# Development of Nanocrystalline Zeolite Materials as Environmental Catalysts

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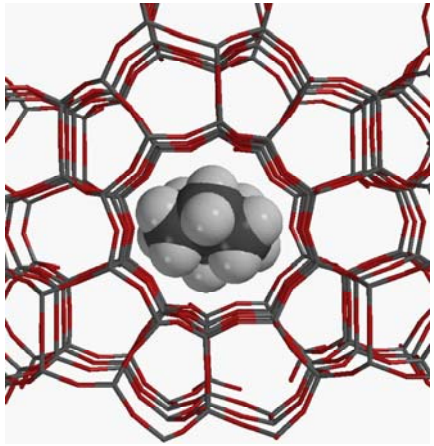
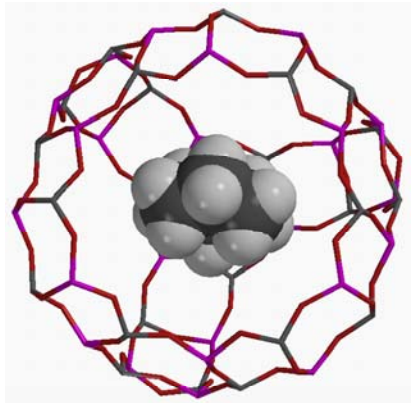
# Zeolites

