Development of Nanocrystalline Zeolite Materials as Environmental Catalysts

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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
Synthesis of Nanocrystalline Zeolites

Silicalite
20 nm
174 (506) m²/g

ZSM-5
15 nm
198 (492) m²/g

Y
23 nm
173 (576) m²/g

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)

![Graph showing external surface area vs. crystal size](image)

External surface area of cubic crystal:

\[
\frac{3214}{x} \text{ m}^2/\text{g}
\]
Adsorption of VOC’s on Nanocrystalline Zeolites

Helium

MFC

Bubbler

Tubular Reactor

MFC

Sample Reference

TCD Detector

Detector Intensity

Adsorption

RT He Purge

TPD

0.2

0.4

0.6

0.8

1

1.2

1.4

1.6

0 100 200 300 400 500 600

Surface area (m²/g)

Adsorption vs. $S_{total}$

Purge vs. $S_{ext}$

TPD vs. $S_{total}$

Silicalite-1-17 (20 nm)

Silicalite-1-15 (149 nm)

Silicalite-1-22 (1000 nm)
Selective Catalytic Reduction of NO$_2$ with Propylene

$2\text{NO}_2 \rightarrow \text{NO}_3^- + \text{NO}^+$

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
473 K
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) → Electrostatic assembly → MS coated with nanocrystalline zeolite seeds → Hydrothermal synthesis → Hollow zeolite sphere (purely silicon forms)

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

Incorporation of Aluminum into Zeolite Shells

Mesoporous silica (hexagonal tubes) → MS coated with nanocrystalline zeolite seeds → Hollow hexagonal zeolite tube

$\text{Al(NO}_3\text{)}_3$

$^{27}\text{Al MAS NMR}$

Before HT

After HT

After Calcination


$^{27}\text{Al MAS NMR}$ 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

$$\text{Si-O-H} \xrightarrow{(\text{SiCl}_3)\text{C}_8\text{H}_{16}} \text{Si-O-Si-C}_x$$

+HCl

Nanocrystalline ZSM-5 Functionalized by Octyltrichlorosilane

\[
\text{Si} - \text{OH} + \text{R}_1\text{Si} - \text{Cl} \xrightarrow{\text{Toluene/Pyridine}} 95 \degree\text{C}, 3 \text{ hours} \quad \Rightarrow \quad \text{Si} - \text{O} - \text{Si} \quad \text{R}_1 \quad \text{R}_2
\]

-110 ppm (framework Si)
-60 ppm (Si-C)

\( ^{29}\text{Si MAS NMR} \)

NanoZSM-5 treated with octyltrichlorosilane

Untreated nano-ZSM-5

Water
Hexane
Functionalization of Zeolites with Different Sizes

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

- ZSM-5 (15 nm): 5.4%
- ZSM-5 (60 nm): 1.7%
- ZSM-5 (200 nm): 0%

- 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.

- The nanocrystalline zeolites can be used as building blocks for hierarchical zeolite structures (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 NO₂ 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