

**IMPROVED CATALYSTS FOR HEAVY OIL UPGRADING BASED ON
ZEOLITE Y NANOPARTICLES ENCAPSULATED IN STABLE
NANOPOROUS HOSTS**

THIRD SEMI-ANNUAL REPORT

REPORT PERIOD: OCTOBER 1, 2003 – MARCH 31, 2004

PRINCIPAL INVESTIGATOR: CONRAD INGRAM, Ph. D.
CO-PRINCIPAL INVESTIGATOR: MARK MITCHELL, Ph. D.

REPORT DATE: JUNE 30, 2004

GRANT NUMBER: DE-FG26-02NT41676

INSTITUTION: CLARK ATLANTA UNIVERSITY
223 JAMES P BRAWLEY DRIVE
ATLANTA, GA 30314

I. Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

II ABSTRACT

The focus of this project is to improve the catalytic performance of zeolite Y for heavy petroleum hydrocracking by synthesizing nanoparticles of the zeolite (~20-30 nm) inside nanoporous silicate or aluminosilicate hosts of similar pore diameters. The encapsulated zeolite nanoparticles are expected to possess pores of reduced diffusional path lengths, hence hydrocarbon substrates will diffuse in, are converted and the products quickly diffused out. This is expected to prevent over-reaction, hence minimizing pore blockage and active sites deactivation. In this phase of the project, research activities were focused on refining procedures to: a) improve the synthesis of ordered, high surface area nanoporous silica, such as SBA-15, with expanded pore size using trimethylbenzene as additive to the parent SBA-15 synthesis mixture; and b) reduce the particle size of zeolite Y such that they can be effectively incorporated into the nanoporous silicas. The synthesis of high surface ordered nanoporous silica containing enlarged pores of diameter of 25 nm (larger than the standard size of 8.4 nm) using trimethylbenzene as a pore size expander was accomplished. The synthesis of zeolite Y nanoparticles with median pore size of approximately 50 nm (smaller than the 80 nm typically obtained with TMAOH) using combined TMABr/TMAOH as organic additives was also accomplished.

III EXECUTIVE SUMMARY

The focus of this project is to improve the catalytic performance of zeolite Y for petroleum hydrocracking by synthesizing nanoparticles of the zeolite (~20-30 nm) inside the nanoporous silicate or aluminosilicate hosts such as SBA-15. The encapsulated zeolite nanoparticles are expected to possess pores of reduced diffusional path lengths, hence hydrocarbon substrates will diffuse in, are converted and the products quickly diffused out. This will prevent over-reaction from occurring and the blocking of the zeolite pores and active sites are minimized. The nanoporous hosts also serves to: a) perform as a mild hydrocracking catalyst in their own right, for the initial disintegration of bulky heavy-oil substrates, and b) screen bulky hydrocarbon substrates from blocking the entrance to the zeolite pores, thus reducing the extent of non selective, undesirable reactions on the external surfaces of the zeolite nanocrystals. The project consists of five major tasks as follows: a) synthesis of the 30 nm pore diameter mesoporous materials. This will be accomplished using poly (alkylene oxide) copolymers as template around which inorganic precursors are organized. Subsequently removal of the copolymer will yield a mesoporous material, the pore sizes of which will depend on the number of poly (alkylene oxide) units; b) synthesis of the nanoparticles of zeolite Y (of various chemical compositions) within the pores of the nanohosts using various techniques such the addition of organics to conventional zeolite Y synthesis, (b) further increase in the thermal stability and acid strength of the encapsulated zeolite Y by dealumination, (c) material characterization, and (e) catalytic testing.

The synthesis of high surface ordered nanoporous silica of expanded pore diameter of 25 nm (larger than the standard size of 8.4 nm) using trimethylbenzene as a pore size expander was accomplished. The synthesis of zeolite Y nanoparticles with median pore size of approximately 50 nm (smaller than the 80 nm typically obtained with TMAOH) using combined TMABr/TMAOH as organic additives was also accomplished. Work in the immediate future will be focused on the following three areas: 1) The synthesis and characterization of all-silica and aluminosilicate mesoporous materials with expanded pore sizes up to 30 nm will continue by increasing the concentration of TMB in the synthesis mixture. The mole ratios of the reactants, synthesis temperature and time will also be controlled towards achieving the desired results. 2) Research efforts to reduce the average particle size of zeolite nanoparticles down to 35-30 nm will continue. The synthesis of zeolite Y nanocrystals within the SBA-15 nanoporous host will also be simultaneously investigated. 3) The resulting composite catalyst system of nanozeolite Y encapsulated within nanoporous SBA-15 will then be evaluated for heavy oil upgrading.

TABLE OF CONTENTS

	Page
I. DISCLAIMER	2
II ABSTRACT	3
III EXECUTIVE SUMMARY	4
IV INTRODUCTION	6
V RESEARCH PROGRESS	7
V-1 EXPERIMENTAL	7
V-1A Synthesis of All Silica Nanoporous Materials	7
V-1B Synthesis of Standard Zeolite Y	7
V-1C Synthesis of “Aluminum and Silicon- Containing” Nanoporous Materials	8
V-1C Characterization	8
VI RESULTS AND DISCUSSION	8
VI-1 Synthesis of All Silica Nanoporous Materials	8
VI-2 Comparison of Synthesis of Standard Zeolite Y and Zeolite Y Nanoparticles	12
VII CONCLUSIONS	16
VIII FUTURE WORK	17
IX TECHNOLOGY/INFORMATION TRANSFER	17
X REFERENCES	18

