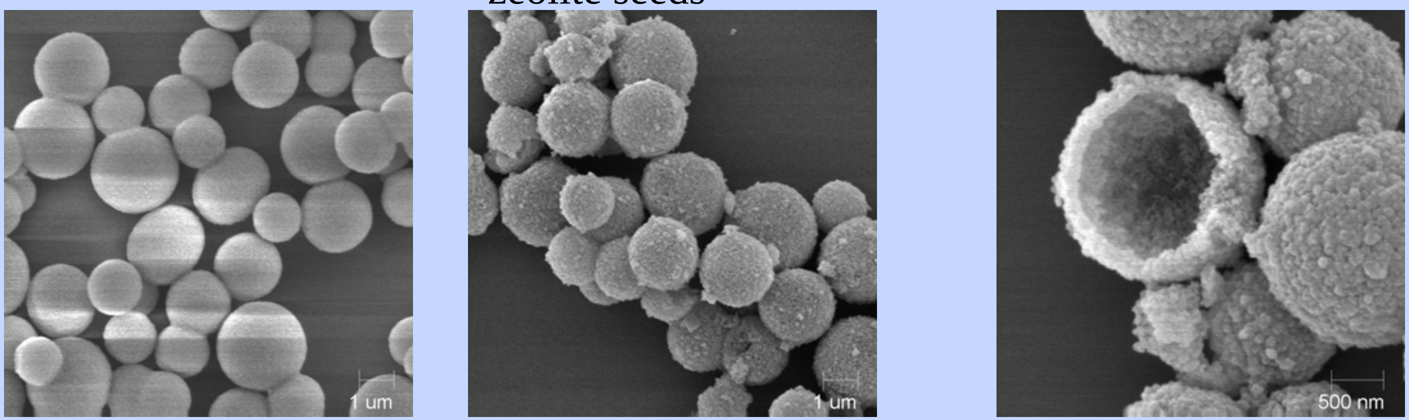
- Nanocrystalline zeolites are used as seeds to coat mesoporous silica (MS) with various morphologies.



Mesoporous silica (spheres, tubes)

MS coated with nanocrystalline zeolite seeds

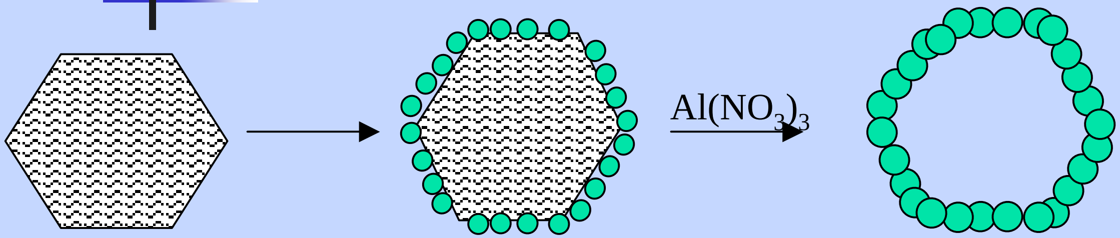
Hollow zeolite sphere (purely silicon forms)



It is also possible to incorporate guest species in the interior.

Reference: Dong, et al. *Microp. Mesopor. Mat.* 64 (2003), 69-81; Schulz-Ekloff, Rathousky, Zukl, Int. J. Inorg. Mater. 1 (1999), 97.

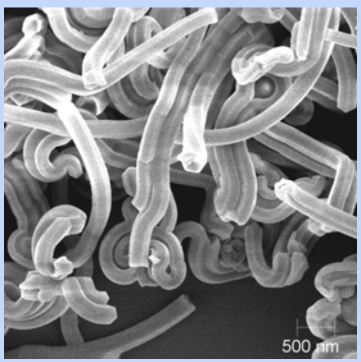
Incorporation of Aluminum into Zeolite Shells