- 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

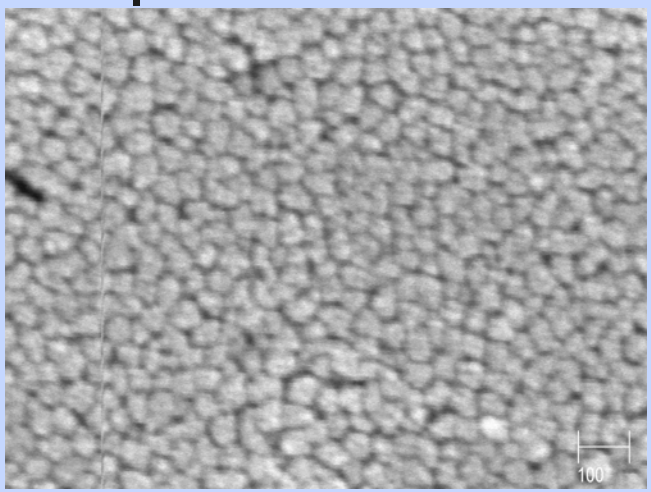


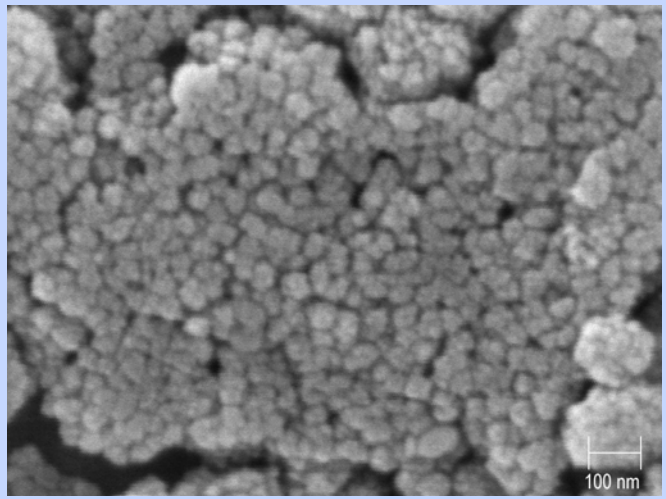
ZSM-5, 0.55 nm

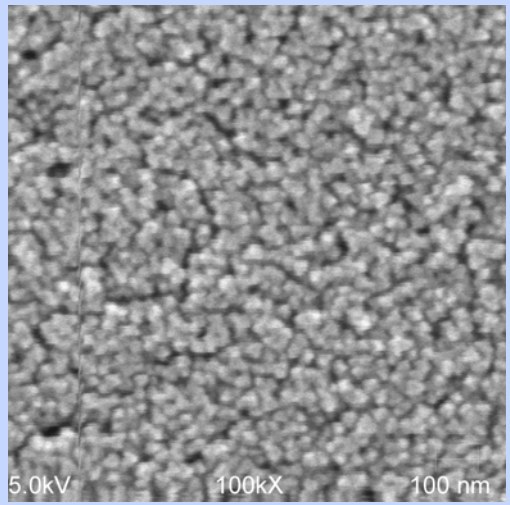


Y, 0.75 nm

# Synthesis of Nanocrystalline Zeolites



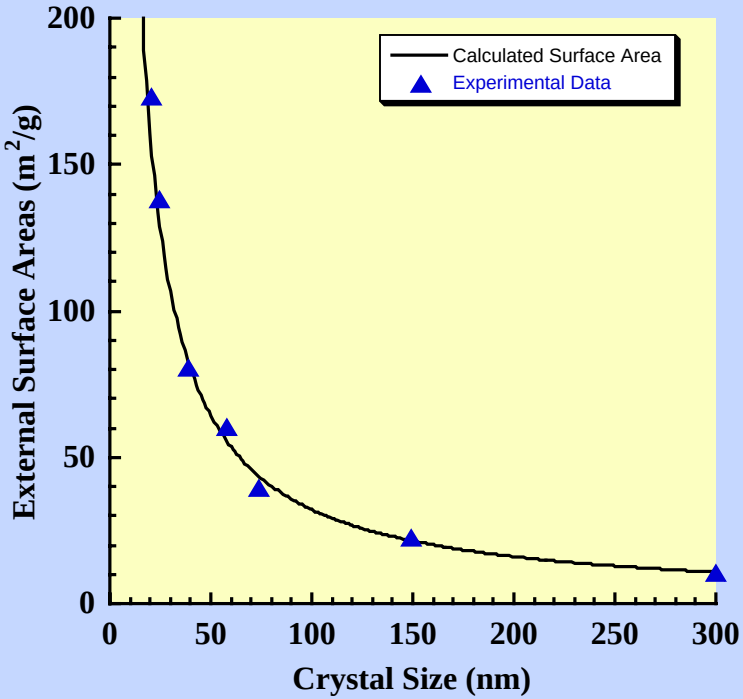



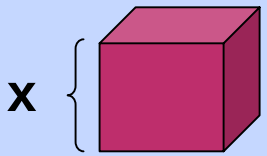

| Silicalite | ZSM-5 | Y |
|---|---|---|
| 20 nm | 15 nm | 23 nm |
| 174 (506) $m^2/g$ | 198 (492) $m^2/g$ | 173 (576) $m^2/g$ |

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)