IV INTRODUCTION

The focus of this project is to improve the catalytic performance of zeolite Y for petroleum hydrocracking by synthesizing nanoparticles of the zeolite (~20-25 nm) inside the mesoporous silicate or aluminosilicate hosts. The encapsulated zeolite nanoparticles are expected to have reduced pores of diffusional path lengths, hence hydrocarbon substrates will diffuse in, undergo catalytic decomposition and the products quickly diffused out. This is expected to prevent over-reactions and the blocking of the zeolite pores and active sites are minimized. The mesoporous hosts also serves to: a) perform as a mild hydrocracking catalyst in their own right, for the initial breaking down of bulky heavy oil substrates and b) screen bulky hydrocarbon substrates from blocking the entrance to the zeolite pores, and reduce the extent of non selective, undesirable reactions on the external surfaces of the zeolite nanocrystals. The project consists of five major tasks as follows: a) synthesis of the 30 nm pore diameter mesoporous materials. This will be done using poly (alkylene oxide) copolymers as template around which inorganic precursors are organized. Subsequently removal of the copolymer will yield a mesoporous material, the pore sizes of which will depend on the number of poly (alkylene oxide) units; b) synthesis of the nanoparticles of zeolite Y (of various chemical compositions) within the pores of the nanohosts using various techniques such as the addition of organic additives conventional zeolite Y synthesis mixtures to suppress zeolite Y crystal growth (c) further increase in the thermal stability and acid strength of the encapsulated zeolite Y by dealumination, (d) material characterization, and (e) catalytic testing.

This phase of the project was focused on materials synthesis on two fronts as follows:

- (1) The synthesis of all silica mesoporous hosts with expanded pore diameters.
- (2) The synthesis zeolite Y nanocrystals

(1) Our research team is developing synthesis methods towards the production of all silica nanoporous host with pore sizes up to 30 nm. The approach is to start with the synthesis of well characterized ordered nanoporous all-silica material, namely SBA-15 with pore sizes in the 3-8 nm range using nonionic surfactants and block copolymers as templates. In order to accommodate 30 nm size zeolite Y nanoparticles within the pores (the main objective of this project) however, the diameter of the pores needs to be expanded at least tenfold from 3 nm to \geq 30 nm. This pore size expansion was attempted by the addition of varying amounts of 1,3,5-trimethylbenze (TMB) to the synthesis mixtures.

(2) We have also simultaneously focused on the synthesis of nanocrystallites of zeolite Y for incorporation within the mesoporous hosts described above. Based on literature, we investigated various approaches for the reducing the crystal size of the zeolite. For example, one approach involved (in addition to the standard sodium, silicon and aluminum sources) the use of TMAOH¹ and/or TMAOH/TMABr combination as crystal growth suppressors.²

Our research progress in these two areas is highlighted below.

V RESEARCH PROGRESS

V-1 EXPERIMENTAL

V-1A Synthesis of All Silica Nanoporous Materials

All-silica nanoporous materials with expanded pore size were synthesized based on the method of Zhou *et. al.*³ Typically, 4.0 g of surfactant (Pluronic 123 block copolymer as templating agent), a known mass of 1,3,5 TMB, 30 g of H₂O and 120g of 2M HCl solution were all mixed under vigorous stirring. 8.5 g of tetraethylorthosilicate (TEOS) was added to the homogenized mixture. The resulting mixture was continuously stirred for 24 h at 40°C. The white solution was finally crystallized in a sealed, high density polyethylene bottle at 100°C for two days. The solid product was centrifuged, filtered, washed with deodorized water and dried in air at room temperature. The composition of the reaction mixture was as follows: 4.0 g P-123: x g TMB: 0.041TEOS:0.24HCl:6.67H₂O, (where x = 0.0, 0.5, 1.5, 3.0, 4.5, 6.0 g).

V-1B Synthesis of Standard Zeolite Y

Standard zeolite Y of submicron size was synthesized for comparison purposes according to procedure of Ginter.⁴ The zeolite was synthesized from a sodium hydroxide: sodium aluminate:sodium silicate reaction mixture. Generally, a solution (Solution A) was first prepared by dissolving 20 g of water, 4.0 g of sodium hydroxide and 2.1g sodium aluminate in a 50 ml plastic bottle. A 23 g aliquot of sodium silicate solution was added, the mixture stirred for 10 minutes and left for 1 day at room temperature. A second solution, (Solution B) was simultaneously prepared by vigorously mixing 131 g of water, 0.14g of sodium hydroxide and 13.1 g sodium aluminate in a beaker. Solutions A and B were combined under high shear mixing in high-speed blender, and left for one day at room temperature, followed by 22 h at 100°C. The product was centrifuged, filtered, washed with deionized water, and dried at 110 °C.

V-1C Synthesis of Zeolite Y Nanoparticles

The synthesis of zeolite Y nanoparticles was based on the presence of organic additives in the reaction mixture. The following reagents were used: NaOH, aluminum isopropoxide-[(CH₃)₂CHO]₃Al, tetraethylorthosilicate (TEOS) – (C₂H₅O)₄Si, 25 Wt % tetramethylammonium hydroxide (TMAOH)- (C₂H₅)₄NOH, and tetramethylammonium bromide (TMABr)-(C₂H₅)₄NBr. A general synthesis procedure was as follows: 12.8 g of [(CH₃)₂CHO]₃Al was dissolved in a solution of 52 g of 25 wt% TMAOH, 0.59 g of NaOH and 78 g of water. Varying amounts of TMABr was then added, followed by 27.7 g of TEOS. The clear solution was stirred in a polypropylene bottle for 1 day at room temperature, followed by several days at 100°C. The solid product was recovered by high speed centrifugation at 15000 g for 40 minutes.

V-1C Characterization

Powdered X-ray diffraction measurements were performed on a Phillips X-Pert X-Ray Diffractometer using Cu-K α radiation ($\lambda = 0.15418$ nm). Nitrogen adsorption isotherms and BET surface area measurements were obtained using a Micromeritics ASAP 2020 Porosimeter. The samples were preheated at 200°C in nitrogen for 2 hr, and then evacuated before adsorption measurements. Atomic force microscopy (AFM) images were taken with a Thermomicroscopes AutoProbe CP Research Scanning Probe Microscope (SPM), a high-resolution SPM which employs ScanMaster, an optically based closed-loop position control system. It measures the sample position and corrects inherent piezo errors such as hysteresis, creep and cross coupling using a feedback loop. The 3-D surface topography was imaged with a gold-coated, V-shaped silicon nitride AFM cantilever having a spring constant of 0.5 N/m. Image sizes ranging from 2 x 2 microns to 500 x 500 nm were scanned at a rate of 500nm/s. The samples were scanned in air in non-contact AFM mode using a cantilever resonant frequency of 117.08 kHz. Dynamic Light Scattering was done on a Horiba 500 Particle Size Analyzer.

