IMPROVED CATALYSTS FOR HEAVY OIL UPGRADING BASED ON ZEOLITE Y NANOPARTICLES ENCAPSULATED STABLE NANOPOROUS HOST

EIGHTH SEMI-ANNUAL TECHNICAL PROGRESS REPORT

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I. ABSTRACT

The addition of hydrothermally-aged zeolite Y precursor to an SBA-15 synthesis mixture under a mildly acidic condition resulted in the formation of mesoporous aluminosilicate catalyst, Al-SBA-15, containing strong Brönsted acid sites and aluminum (Al) stabilized in a totally tetrahedral coordination. The physicochemical characteristics of the catalyst varied as a function of the synthesis conditions. The catalyst possessed surface areas ranging between 690 and 850 m^2/g, pore sizes ranging from 5.6 to 7.5 nm, and pore volumes up 1.03 cm^3, which were comparable to the parent SBA-15 synthesized under similar conditions. Two wt % Al was present in the catalyst that was obtained from the reaction mixture that contained the highest Al content. The Al remained stable in totally tetrahedral coordination after calcination at 550˚C. The Al-SBA-15 mesoporous catalyst showed significant catalytic activity for cumene dealkylation, and the activity increased as the amount of zeolite precursor added to the SBA-15 mixture was increased. In preparation for the final phase of the project, the catalyst was embedded into psuedoboemite alumina (catapal B) matrix and then formed into pellets. In the final phase of the project, the pelletized catalyst will be evaluated for the conversion of heavy petroleum feedstocks to naphtha and middle distillates.

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II DISCLAIMER

III LIST OF ABBREVIATIONS

Al	Aluminum
SBA-15	University of California-Santa Barbara Mesoporous Material No 15
Al-SBA-15	Aluminum-containing SBA-15
MPa	Mega pascal
GC/FID	Gas chromatograph with Flame Ionization Detector
ASTM	American Society for Testing Materials

IV EXECUTIVE SUMMARY

The objective of this project is to synthesize nanocrystals of highly acidic zeolite Y nanoculsters, 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 catalysts 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 deactivation of the catalyst and prolong the life of catalyst. 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). The project consists of four major tasks as follows: 1) synthesis of the nanoparticles of zeolite Y (of various chemical compositions) using various techniques such as the addition of organic additives to conventional zeolite Y synthesis mixtures to suppress zeolite Y crystal growth; 2) synthesis of nanoporous silicate host materials of up to 30 nm pore diameter, using poly (alkylene oxide) copolymers which when removed will yield a mesoporous material; 3) synthesis of zeolite Y/Nanporous Host composite materials as potential catalysts; and (4) evaluation of the catalyst for the upgrading of heavy petroleum feedstocks.

This report highlights the progress in preparation for the final phase of the project. Several samples of Al-SBA-15 mesoporous catalysts were fabricated into pellets (extrudates). The preparation of the catalyst pellets involved two successive steps. First alumina paste suitable for extrusion was prepared from psuedoboemite catapal B by kneading the psuedoboemite powder with a 5 % acetic acid (peptizing) solution. The paste was then mixed with SBA-15 /Zeolite-Y composite catalyst with kneading until it formed a "plastic-feeling" paste. In a typical experiment, 8.0g of the psuedoboehmite powder, 2.0g of SBA-15/Zeolite-Y composite, 6.5g water, and the appropriate quantities of peptizing agent was used each batch. The peptizing agent was added slowly over 20 minutes with continuous mixing and kneading. The paste was extruded through a garlic press, and then dried in a thermolyne tube furnace at 250˚C for 1 hour.

The dried extradites were then calcined at 250˚C for 1 hour and 500˚C for 2 hours in the presence of flowing dry air. The pellets were then impregnated with 15 wt % ammonium heptamolybdate solution, dried for 12 hours at 100˚C in an air oven, and calcined for 2 hours at 500˚C under dry air circulation. Nickel was then introduced by a second impregnation with a 16 wt % nickel nitrate solution, followed by drying at 100˚C in an air oven and final calcinations for 1 hour at 500˚C. In the final phase, the samples will be evaluated for the conversion heavy petroleum feedstocks.

The Al-SBA-15 mesoporous catalysts that were formed into pellets were prepared according to procedures detailed in earlier reports. The catalysts with strong Brönsted acid sites and Al stabilized in a totally tetrahedral coordination were synthesized from the addition of hydrothermally aged zeolite Y precursor to SBA-15 synthesis mixture under a mildly acidic condition of pH 5.5. The materials possessed surface areas between 690 and 850 m^2/g, pore sizes ranging from 5.6 to 7.5 nm and pore volumes up 1.03 cm^3, which were comparable to the parent SBA-15 synthesized under similar conditions. Two wt % Al was present in the catalyst that was obtained from the reaction mixture that contained the highest Al content. The Al remained stable in totally tetrahedral coordination after calcination at 550˚C. It was also highlighted in previous reports that the Al-SBA-15 mesoporous catalyst showed significant catalytic activity for cumene dealkylation. The catalytic activity was found to increase as the amount of zeolite precursor added to the SBA-15 mixture was increased. The activity of the catalyst was not affected by the aging time of the precursor for up to the 24-hour aging period. This method of introducing Al and maintaining it in a total tetrahedral coordination is very effective when compared to other direct and post synthesis alumination methods reported.