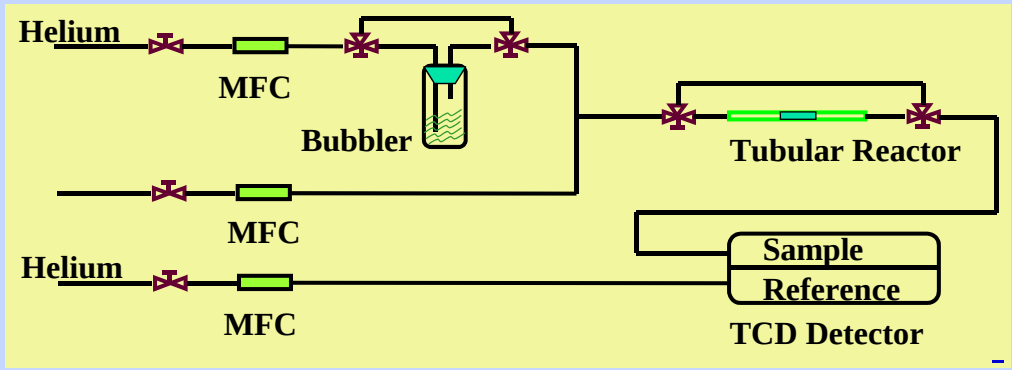


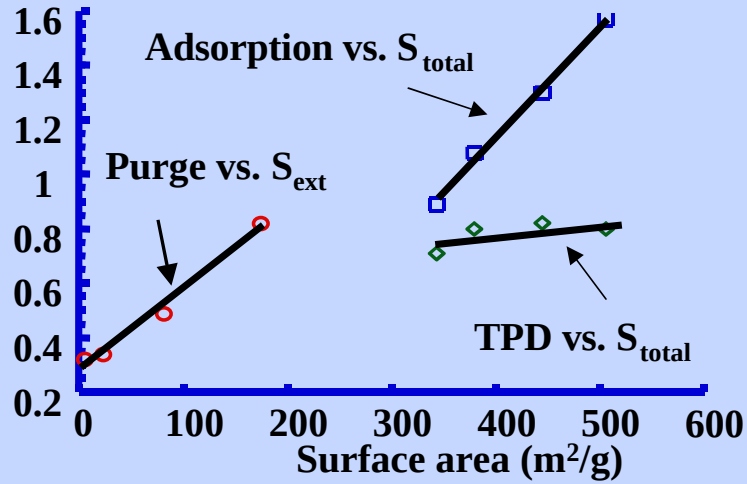



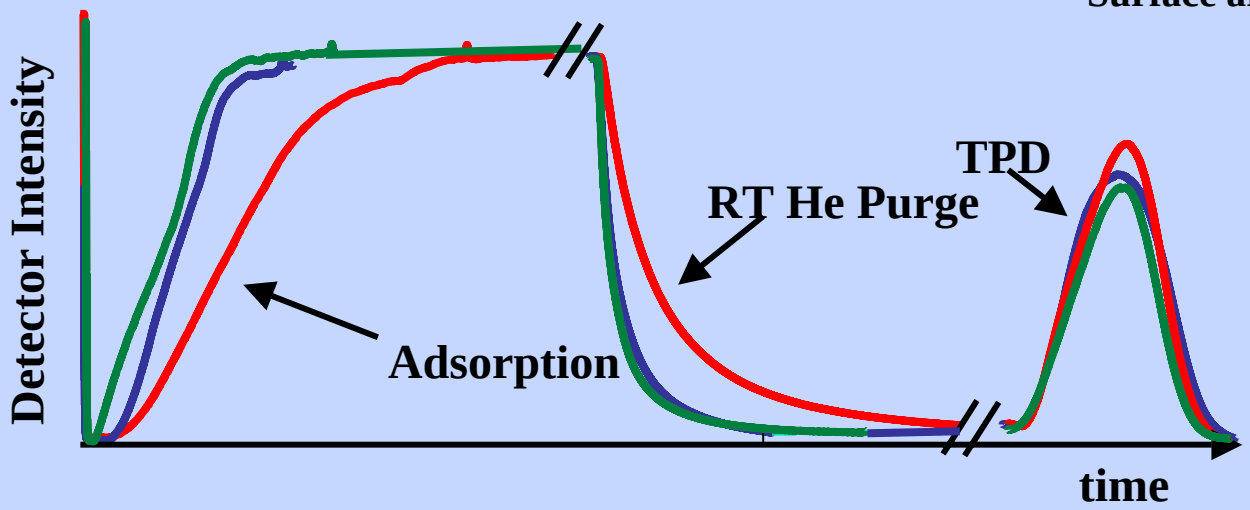

External surface area of cubic crystal:

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

# Adsorption of VOC's on Nanocrystalline Zeolites



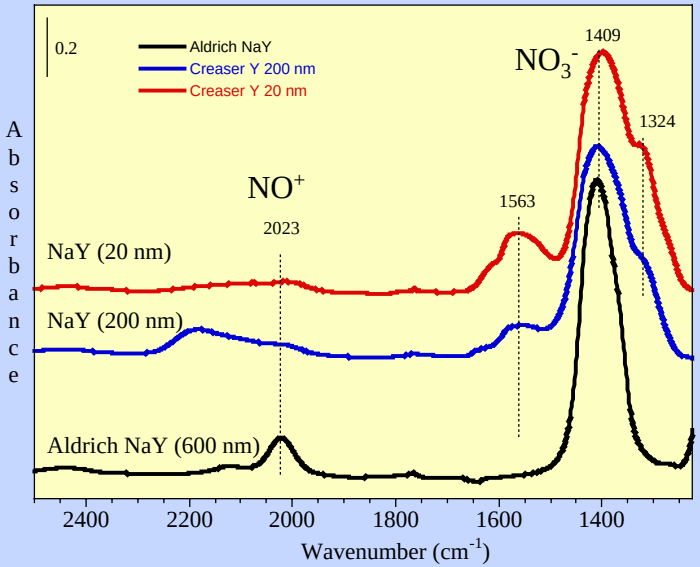




Silicalite-1-17 (20 nm) Silicalite-1-15 (149 nm) Silicalite-1-22 (1000 nm)