VI Results and Discussion

VI-1 Synthesis of All Silica Nanoporous Materials

Figure 1. shows product obtained from the reaction mixture of molar composition 4.0 g P-123: 0g TMB: 0.041TEOS:0. 24HCl: 6.67H₂O. The three peaks observed (1 major peak at 2θ angle of $\sim 1^\circ$ and two smaller peaks at higher angles) are consistent with three dimensional hexagonally ordered nanoporous SBA-15.³ However, peaks in X-Ray diffraction patterns of samples synthesized in the presence of TMB, (not shown), could not be resolved from the very large background scattering generated by the instrument at very low angles. The presence of TMB in the synthesis mixture is expected to enlarge the pore diameters and unit cell size of SBA-15, thus shifting the diffraction peaks to lower 2θ angles. At angles of less than 1° significant background scattering was experienced on the XRD instrument, hence diffraction peaks, if present, could not be observed.

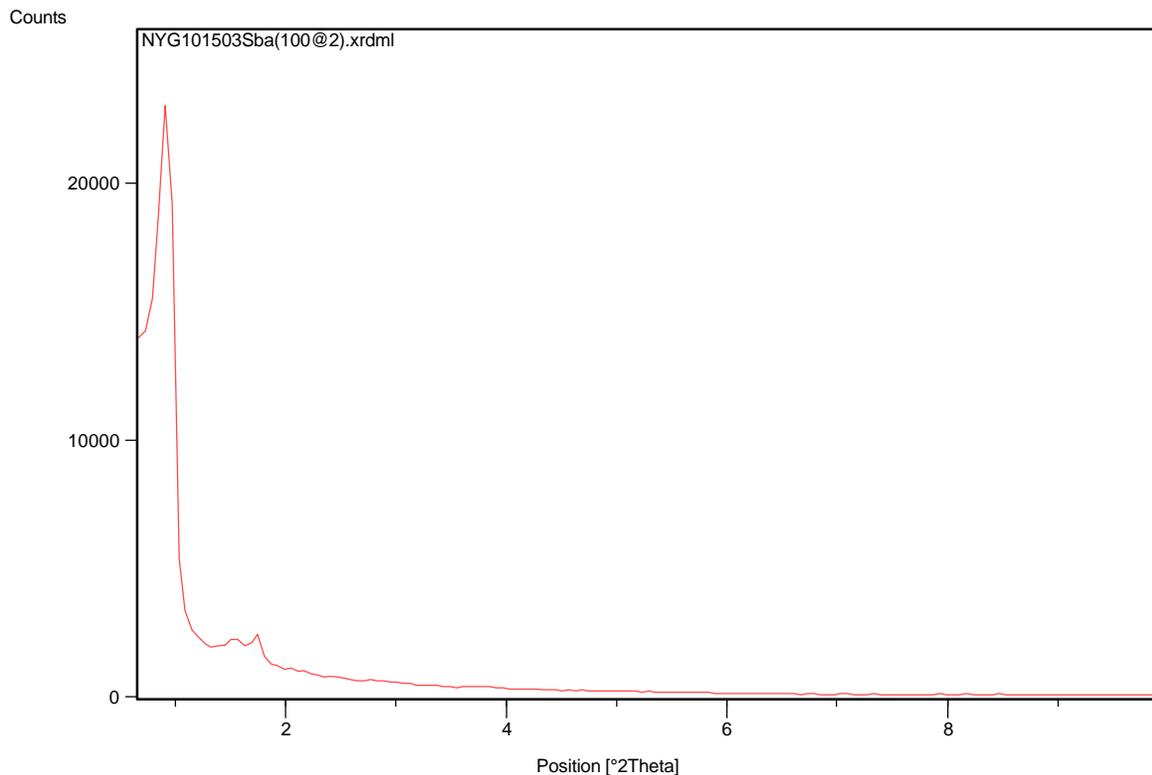


Figure 1. X-Ray Diffraction Pattern of the “as-synthesized” product obtained in the presence of surfactant P-123.

In the interim, the pore size distributions in these samples were investigated using nitrogen porosimetry. Figure 2 (top) shows the adsorption-desorption isotherms from a standard SBA-15 synthesized in the absence of TMB. A type IV isotherm was observed, with filling of nanopores commencing at P/P_0 around 0.74 during the adsorption phase. A hysteresis loop, typical of this material was also observed at P/P_0 values between 0.5 and 0.9. The sample shows BET surface area of $653 \text{ m}^2/\text{g}$, pore volume $0.67 \text{ cm}^3/\text{g}$ and average BJH adsorption diameter of 8.4 nm.

However, SBA -15 sample synthesized in the presence of TMB (Figure 2 bottom) shows adsorption-desorption isotherms with pore filling at P/P_0 around 0.88 during the adsorption phase. The sample shows BET surface area of $466 \text{ m}^2/\text{g}$, pore volume of $1.13 \text{ cm}^3/\text{g}$ and average BJH adsorption pore diameter of 25 nm. Pore size distribution curves for these samples are shown in Figure 3. Progress is therefore been made towards the synthesis of SBA-15 with expanded pore size in the range of 30 nm for use in the encapsulation of zeolite Y nanoparticles.