V INTRODUCTION

The objective of this project is to synthesize 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 catalysts of micron size particles, the nanocrystals (< 100 nm particle size) which contain shorter path lengths, will allow faster diffusion of large hydrocarbon substrates through the channels and cages (<1 nm size) of the zeolite. This is expected to significantly reduce catalyst deactivation and prolong the life of the prolong catalyst. 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). The project consists of four major tasks as follows: 1) synthesis of the nanoparticles of zeolite Y (of various chemical compositions) using various techniques such as the addition of organic additives to conventional zeolite Y synthesis mixtures to suppress zeolite Y crystal growth; 2) synthesis of nanoporous silicate host materials of up to 30 nm pore diameter, using poly (alkylene oxide) copolymers which when removed will yield a mesoporous material; 3) synthesis of zeolite Y/Nanporous Host composite materials as potential catalysts; and 4) evaluation of the catalyst for the upgrading of heavy petroleum feedstocks.

V-1 BACKGROUND

In previous reports, the synthesis and characterization of Al-SBA-15 mesoporous catalysts was highlighted. The details were also published in the December 2006 issue of Journal of Porous Materials. In summary, the catalysts with strong Brönsted acid sites and Al stabilized in a totally tetrahedral coordination were synthesized from the addition of hydrothermally aged zeolite Y precursor to SBA-15 synthesis mixtures under a mildly acidic condition of pH 5.5. The materials possessed surface areas between 690 and 850 m^2/g, pore sizes ranging from 5.6 to 7.5 nm, and pore volumes up 1.03 cm^3. These properties are comparable to parent SBA-15 synthesized under similar conditions. Two wt % Al was present in the catalyst that was obtained from the reaction mixture that contained the highest Al content. The Al remained stable in

totally tetrahedral coordination after calcination at 550˚C. It was also highlighted in previous report that the Al-SBA-15 mesoporous catalyst showed significant catalytic activity for cumene dealkylation, and that the activity increased as the amount of zeolite precursor added to the SBA-15 mixture was increased. The activity of the catalyst was not affected by the aging time of the precursor for up to the 24 hour aging period. This method of introducing Al and maintaining it in a total tetrahedral coordination is very effective, in comparison to other direct and post synthesis alumination methods reported. In the final phase of the project the fabrication of the catalysts into extrudates was accomplished and mild hydro-cracking reactions will be conducted in the laboratory to evaluate the catalysts for petroleum conversion.

VI EXPERIMENTAL DETAILS

Fabrication of Pellets

The preparation of the catalyst pellets involved two successive steps. First alumina paste suitable for extrusion was prepared from psuedoboemite catapal B by kneading the psuedoboemite powder with a 5 % acetic acid (peptizing) solution. The paste was then mixed with SBA-15 /Zeolite-Y composite catalyst with kneading until it formed a “plastic-feeling” paste. In a typical experiment, 8.0g of the psuedoboehmite powder, 2.0g of SBA-15/Zeolite-Y composite, 6.5g water, and appropriate quantities of peptizing agent was used in each batch. The peptizing agent was added slowly over 20 minutes with continuous mixing and kneading. The paste was extruded through a garlic press, and then dried in a thermolyne tube furnace at 250˚C for an hour. The dried extradites were then calcined at 250˚C for one hour and 500˚C for 2 hour in the presence of flowing dry air. The pellets were then impregnated with a 15 wt % ammonium heptamolybdate solution, dried for 12 hour at 100˚C in an air oven, and calcined for 2 hours at 500˚C under dry air circulation. Nickel was then introduced by a second impregnation with a 16 wt % nickel nitrate solution, followed by drying at 100˚C in an air oven and final calcinations for one hour at 500˚C (Figure 1). The pellets will be further analyzed for final surface area, and the

nickel and molybdenum loadings through chemical analysis with a Perkin Elmer Elan 9000 Inductively Coupled Plasma/Mass spectrometer.

VII RESULTS AND DISCUSSION

Pellets Preparation

Figure 1. Catalysts pellets loaded with nickel and molybdenum

Figure 1 shows various samples of catalysts pellets loaded with nickel and molybdenum.

The samples will be evaluated for the conversion if heavy petroleum feedstocks to naptha and middle distillates under mild-hydrocracking reaction conditions.

VIII CONCLUSIONS

Composite catalysts of mesoporous materials were successfully formed into pellets for further evaluation for the mild-hydrocracking of heavy petroleum feedstocks to naptha and middle distillates.