# Selective Catalytic Reduction of $NO_2$ with Propylene

## $NO_2$ Adsorption

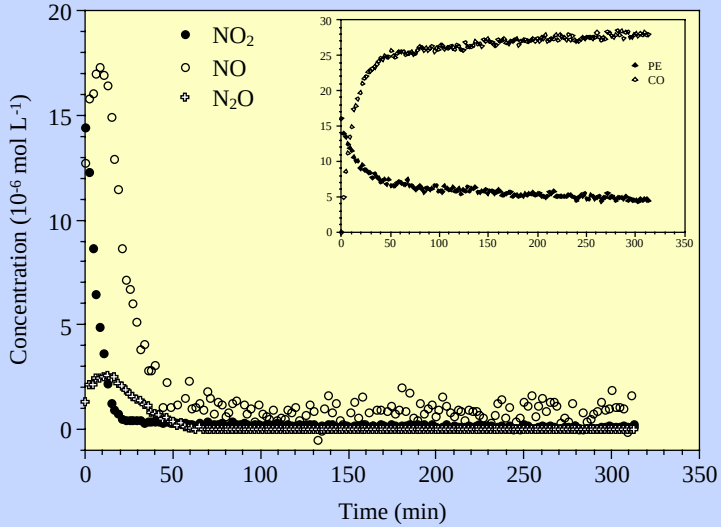



$2NO_2 \rightarrow NO_3^- + NO^+$

$NO_2$ 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

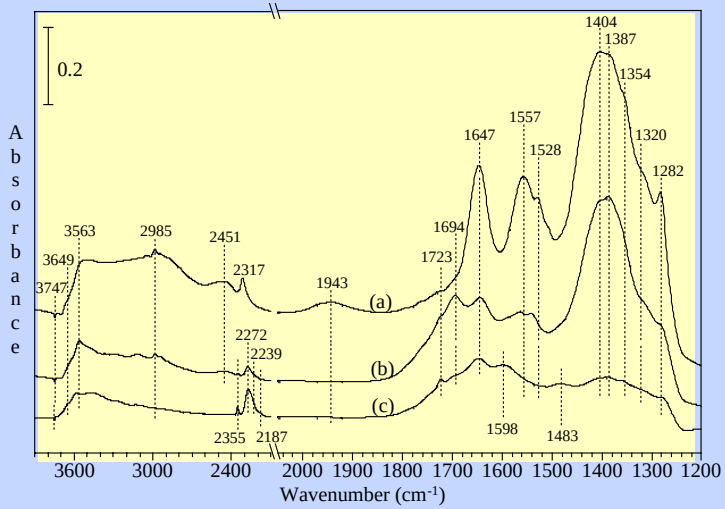



Surface species

298 K

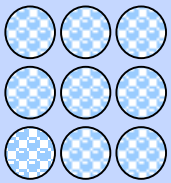
373 K

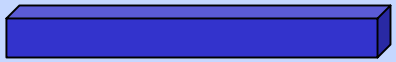
473K



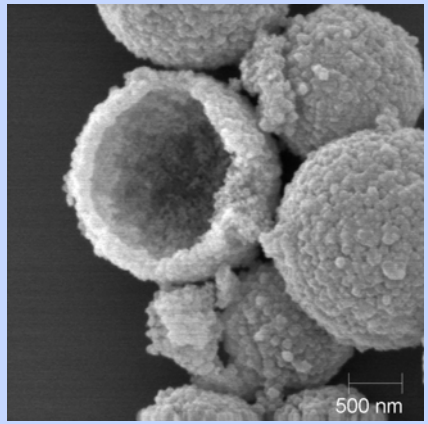
# Hierarchical Assemblies of Nanocrystalline Zeolites

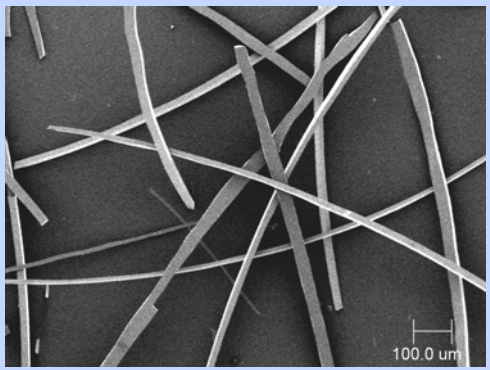
- A variety of nanoarchitectures can be constructed using nanocrystalline zeolites as building blocks.



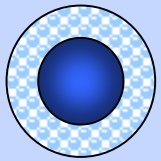


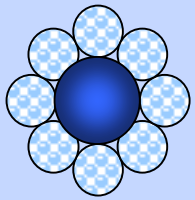
Hollow zeolite spheres or tubes

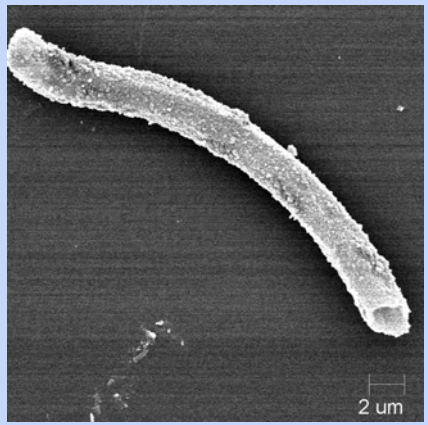





Self-assembled films and fibers

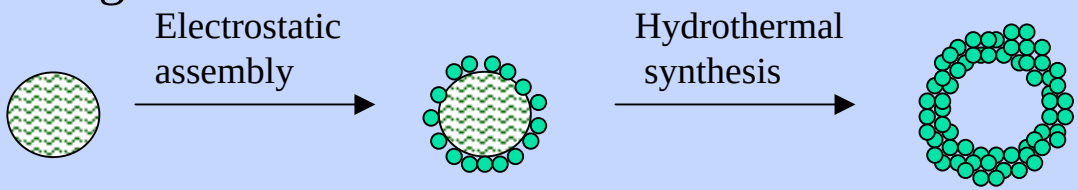






# Preparation of Hollow Zeolite Structures

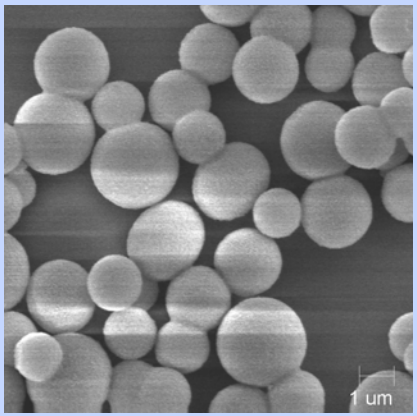
- Nanocrystalline zeolites are used as seeds to coat mesoporous silica (MS) with various morphologies.

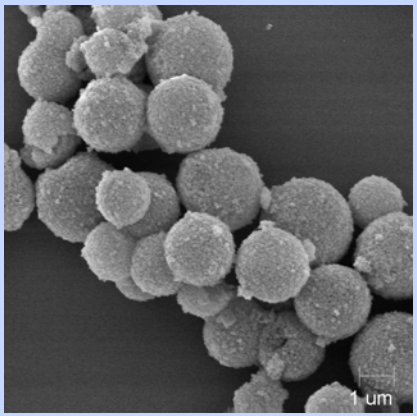


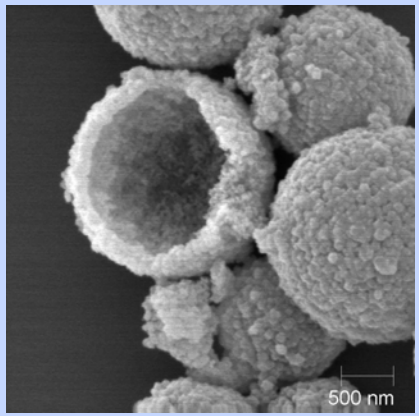

Mesoporous silica (spheres, tubes)