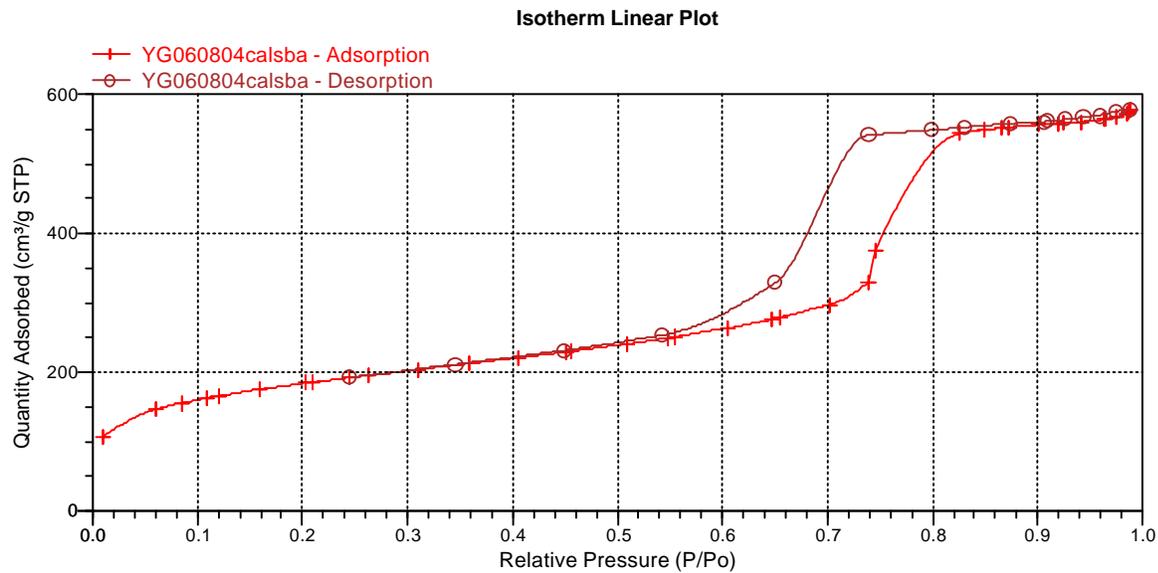


Figure 2. Adsorption-desorption isotherms of nanoporous SBA-15 synthesized in the presence of 0 g TMB (top) and 3 g of TMB (bottom) in synthesis mixture.

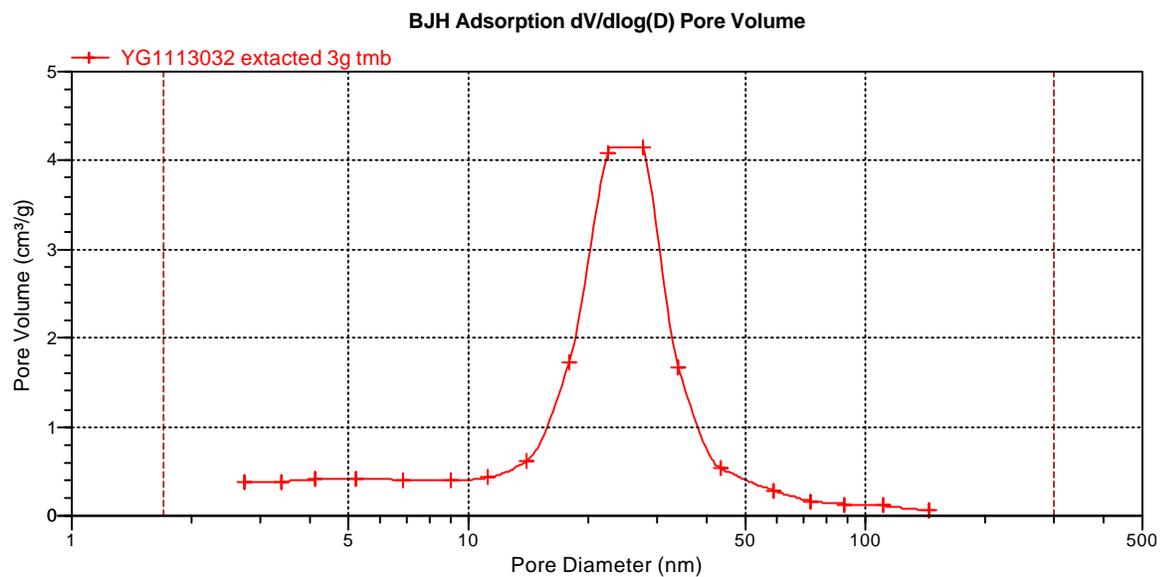
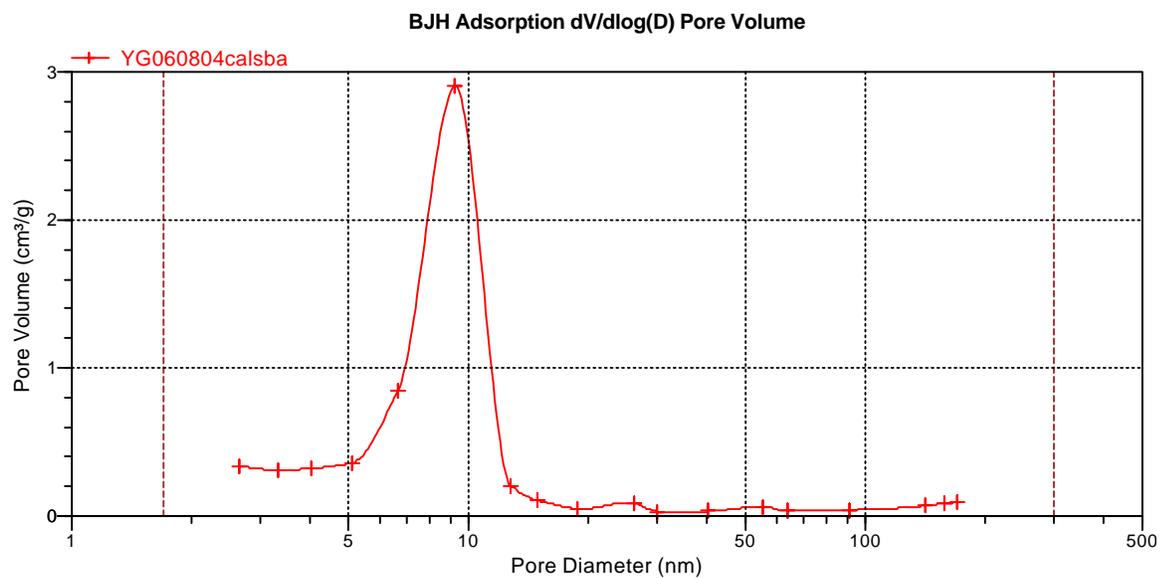


Figure 3. Pore size distribution curves of nanoporous SBA-15 synthesized with 0 g TMB (top) and 3 g of TMB (bottom) .

