

ABSTRACT

Title: Improved Catalyst for Heavy Oil Upgrading Based on Zeolite Y Nanoparticles Encapsulated Stable Nanoporous Host

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OBJECTIVES

The objective of this project is to synthesis nanocrystals of highly acidic zeolite Y, encapsulate them within the channels of mesoporous (nanoporous) silicates or nanoporous organosilicates and evaluate the “zeolite Y/Nanoporous host” composites as catalysts for the upgrading of heavy petroleum feedstocks. In comparison to conventionally-used zeolite Y catalyst of micron size particles, the nanocrystals (< 100 nm particle size) which will contain shorter path lengths, will allow faster diffusion of large hydrocarbon substrates and the catalysis products within and out of the zeolite’s channels and cages (<1 nm size). This is expected to significantly reduce catalysts deactivation. Encapsulating zeolite Y nanocrystals within the nanoporous materials will protect its external surfaces and pore entrances from being blocked by large hydrocarbon substrates, since these substrates will initially be converted to small molecules by the nanoporous host (a catalyst in its own right).

ACCOMPLISHMENTS TO DATE

We initially investigated methods to synthesize nanocrystals of zeolite Y (< 30 nm), including, the addition of organic additives, such as tetramethylammonium hydroxide/bromide (TMAOH/Br), to conventional zeolite Y synthesis mixtures to facilitate its nucleation and reduce the growth of the crystals. Thus, the synthesis of zeolite Y nanoparticles with median pore size of approximately 40 nm was accomplished by adding TMABr/TMAOH as organic additives to aged synthesis mixtures in typical molar chemical compositional ratio as follows: $1.0\text{Al}_2\text{O}_3:4.4\text{SiO}_2:2.4\text{TMAOH}:1.19\text{TMABr}:0.048\text{Na}_2\text{O}:249\text{H}_2\text{O}$. From dynamic light scattering measurements suggest that the 40 nm size zeolite Y crystallized from an initially formed larger aluminosilicate amorphous gel network of 80 nm. Within this pore size distribution, 20-30 nm size zeolite particles were also available which could be captured and encapsulated within nanoporous hosts of pore size up to 30 nm.

We investigated methods to expand the pore size of the standard nanoporous silicate material called SBA-15. The synthesis of high surface ordered nanoporous silica of expanded pore diameter up to 25 nm (larger than the standard size of 4.8 nm) was accomplished. This was conducted by adding trimethylbenzene to standard synthesis mixture containing poly(ethylene oxide) copolymers (P123- $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) as template around which the added inorganic silicate precursors are organized.

Subsequent removal of the copolymers yielded nanoporous the materials. Bases on the results form experiments above, the synthesis of zeoliteY/Nanoporous silica composite materials was investigated. To accomplish this, zeolite Y precursor mixtures were vigorous stirred and aged at room for 3 days followed by 100°C for up to 7 days. The Si/Al ratio of mixture was modified with addition silicate, sulfuric acid and copolymer template, P123 (EO₂₀PO₇₀EO₂₀) and the acidic final mixture further heated at 100°C. Products obtained showed X-Ray diffraction two theta peaks at low diffraction angles, suggesting that they are nanostructured. BJH N₂ absorption isotherms of the calcined materials (500°C) were of type IV, thus indicating that the materials were nanoporous, with pore size ranging from 4.8 nm for the pure nanoporous SBA-15 silicate (synthesized in the absence of zeolite Y precursor) to 11.2 nm for the zeolite Y/Sba-15 composite materials which were synthesized in the presence of the zeolite Y precursor. The pure SBA-15 gave high surface area of 615 m²/g whereas as the composite materials showed significantly low surface around 270 m²/g. Evidence for the presence of zeolite Y in the composite was seen as a 570 cm⁻¹ band in the in FTIR spectra.

FUTURE WORK

Further work will be conducted on: a) the synthesis and characterization of the zeolite Y/SBA-15 composites to unambiguously confirm the presence of zeolite Y, b) to increase the surface areas c) and to evaluate the materials as catalysts for petroleum upgrading catalysts.

LIST OF PUBLISHED /CONFERENCE PRESENTATIONS

- 1) Preparation of Nanosized micro/mesoporous composites via sequential synthesis of zeolite Y/SBA-15 phases; Yohannes Ghirmazion and Conrad W. Ingram, to be presented at the ACS National Meeting, Washington DC, August, 2005 .
- 2) On the Synthesis of Zeolite Y Nanocrystals in the Presence of Tetramethylammonium Bromide, Yohannes Ghirmazion* and Conrad W. Ingram, presented at the 227 ACS National Meeting, Anaheim, California, March 28 - April 1, 2004 .
- 3) Non Ionic Surfactant Mediated Templated Synthesis of Phenylene-Bridged Organosilicate, Yohannes Ghirmazion*, Conrad Ingram, presented at the 55th Southeast Regional Meeting (SERMACS), Atlanta, GA, November 16-19, 2003.
- 4) A Comparison of Synthesis Strategies for Aryl Functionalized Ordered Nanoporous Organosilicates using Nonionic and Cationic Surfactants, Yohannes Ghirmazion*, Conrad Ingram presented at the 55th Southeast Regional Meeting (SERMACS), Atlanta, GA, November 16-19, 2003.
- 5) Phenylene-Bridged Mesoporous Organosilicate from Nonionic Surfactant Templated Synthesis, Conrad Ingram* and Yohannes Ghirmazion, presented at the 4th International Mesostructured Material Symposium, May 1-4, 2004, Cape Tow, South Africa.
- 6) Synthesis of Aromatic Bridged Ordered Mesoporous Organosilicate with Cetyltrimethylammonium Cation as Templating Agent was presented at the 4th International Mesostructured Material Symposium, May 1 -4, 2004, Cape Tow, South Africa.

STUDENTS SUPPORTED UNDER THIS GRANT

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