MS coated with nanocrystalline zeolite seeds

Hollow zeolite sphere (purely silicon forms)



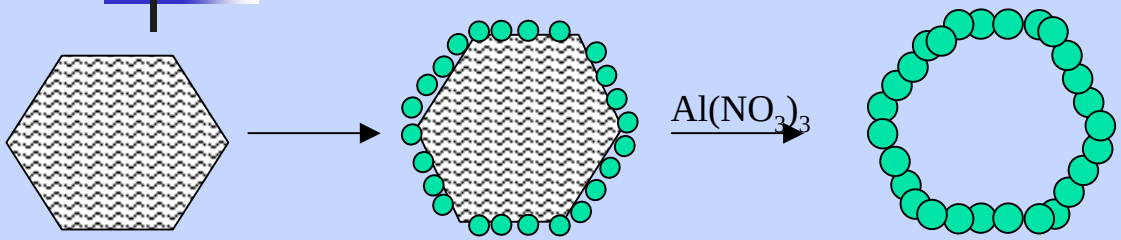




**It is also possible to incorporate guest species in the interior.**

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

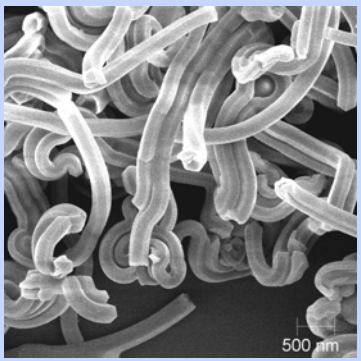
# Incorporation of Aluminum into Zeolite Shells

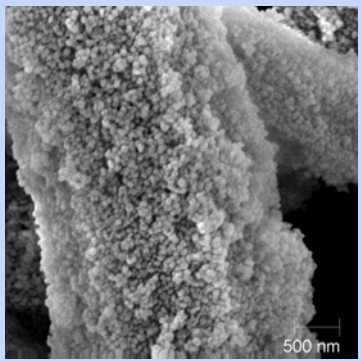


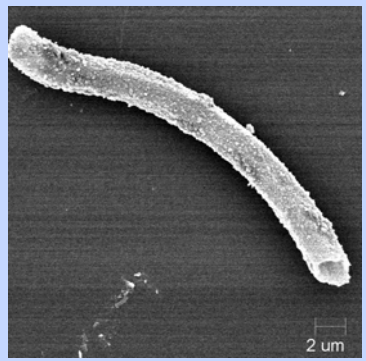

Mesoporous silica (hexagonal tubes)

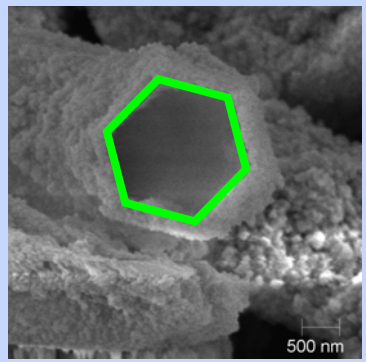
MS coated with nanocrystalline zeolite seeds