VI-2 Comparison of Synthesis of Standard Zeolite Y and Zeolite Y Nanoparticles

Figure 4 shows the diffraction pattern of the zeolite Y synthesized (according to Ginter's method⁴) for comparison purposes. The first 5 reflections at 2 angles of 7.14°, 10.1°, 12.4°, 16.1° and 20.4° are characteristic of zeolite Y.^{4,5} The low background and strong reflections indicate that the sample is highly crystalline.

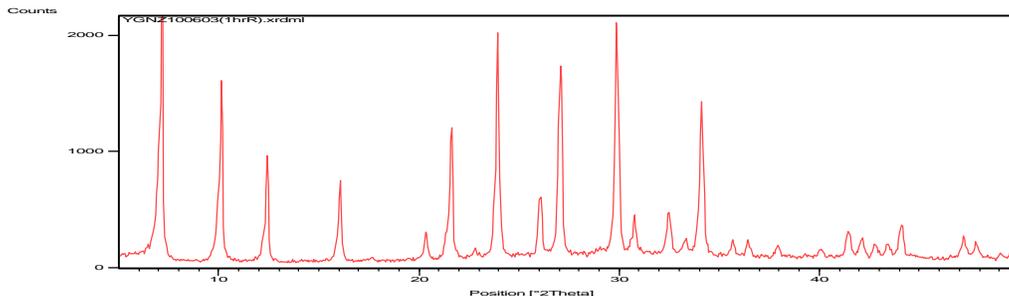


Figure 4. XRD of standard zeolite Y synthesized in the absence of TMA cations

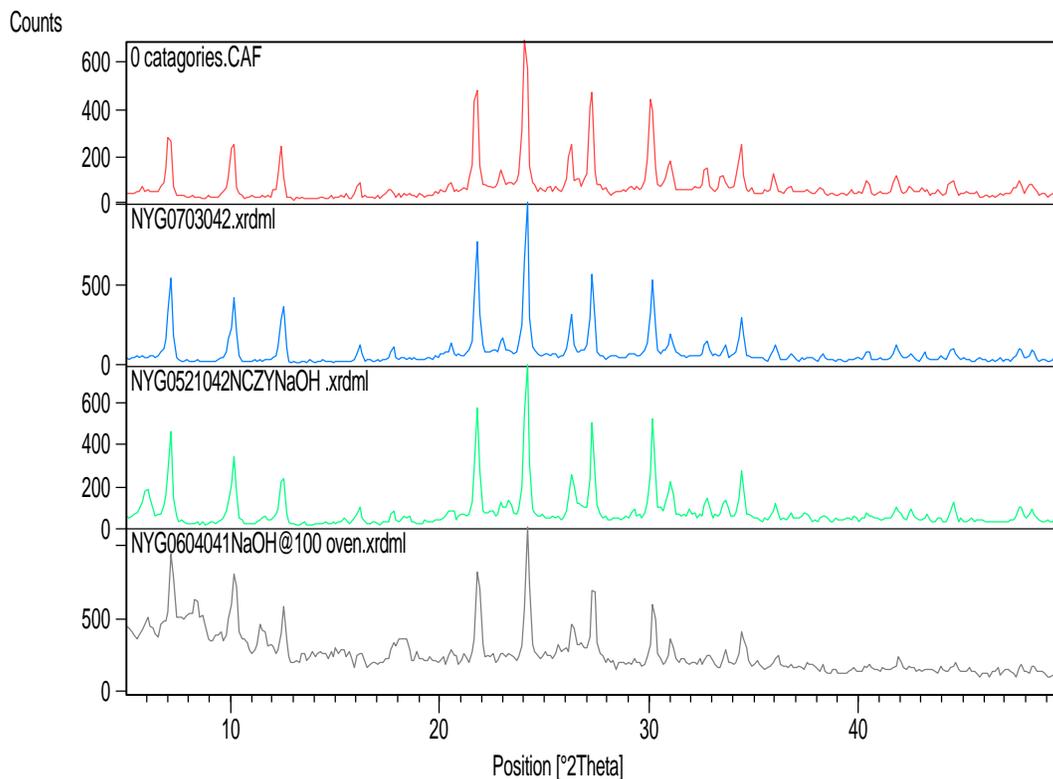


Figure 5. XRD Diffraction patterns of zeolite Y synthesized in the presence of TMAOH at 100°C for various times (45 hrs to 168 hr from top to bottom).

Figure 5 shows XRD patterns of zeolite Y synthesized in the presence of TMAOH at 100°C at various crystallization times (45 h to 168 h from top to bottom). No significant differences were

observed between the patterns, suggesting that zeolite Y crystals are formed as early as 45 h at 100°C in the presence of TMAOH.

In contrast, Figures 6 and 7 show XRD patterns for samples obtained when TMABr was added to the TMAOH-containing mixtures. For both figures, XRD analysis shows that highly crystalline zeolite Y products were obtained in the presence of TMABr, but a sharp peak at 2θ angle around 23° is predominant in all patterns (Figure 6). This peak became more predominant as the concentration of TMABr was increased (Figure 7) and is possibly due to the precipitation/recrystallization of the TMABr salt within the pores of the zeolite.