IX FUTURE WORK

Mild hydrocracking reactions will be conducted in a 500 ml batch high-temperature, high-pressure Parr autoclave. The catalysts will first be sulfided with 5% H_2S. The gas oil feedstock to be tested is a metal-free, low-sulfur gas oil containing a 79 wt % heavy fraction. Reaction conditions will be at a temperature of 400-500˚C and a hydrogen pressure of 5.5 MPa. Liquid reaction products will be collected and analyzed by GC/FID using ASTM D2887 simulated distillation method. Gaseous product will be sampled and analyzed by GC/FID. The effect of reaction temperature, time, and catalyst concentration on conversion and products distribution will be assessed.

X TECHNOLOGY/INFORMATION TRANSFER

Students:

The following students have been working on the project since inception:

Tesfamariam Mehreteab	M.S. graduate student (Chemistry)
Yohannes Ghirmazion	M.S. graduate student (Chemistry)
Fengling Ding	M.S. graduate student (Chemistry)
Ifedapo Adeniyi	Sophomore undergraduate (Chemistry & Engineering)
Taurean Hodges	M.S. graduate student (Chemistry)
Selassi Blavo	Senior (Chemistry and Chemical Engineering)

Presentations and publications:

1) *Mesoporous Aluminosilicate Catalysts from FAU Precursor under Mild Acidic Conditions and with Al in Totally Tetrahedral Coordination*, Conrad W. Ingram, Yohannes Ghirmazion and Tesfa Mehreteab. Published in *Journal of Porous Materials*, December 2006.

2) "*On the Incorporation of Tetrahedral Aluminum in SBA-15 from Zeolitic Seeds"* Conrad W. Ingram, Yohannes Ghirmazion and Tesfamariam Mehreteab presentated at the XXIX Annual British Zeolite Association Conference to be held in Ambleside, UK from 30th July to 4th August.

3) *Development of potential gas oil cracking catalysts by incorporating tetrahedral aluminum in SBA-15* submitted for presentation to Division of Petroleum Chemistry for the 232nd ACS National Meeting, San Francisco, CA, September 10-14, 2006 in San Francisco (from 09-10-2006 to 09-14-2006 .

4) *Improved Catalysts for the Heavy Oil Upgrading Based on Zeolite Y Nanoparticles Encapsulated in Stable Nanoporous Host*, Yohannes Ghirmazion and Conrad Ingram, to presented at the University Coal Research/HBCU/MIs Contractors' Review Conference, June 7-8 2005, Pittsburgh, Pensylvania.

5) *Mesoporous Composites from the Sequential Combination of Hydrothermally Treated Colloidal Zeolitic Silicate Precursors*: Yohannes Ghirmazion and Conrad Ingram: presented at Division of Colloid and Surface Chemistry for the 230th ACS National Meeting, in Washington, DC, Aug 28-Sept 1, 2005 in Washington (from 08-28-2005 to 09-01-2005).

6) *Synthesis of Mesoporous Solids Containing Zeolitic Phase from Hydrothermal Treatment of Colloidal Zeolite Y Precursors* " Yohannes Ghirmazion and Conrad Ingram; presented at Pacifichem 2005, Hawaii, December 2005.

7) *Synthesis and Catalytic Properties of Hierarchical Mesoporous Aluminosilicate Assembled from Zeolite Y Precursors*, Conrad W. Ingram, Yohannes Ghirmazion, and Ifedapo Adeniyi, presented at the Singapore International Chemical Conference 4, December 8-10, 2005, Singapore.

8) *Enhancing the Catalytic Properties of Ordered Nanoporous Silicate Using Hydrothermally Treatment Zeolitic Precursors*, Conrad W. Ingram, Yohannes Ghirmazion, and Ifedapo Adeniyi; Nanomaterials and Composites: Synthesis, Properties and Applications II57th Southeast / 61stSouthwest, Joint Regional Meeting of the American Chemical Society, November 1 - 4, 2005, Memphis, Tennesse.

9) *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 .

10) *On the Synthesis of Zeolite Y Nanocrystals in the Presence of Tetramethylammonium Bromide*, Yohannes Ghirmazion* and Conrad W. Ingram, presentated at the 227 ACS National Meeting, Anaheim, California, March 28 - April 1, 2004 .

11) 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.

12) *A Comparison of Synthesis Strategies for Aryl Functionalized Ordered Nanoporous Organosilicates using Nononionic and Cationic Surfactants*, Yohannes Ghirmazion*, Conrad Ingram presented at the 55th Southeast Regional Meeting (SERMACS), Atlanta, GA, November 16-19, 2003.

13) *Phenylene-Bridged Mesoporous Organosilicate from Nonionic Surfactant Templated Synthesis*, Conrad Ingram* and Yohannes Ghirmazion, presentated at the 4th International Mesostructured Material Symposium, May 1-4, 2004, Cape Tow, South Africa.

14) *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.

XI REFERENCES

None in this report.