Hollow hexagonal zeolite tube



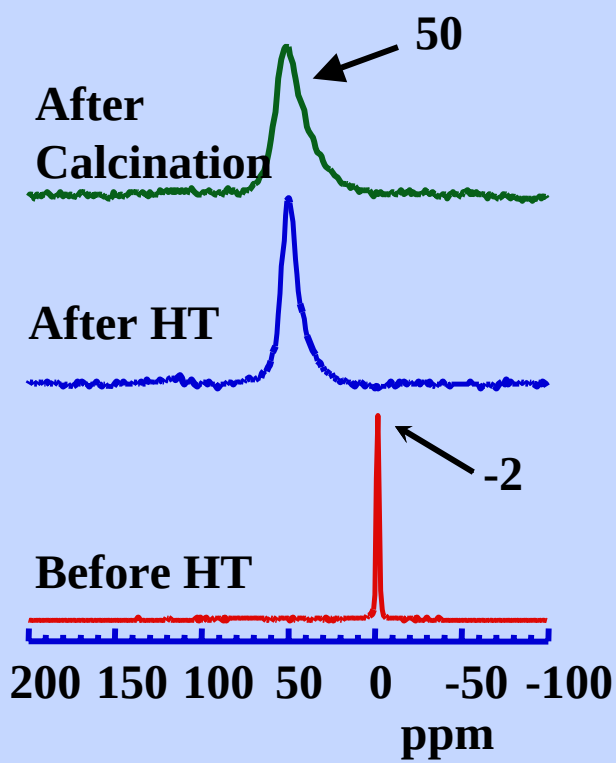



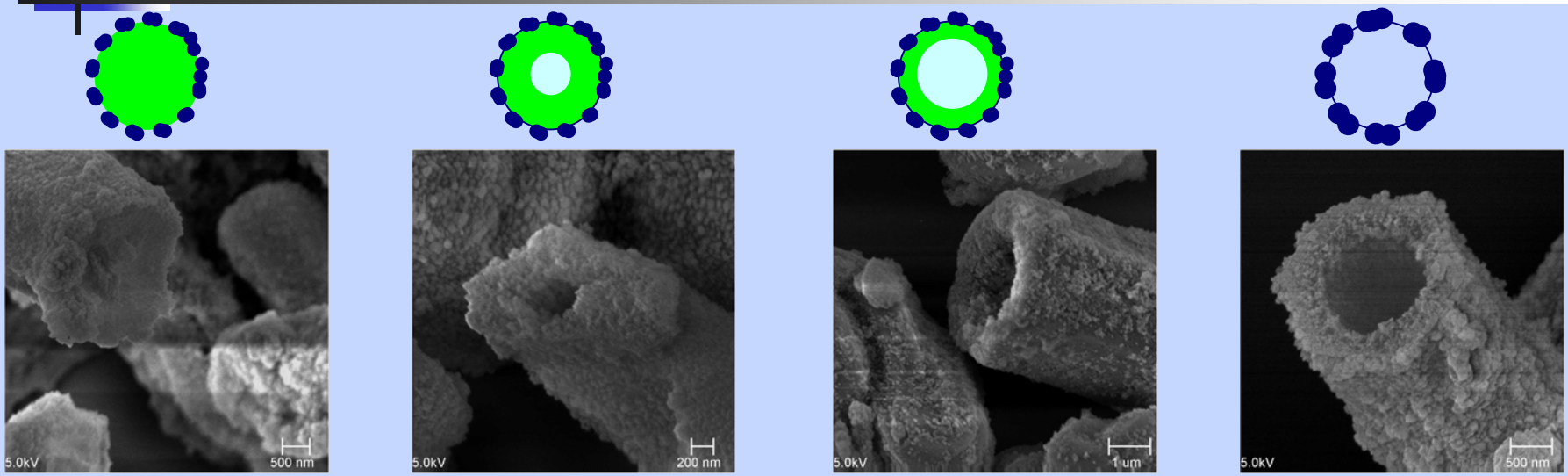

Reference: Song, Grassian and Larsen, Chem. Comm., **2004**, in press (*Chem Comm Hot Article*)

$^{27}$Al MAS NMR




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

# Synthesis Mechanism and Applications

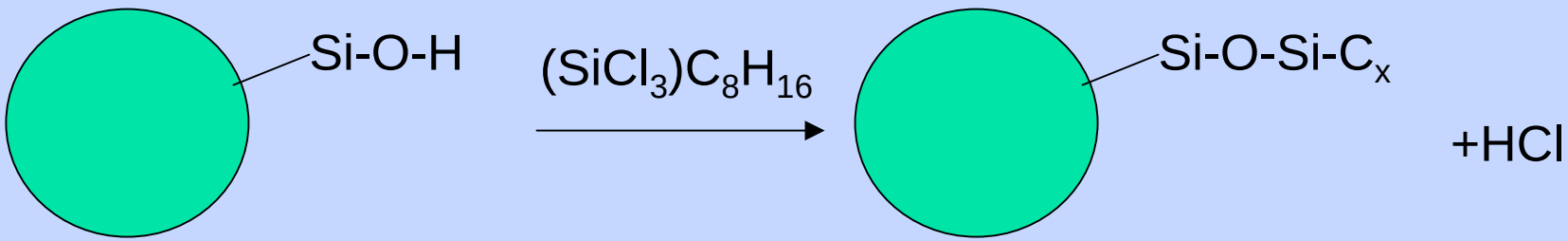



SEM images of MS seeded with nanocrystalline silicalite after hydrothermal treatment 0, 1, 4, and 16 h.