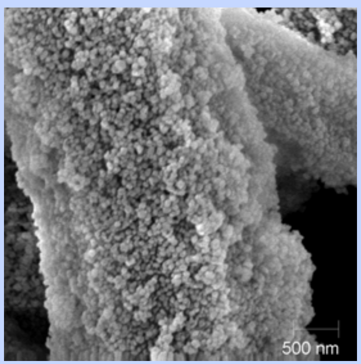


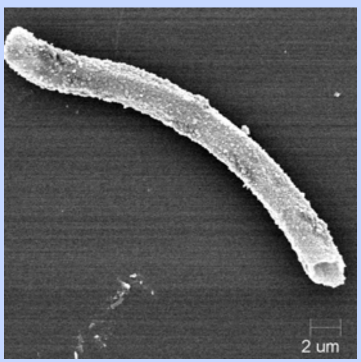
Mesoporous silica (hexagonal tubes)

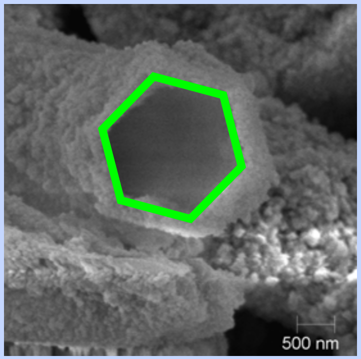
MS coated with nanocrystalline zeolite seeds

Hollow hexagonal zeolite tube



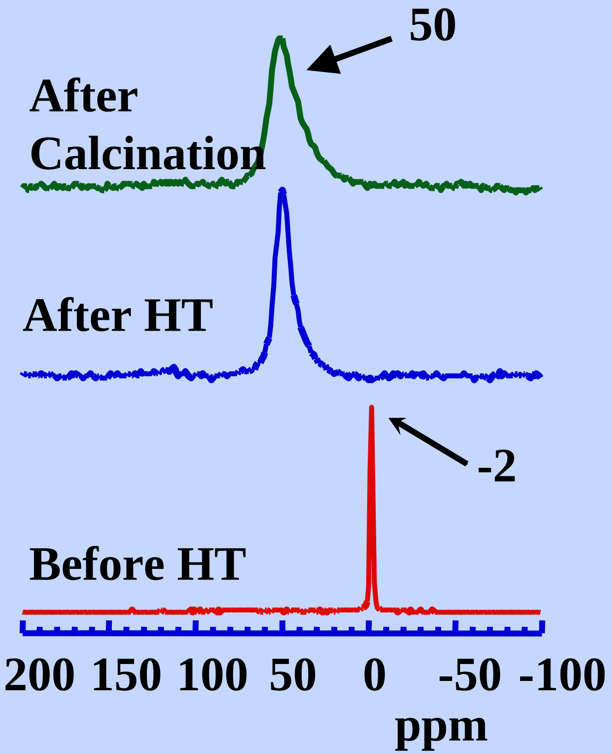






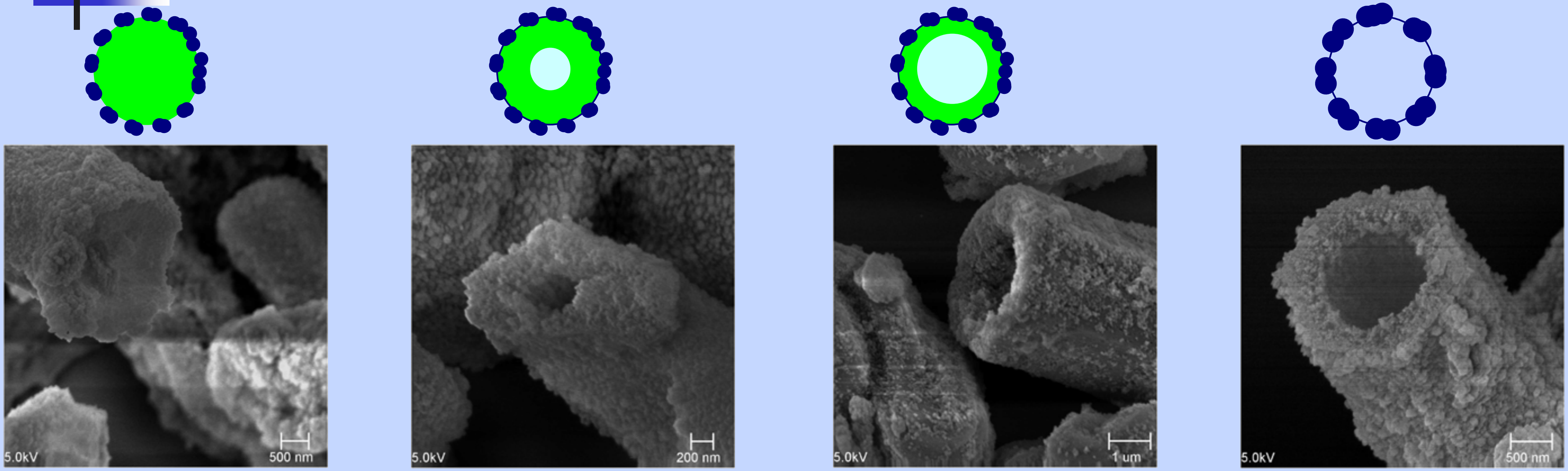
Reference: Song, Grassian and Larsen, Chem. Comm., **2004**, in press (*Chem Comm Hot Article*)

