Improved Catalysts for Heavy Oil Upgrading Based on Zeolite Y Nanoparticles Encapsulated in Stable Nanoporous Hosts

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Outline of Presentation

• Research objectives and background

• Research progress on the synthesis of zeolite Y nanoparticles

• Research progress on the synthesis of nanoporous hosts

• Summary

• Future plans for synthesis of nanocomposite catalysts and catalysts testing

• Acknowledgements
Research Objective

To synthesize a composite catalysts system (comprised of Zeolite Y nanoparticles encapsulated in stable nanoporous hosts) that is useful for heavy oil upgrading.
Motivation

Increasing demand for stable, resistant and very active catalysts for the conversion of heavy petroleum feedstock and residue to useful fuels (naptha and middle distillates).
Zeolite Y as Petroleum Catalyst

- Porous aluminosilicates with SiO$_2$ and AlO$_2$ tetrahedra
- Si/Al ratio of zeolite $\sim$ 2.5
- Synthetic counterpart to natural faujasite
- Extensively used as a component of FCC process in the petroleum industry (Steam stabilized version-USY with Si/Al= 9)
- Typical particle is in micron size range

**Limitation as catalyst:**
- catalyst deactivation
Advantages of Zeolite Y Nanoparticles over Conventional Micron-Size Zeolite Y

- Reduced diffusion path length, hence hydrocarbon substrates will diffuse in, are converted and the products quickly diffused out.

- Reduced over-reaction and hence reduced pore blockage and active sites deactivation.
Our Research Approach

• Synthesis of aluminosilicate nanoporous materials with pore diameter up to 30 nm (300 Å).

• Synthesis of zeolite Y nanoparticles (~30 nm) within the pores of the nanohosts.

• Testing the nanocomposite catalysts for the catalytic conversion of heavy petroleum substrates.
Role of the Nanoporous Host

• Perform as a mild hydrocracking catalyst for the initial conversion of bulky heavy oil substrates.

• Screen bulky hydrocarbon substrates from blocking the entrance to the zeolite pores, (reduce the extent of non selective, undesirable reactions on the external surfaces of the zeolite nanocrystals).
Synthesis of Nanoporous Silicate

**Surfactant templating mechanism**

Inserting Zeolite Y Nanoparticles Through Direct Synthesis
Progress on Zeolite Y Synthesis

Standard Zeolite Y synthesis:

• sodium hydroxide (NaOH)
• sodium aluminate (NaAlO_2)
• sodium silicate
• High shear mixing conditions, 24 h at RT and 22 h at 100°C.
  (molar composition: 4.62Na_2O:Al_2O_3:SiO_2:180 H_2O)

(Verified Synthesis Recipe for Zeolites, H. Robson, 1997)
Nanoparticles Zeolite Y Synthesis:

**Method 1**
- sodium chloride
- aluminum isopropoxide- [(CH₃)₂CHO]₃Al
- tetraethylorthosilicate (TEOS) – (C₂H₅O)₄Si
- tetramethylammonium hydroxide (TMAOH)- (C₂H₅)₄NOH
- filter clear solution
- stir for 3 days RT, 4 days at 100ºC
- recover product by centrifuge at 15000 g for 40 minutes

**Method 2**
method 1 + with NaOH instead of NaCl

**Method 3**
method 1 + tetramethylammonium bromide (TMABr)
- (C₄H₁₂NBr)

(1Al₂O₃:4.36SiO₂:2.3TMAOH:0.6TMABr:0.048Na₂O)

*Yan et al., Microporous and Mesoporous materials, 2003*
X-Ray Diffraction Patterns of Zeolite Y

Method 1
NaCl+TMAOH+Al Iso.

Method 3
Method 1+ TMABr

Method 2
NaOH+TMAOH+Al Iso

Standard
(gel, no organics)

No crystals using Ludox AS-30, HS-30 as SiO₂
Dynamic Light Scattering Particle Size Analysis

**Range = 100-1000 nm**
Median = 284 nm

**Median = 75 nm**
Method 2
NaOH + TMAOH + Al Iso.

**Median = 91 nm**
Method 1
NaCl + TMAOH + Al Iso.

**Median = 100 nm**
Method 3
(Method 1 + TMABr)
Atomic Force Microscope Image of Zeolite Nanoparticles from NaCl+TMAOH+ TMABr + Al Iso.

110 x 60 x 27 nm
Future Work on Zeollite Y synthesis

Continue to explore synthesis variables to reduce the size of the nanocrystals.
Progress on the Synthesis of Nanoporous Host

**General synthesis approach**

Precursor: (TEOS, Al Isopropoxide)

\[ \text{H}^+ \quad (C_{18}H_{35}(OCH_2CH_2)_{10}OH) \]

40°C, 24 hr, then 90°C 24 hr.