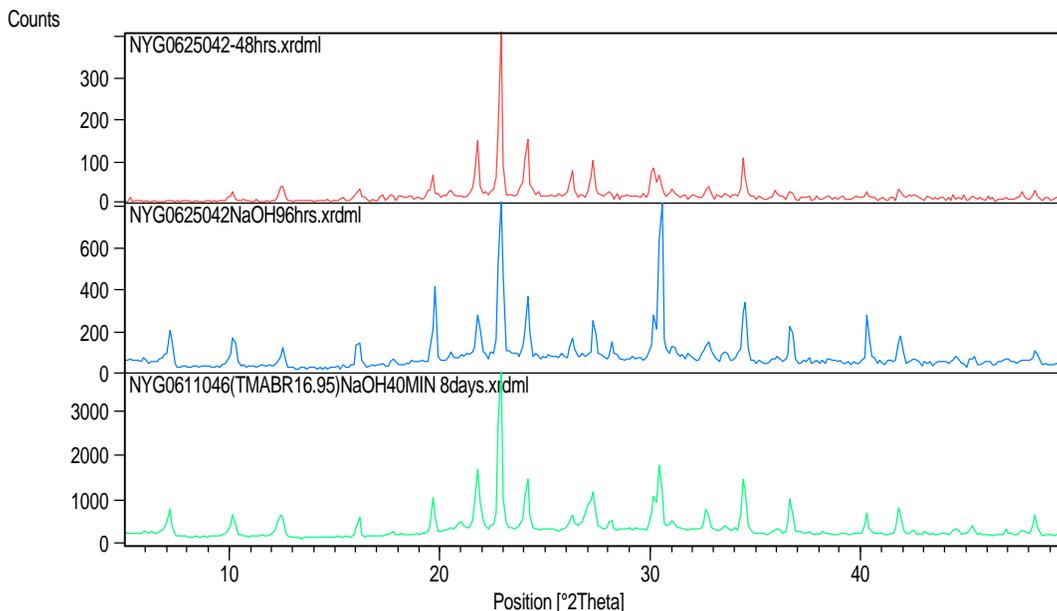


Figure 6. XRD patterns of zeolite Y samples synthesized in the presence of TMABr/OH (TMABr/OH ratio = 0.64) with increasing synthesis time up to eight days.

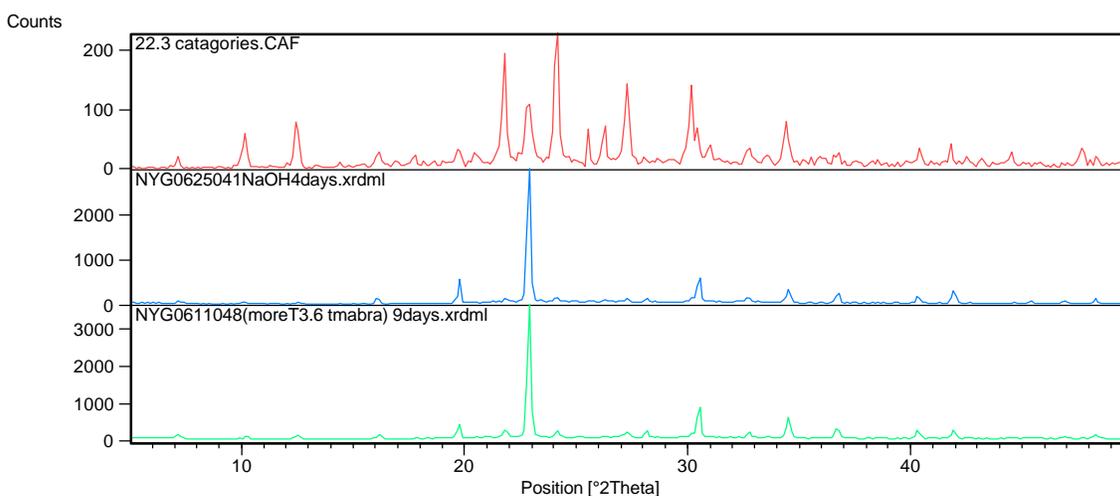


Figure 7. XRD Patterns of zeolite Y samples synthesized in the presence of TMABr/OH (TMABr/OH ratio = 1.07) with increasing synthesis time up to nine days.

The impact TMAOH and TMABr can be observed in the particle size distribution of the resulting zeolite Y products. Dynamic light scattering results (Figure 8) show that the particles size of zeolite Y synthesis under standard conditions and in the absence of organics, ranged from 100 to 1000 nm with a median of 284 nm and mean of 267 nm. However, zeolite Y synthesized in the presence of TMAOH under conditions defined above are of median sizes around 75 nm after 4 to 7 days at 100°C (Figures 9, 10 and 11). The morphology of these particles as obtained by AFM is show in Figure 10. At longer crystallization time (up to 196 h) particle size increased to approximately 80 nm (Figure 11).

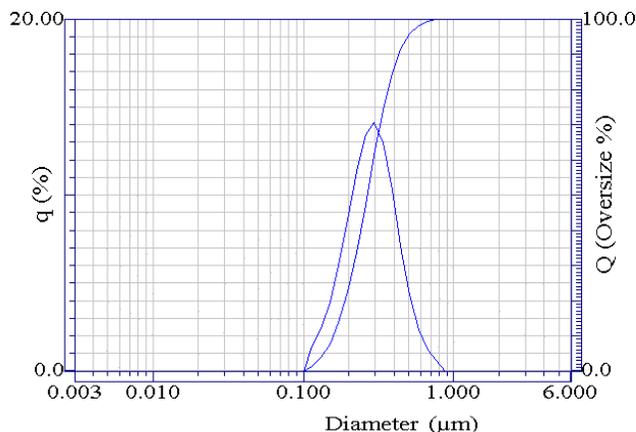


Figure 8. DLS particle size distribution of zeolite Y synthesized in the absence of TMA cation.