^{27}Al MAS NMR



^{27}Al MAS NMR confirms the presence of aluminum in the zeolite framework

Synthesis Mechanism and Applications

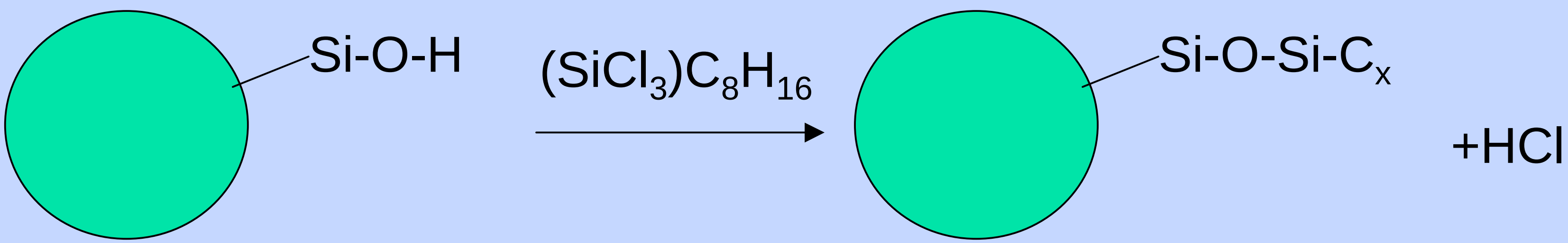


SEM images of MS seeded with nanocrystalline silicalite after hydrothermal treatment 0, 1, 4, and 16 h.

- The next step is to incorporate active species into the interior of the hollow zeolite structures (metal nanoparticles, catalysts)
- Potential applications
  - Cr(VI) reduction on iron-loaded zeolite tubes
  - Encapsulate magnetic materials into interior space so that hollow zeolite structures can be recovered from the environment after use as adsorbents

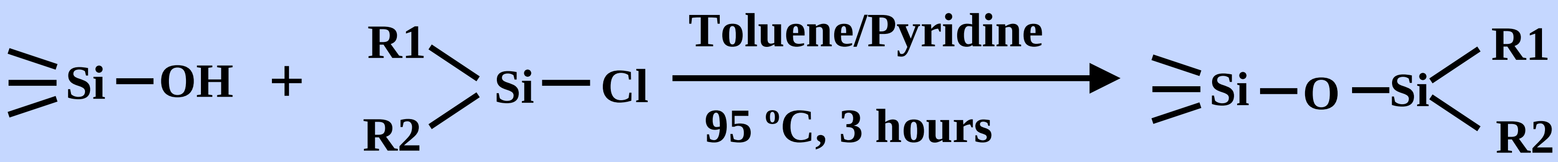
Functionalization of Zeolite Surfaces

- Functionalize external and internal surfaces with different functional groups
- Vary "solubility", acid base properties
  - Expand environments in which zeolites may be useful for applications in remediation and environmental catalysis