Nanostructured Organosilicate

Extraction in EtOH/HCl

Nanoporous Organosilicate
Organic Templates Used

Nonionic Alkyl (polyethylene oxide) Surfactants
Brij $\text{30}$ \hspace{1cm} C$_{12}$ (EO)$_4$
Brij $\text{78}$ \hspace{1cm} C$_{16}$ (EO)$_{10}$
Brij $\text{76}$ \hspace{1cm} C$_{18}$ (EO)$_{10}$

Nonionic Triblock Copolymers
Pluronic L-121 \hspace{1cm} EO$_5$PO$_{70}$EO$_5$
Pluronic P-64 \hspace{1cm} EO$_{13}$PO$_{30}$EO$_{13}$
Pluronic F-68 \hspace{1cm} EO$_{80}$PO$_{30}$EO$_{80}$
Pluronic P-123 \hspace{1cm} EO$_{20}$PO$_{70}$EO$_{20}$

Cationic Surfactants
Cetyltrimethylammonium $\text{CH}_3(\text{CH}_2)_{15}\text{N(CH}_3)_3^+$

(EO = ethylene oxide units, PO = propylene oxide units)
Results for Synthesis of All Silica/Aluminosilicate Nanoporous Host

X-Ray Diffraction Pattern of Nanoporous SBA 15 (all silica) with P123
Nitrogen Adsorption Isotherm of Nanoporous SBA 15

**Pore size 4 nm (40 Å)**

**Surface area : 980 m\(^2\)/g**
Synthesis of Organosilicate Nanoporous Host
(Acid condition and nonionic surfactant)

Precursor: 1,4 bis-triethoxysilyl benzene (BTEB)

\[
\begin{array}{c}
\text{EtO} \\
\text{EtO} \\
\text{EtO} \\
\text{Si} \\
\text{Si} \\
\text{EtO} \\
\text{EtO} \\
\end{array}
\]

\[
(C_{18}H_{35}(OCH_2CH_2)_{10}OH)
\]

H⁺

40°C, 24 hr, then 90°C 24 hr.

Nanostructured Organosilicate

Extraction in EtOH/HCl

Nanoporous Organosilicate
X-Ray Diffraction Patterns

**Extracted Organosilicate**

\[ 2\theta = 1.6^\circ \ (d = 55.3 \text{ Å}) \]

\[ 2\theta = 3.3^\circ \ & \ 4.1^\circ \]

\( (d = 27.1 \text{ Å} \ & \ 21.4 \text{ Å}) \)

**“As Synthesized” organosilicate**

\[ 2\theta = 1.6^\circ \ (d = 55.3 \text{ Å}) \]
Nitrogen Adsorption-Desorption Isotherms

- Pore diameter 27.4 Å
- Surface area 784 m²/g

Isotherms acquired on a Micromeretics ASAP 2010 Porosimeter
$^{13}$C Solid State Magic Angle Spinning NMR Spectrum of Extracted Sample

This shows that Si-C bond remained in-tact in the product.
$^{29}\text{Si}$ Solid State Magic Angle Spinning NMR Spectrum of Extracted Sample

67\% condensation of the organosilicate precursor was observed.
Weight-Loss Thermogram of “As-synthesized” Phenylene-bridged Organosilicate
Weight-Loss Thermogram of “Ethanol/HCl Extracted” Phenylene-bridged Organosilicate

Weight (%)  vs  Temperature (°C)

- H₂O = 8%
- Residual surfactant = 8%
- -C₆H₄⁻
Synthesis of Organosilicate Nanoporous Host
(Base condition & cationic template)

40°C, 24 hr, then 90°C 24 hr.

Nanostructured Organosilicate

Extraction in EtOH/HCl

Nanoporous Organosilicate
X-Ray Diffraction
Adsorption/Desorption Isotherm

Pore diameter 31 Å
Surface area 876 m²/g
Weight-Loss Thermogram of “As-synthesized” Phenylene-bridged Organosilicate
$^{13}$C Solid State Magic Angle Spinning NMR Spectrum of Extracted Sample
87% condensation of the organosilicate precursor was observed.
AFM Topography of Phenylene-Bridged Nanoporous Organosilicate

**Instrument**: Thermomicroscopes AutoProbe CP Research Scanning Probe Microscope (SPM)

**Scan mode**: Non-contact mode in air at a rate of 500nm/s.

**Canilever**: Gold coated V-shaped silicon nitride cantilever with resonant frequency =117.08 kHz and spring constant of 0.5 N/m. Tip radius= 10 nm
Summary

• Successful synthesis of zeolite Y nanoparticles in the presence of organics to < 100 nm, but further reduction in particle size needed.

• Successful synthesis of a wide range of silicate, aluniosilicate, and organosilicate nanoporous hosts up 3+ nm, but further expansion of pore diameter needed.
Summary of Organosilicate Synthesis

A.
• High surface area nanoporous phenylene-bridged organosilicate was synthesized by acid catalyzed hydrolysis and condensation in the presence of 1,4 bis-triethoxysilyl benzene and non-ionic oligomeric surfactant Brij 76 ($C_{18}H_{35}(OCH_2CH_2)_{10}OH$) as template.

• Material has pore diameter of 27.4 Å, pore volume 0.46 cm$^3$/g, and surface area of 784 m$^2$/g.

• Approximately 67 % condensation of the precursor was achieved.

B. High surface area nanoporous phenylene-bridged organosilicate was also synthesized by base catalyzed hydrolysis and condensation in the presence of 1,4 bis-triethoxysilyl benzene and catonic surfactant ($C_{16}H_{33}N(CH_3)_3Br$ as template.

• Material has pore diameter of 31 Å, and pore volume of 0.58 cm$^3$/g, and surface area of 876 m$^2$/g.

• Approximately 80 % of the precursor was achieved.
Future Work

- Continue to explore synthesis variables to reduce the size of the nanocrystals

- Expand the pore dimension of nanoporous hosts from 4 nm towards 30 nm using pore size expanders e.g. trimethylbenzene

- Insert zeolite Y nanocrystals in nanoporous materials

- Catalysts testing.
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