- 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

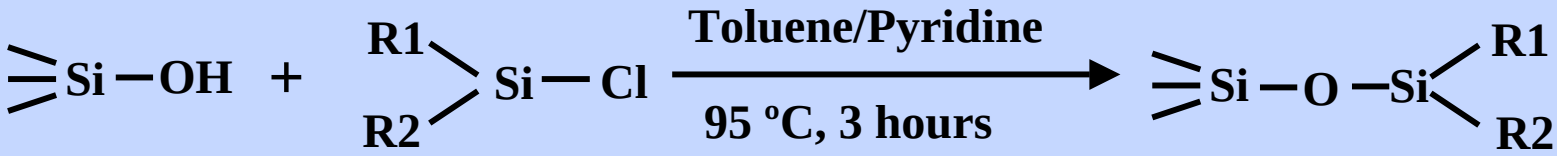
# Functionalization of Zeolite Surfaces

- 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

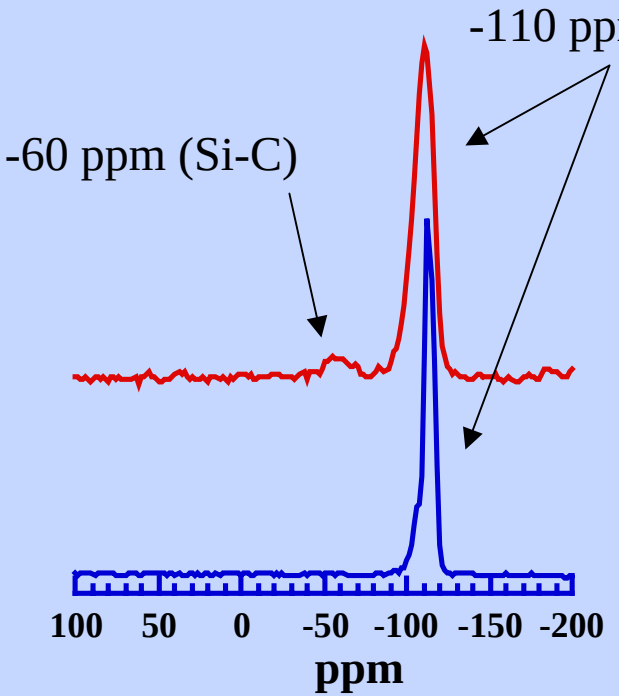



References: a) Usher, Michel, Stec and Grassian, *Atmos. Env.* 37 (2003) 5337-5347
b) Zhan, White, Lumsden, *Langmuir 2003*, 19, 4205-4210.