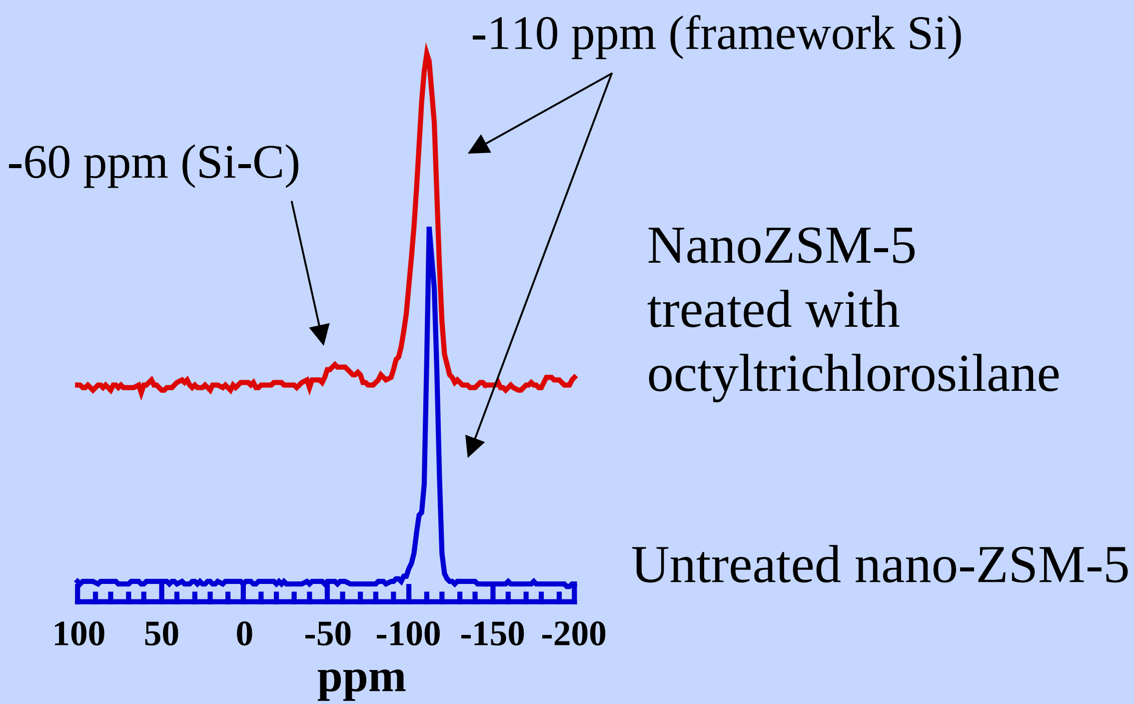


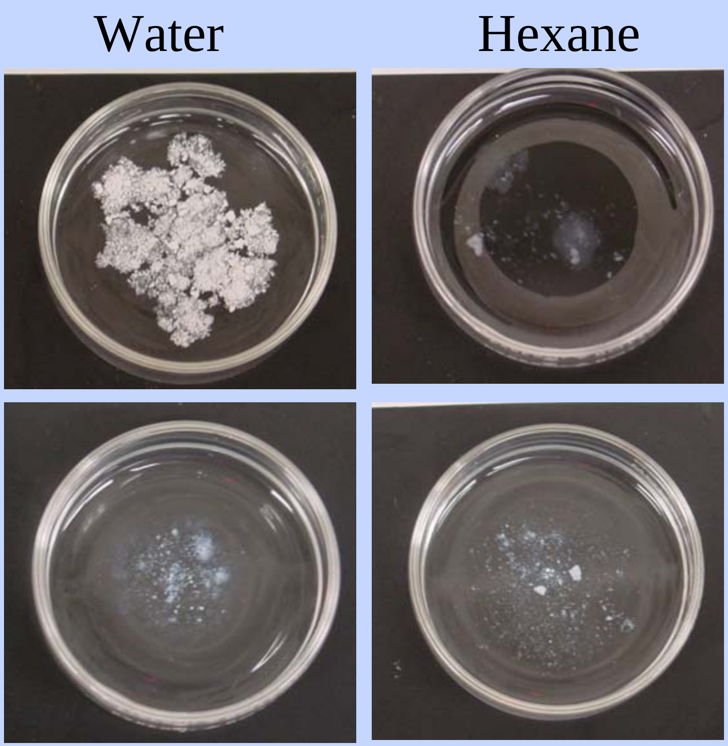
References: a) Usher, Michel, Stec and Grassian, *Atmos. Env.* 37 (2003) 5337-5347
b) Zhan, White, Lumsden, *Langmuir 2003*, 19, 4205-4210.