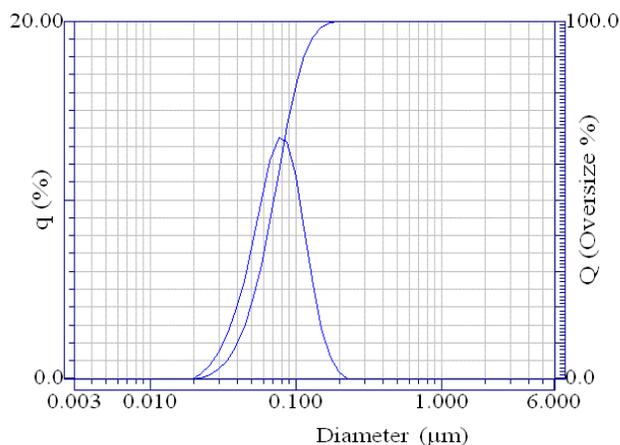


Figure 9. DLS particle size distribution of zeolite Y synthesized in the presence of TMAOH.

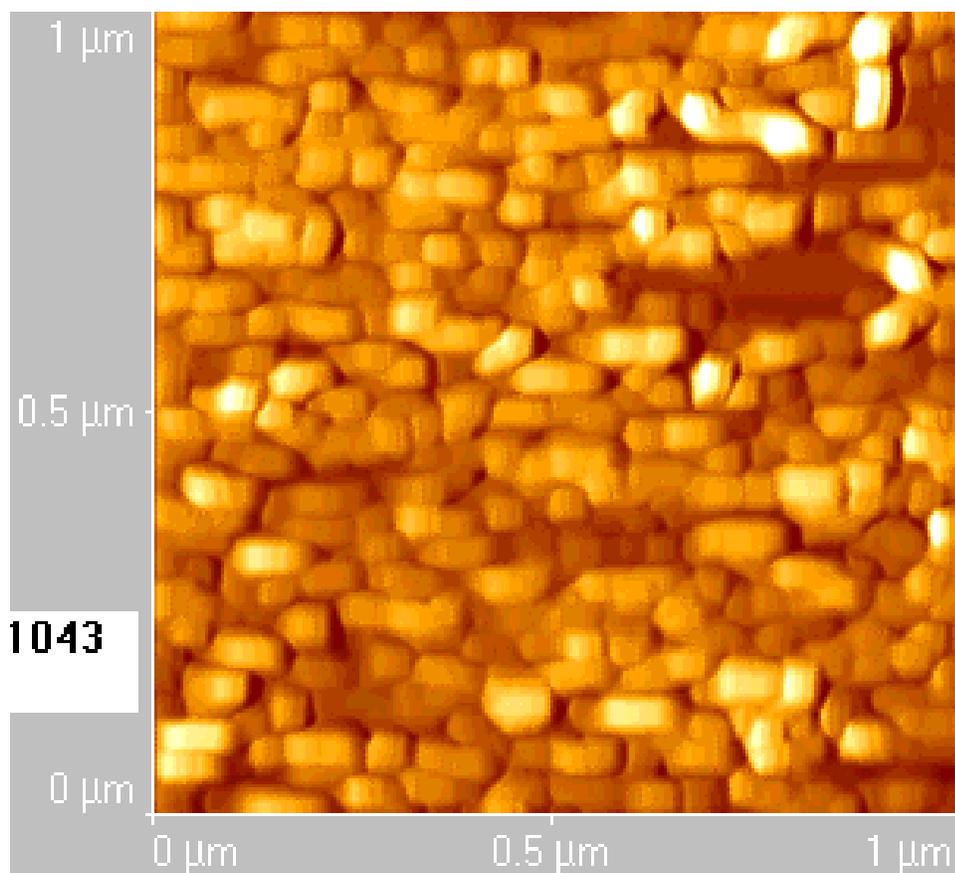


Figure 10. AFM scan showing morphology of zeolite Y synthesized in the presence of TMAOH

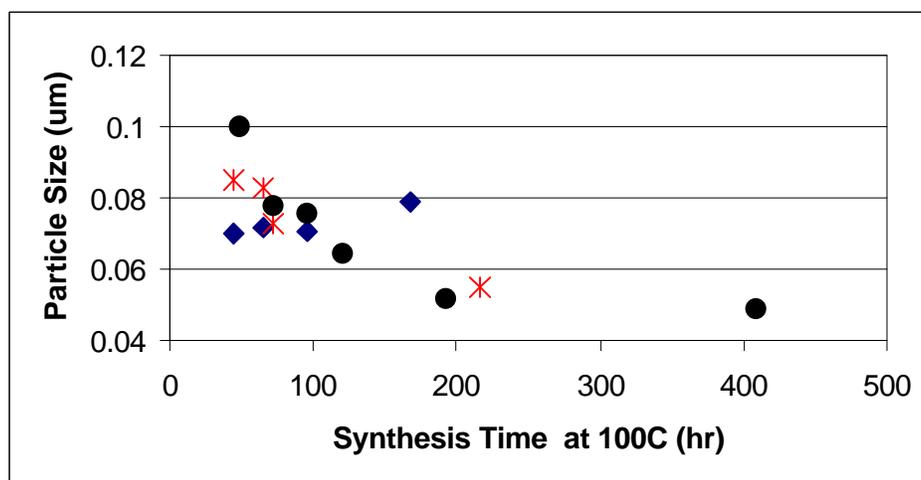


Figure 11. Median particle size of Zeolite Y nanocrystals as a function of synthesis time and with increasing concentration of TMABr (◊ - 0 TMABr, • -TMABr/ TMAOH = 0.64, * -TMABr/ TMAOH = 1.07).

In the presence of TMABr however, particle size decreased with increase in synthesis time (Figure 11). After 196 h at 100°C, the median particle size obtained in the TMABr/ TMAOH system (of mole ratio 0.64) was approximately 55 nm. Increasing the TMABr to TMAOH molar ratio of 1.07 showed no additional decrease in particle size of the zeolite, but XRD patterns of products obtained from the presence of additional TMABr show sharp peaks around 2 θ angle of 23° mentioned earlier (Figures 6 and 7) which is assumed to have resulted from the precipitation of crystalline TMABr salt. On calcination of one of these samples at 400°C, the peak disappeared (Figure 12) possibly as a result of thermal decomposition of the salt. Higher background in the calcined sample in comparison to its as-synthesized parent, suggests that the zeolite Y loses some crystallinity during the calcinations process.