# Nanocrystalline ZSM-5 Functionalized by Octyltrichlorosilane

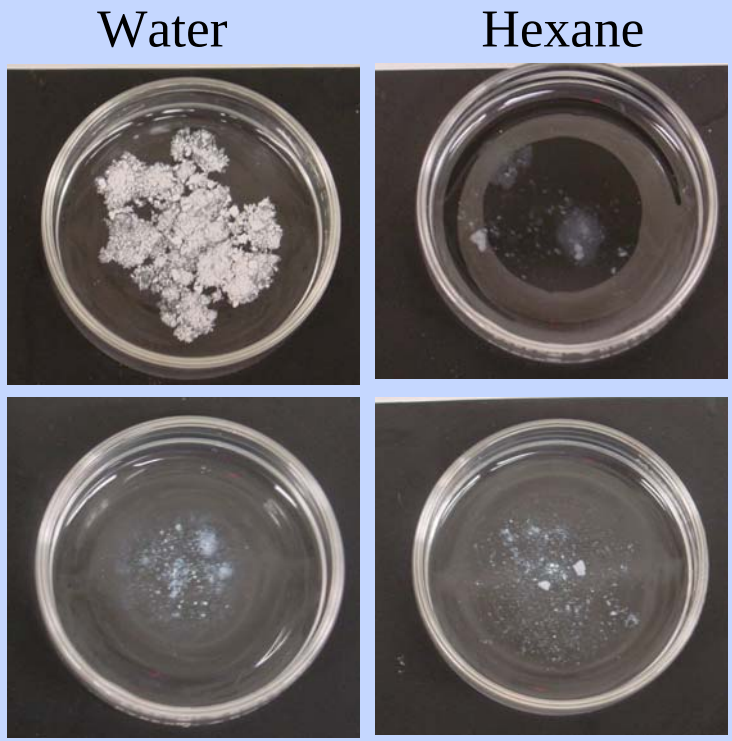



**$^{29}$Si MAS NMR**



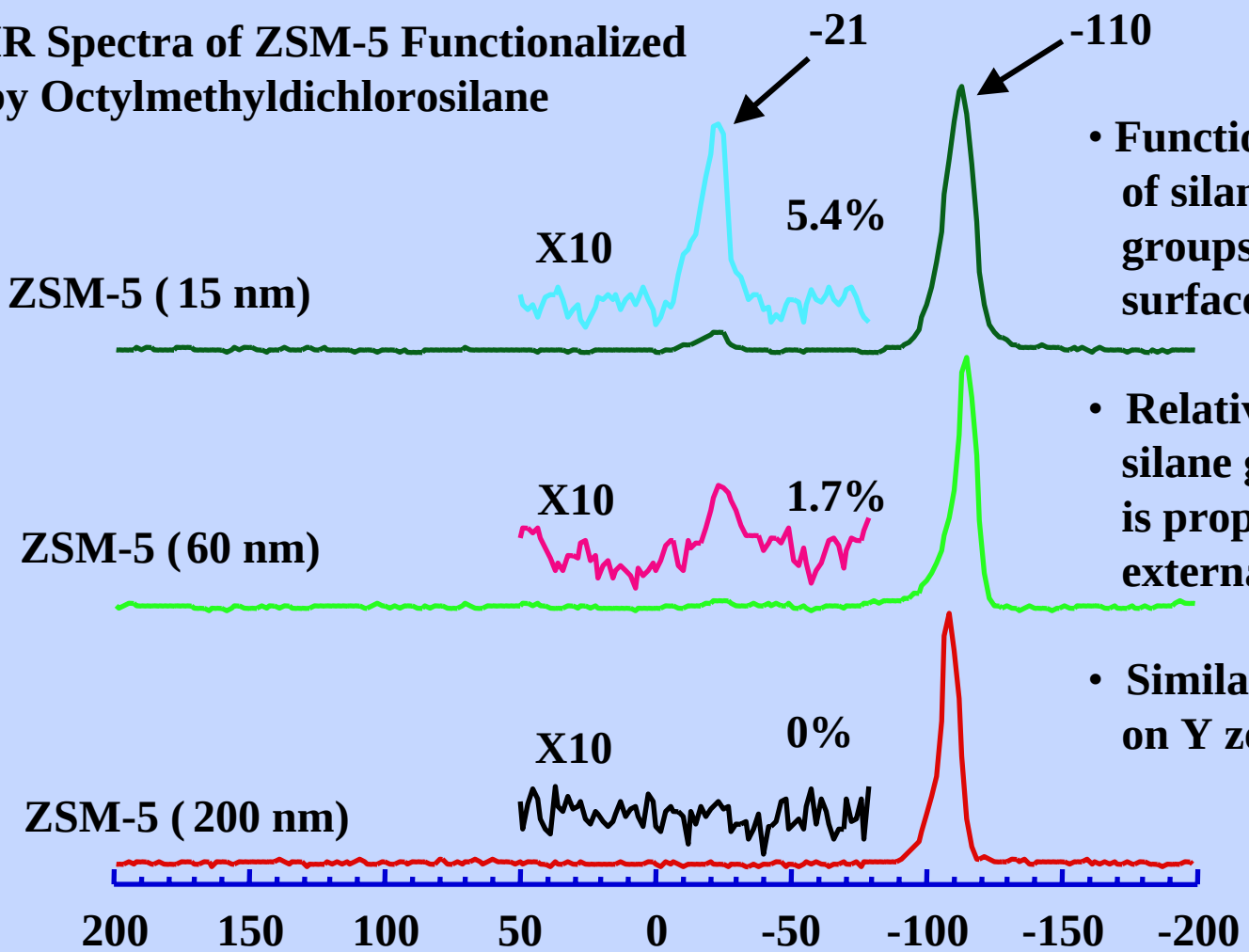

NanoZSM-5 treated with octyltrichlorosilane

Untreated nano-ZSM-5



# Functionalization of Zeolites with Different Sizes

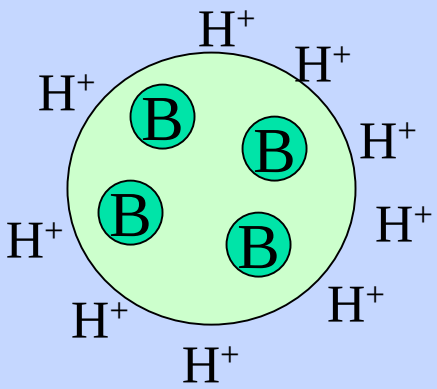
$^{29}$Si NMR Spectra of ZSM-5 Functionalized by Octylmethyldichlorosilane




- 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

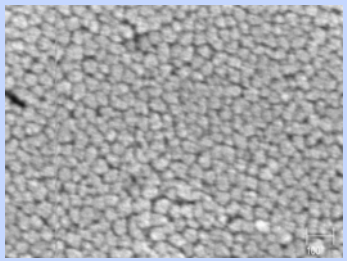
# Applications for Functionalized Zeolites

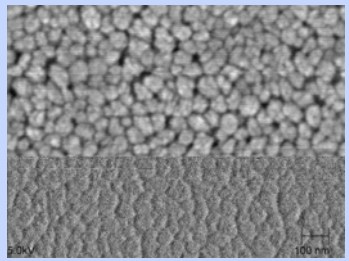
- Adsorption of VOC's, such as toluene, from humid or aqueous environments
- Bifunctional Catalysts
  - Design catalyst for specific applications by incorporating acid/base, hydrophobic/hydrophilic properties
  - Exterior surface is functionalized with acid sites- can break a reactant molecule up on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

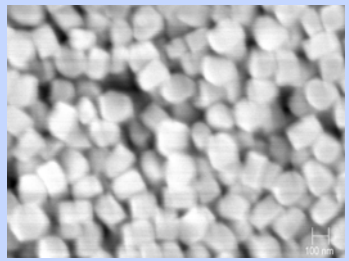


# Development of Nanocrystalline Zeolite Materials - Summary

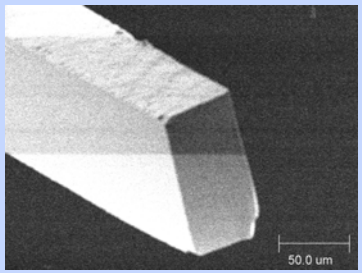
- Zeolite particle size can be **systematically** tuned in the nanometer range by varying reaction conditions.

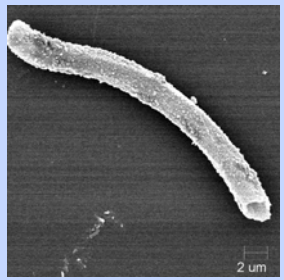

**20 nm**

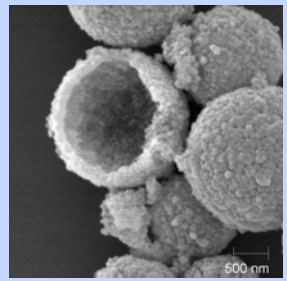

**39 nm**


**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