Nanocrystalline ZSM-5 Functionalized by Octyltrichlorosilane



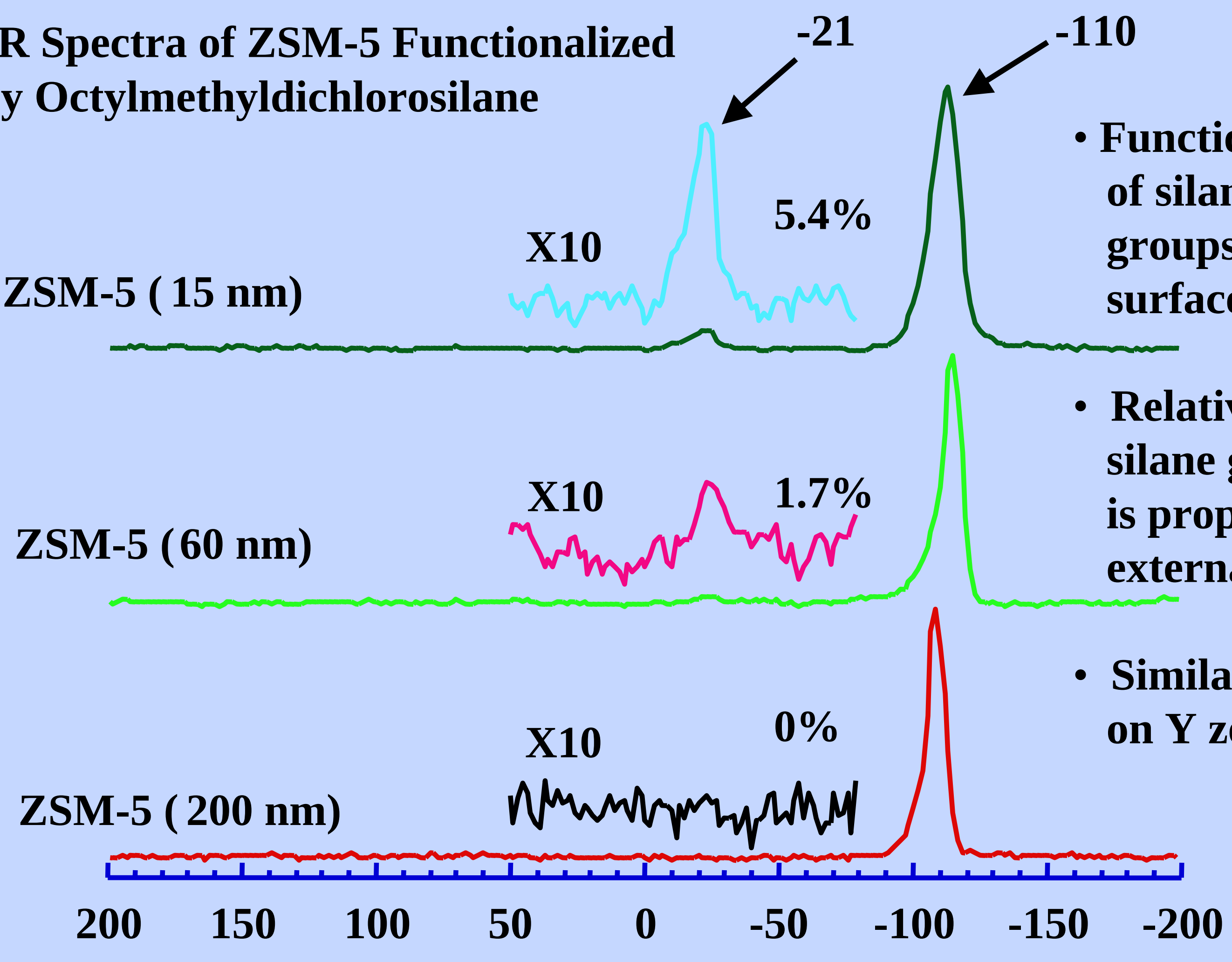
^{29}Si MAS NMR





Functionalization of Zeolites with Different Sizes

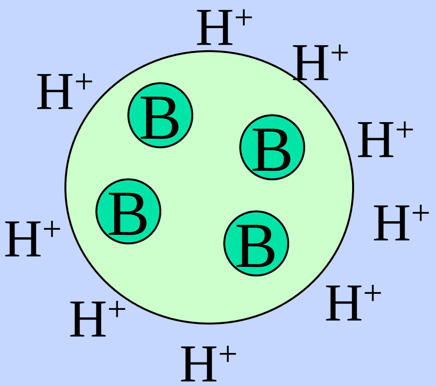
^{29}Si NMR Spectra of ZSM-5 Functionalized by Octylmethyldichlorosilane



- Functionalization of silanol groups on the external surface
- Relative amount of silane grafted on zeolites is proportional to external surface areas.
- Similar results observed on Y zeolites

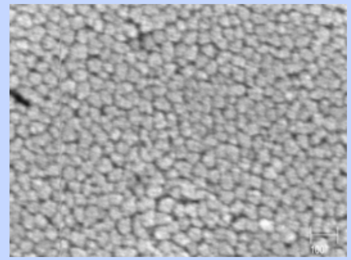
Applications for Functionalized Zeolites

- Adsorption of VOC's, such as toluene, from humid or aqueous environments
- Bifunctional Catalysts
  - Design catalyst for specific applications by incorporating acid/base, hydrophobic/hydrophilic properties
  - Exterior surface is functionalized with acid sites- can break a reactant molecule up on external surface- into smaller pieces that can diffuse into the zeolite pores for further reaction.

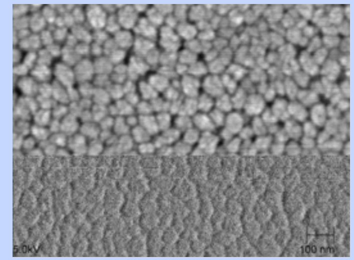


Development of Nanocrystalline Zeolite Materials - Summary

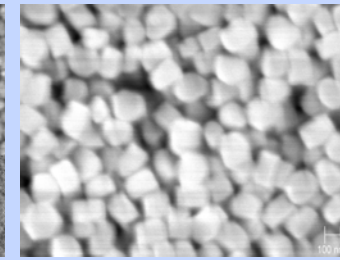
- Zeolite particle size can be **systematically** tuned in the nanometer range by varying reaction conditions.



20 nm

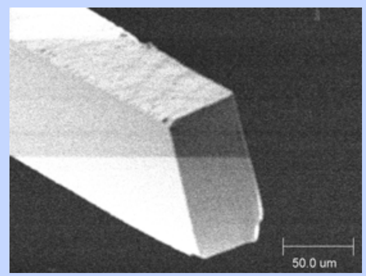


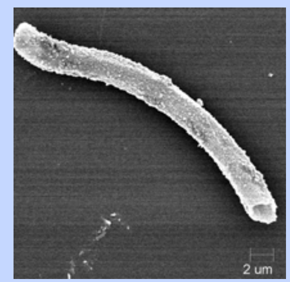
39 nm

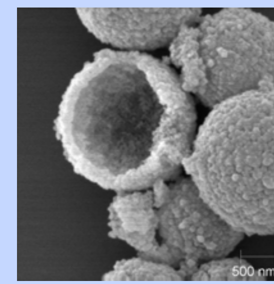


149 nm

- The nanocrystalline zeolites can be used as building blocks for <u>hierarchical zeolite structures</u> (fibers, films, hollow zeolite structures)







- Environmental applications for nanocrytalline zeolites and hierarchical structures:
  - Adsorption of volatile organic compounds (VOCs)
    - Toluene on silicalite, ZSM-5 and Y
  - Adsorption of VOCs from aqueous solutions or humid environments on functionalized zeolites
  - Selective Catalytic Reduction(SCR) of NO_2 with hydrocarbons on nanocrystalline Y zeolites
  - Cr(VI) Reduction on iron-loaded hollow zeolite structures
  - Demonstration of a bifunctional nanocrystalline zeolite catalyst
    - Different functionality on external and internal surfaces