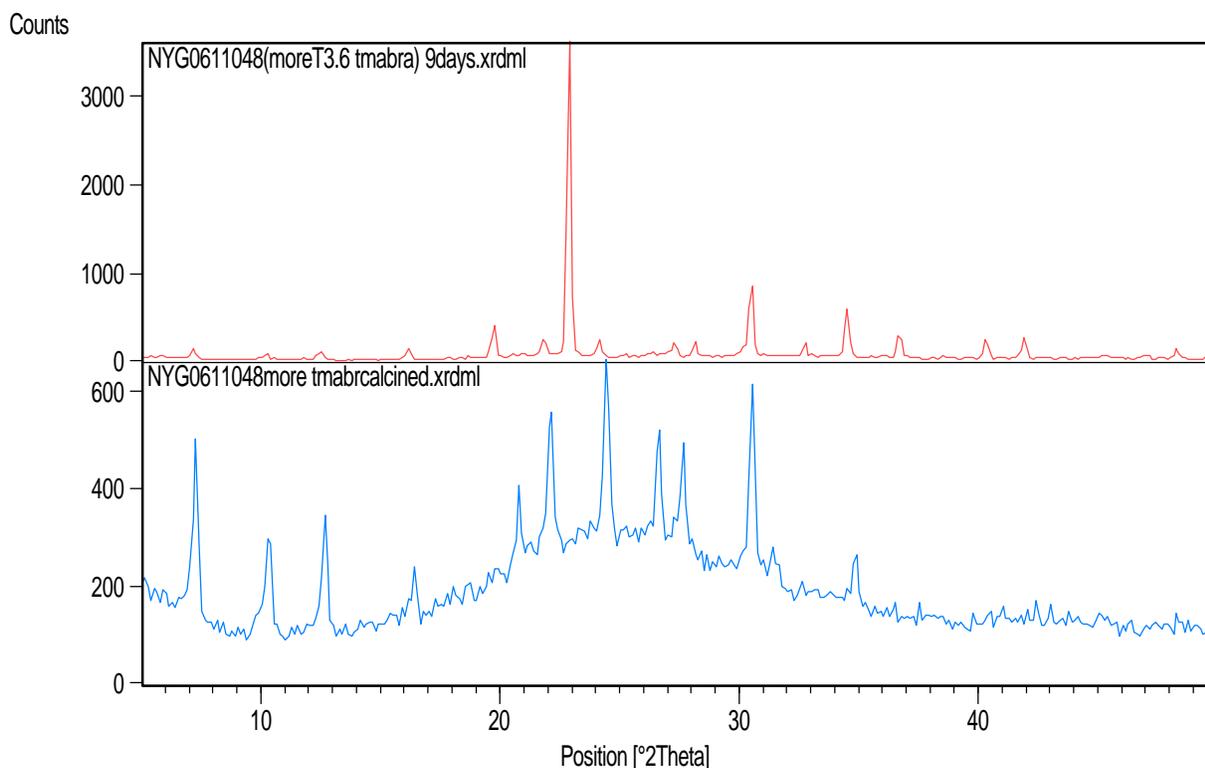


Figure 12. XRD pattern of “as-synthesized” (top) and calcined (bottom) zeolite Y nanocrystals synthesized in the presence of TMAOH/TMABr system (TMABr/ TMAOH = 1.07).

VII CONSLUSIONS

The synthesis of high surface ordered nanoporous silica of expanded pore diameter of 25 nm (larger than the standard size of 8.4 nm) using trimethylbenzene as a pore size expander was accomplished. The synthesis of zeolite Y nanoparticles with median pore size of approximately

50 nm (smaller than the 80 nm typically obtained with TMAOH) using combined TMABr/TMAOH as organic additives was also accomplished.

VIII FUTURE WORK

Work in the immediate future will be focused on the following three areas: 1) The synthesis and characterization of all-silica and aluminosilicate nanoporous materials with expanded pore sizes up to 30 nm will continue by increasing the concentration of TMB in the synthesis mixture. The mole ratios of the reactants, synthesis temperature and time will also be controlled towards achieving the desired results. 2) Research efforts to reduce the average particle size of zeolite nanoparticles down to 35-30 nm will continue. The synthesis of zeolite Y nanocrystals within the SBA-15 nanoporous host will also be simultaneously investigated. 3) The resulting composite catalyst system of nanozeolite Y encapsulated within nanoporous SBA-15 will then be evaluated for heavy oil upgrading.

IX TECHNOLOGY/INFORMATION TRANSFER

Students:

Two following two students have been working on the project since inception:

Yohannes Ghirmazion	Second year graduate student (Chemistry)
Ifedapo Adeniyi	Sophomore undergraduate (Chemistry & Engineering)
Taurean Hodges	Senior (Chemistry undergraduate)

Presentation:

- 1) Abstract entitled “*Improved Catalysts for the Heavy Oil Upgrading Based on Zeolite Y Nanoparticles Encapsulated in Stable Nanoporous Host*” was presented at the University Coal Research Contractors Review Conference June 3-4 2003, at the Marriott City Center in Pittsburgh, Pennsylvania.
- 2) Paper entitled “*Improved Catalysts for the Heavy Oil Upgrading Based on Zeolite Y Nanoparticles Encapsulated in Stable Nanoporous Host*” was presented at the University Coal Research Contractors Review Conference June 8-9, 2004, at the Marriott City Center in Pittsburgh, Pennsylvania
- 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) 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 .
- 6) Phenylene-Bridged Mesoporous Organosilicate from Nonionic Surfactant Templated Synthesis, Conrad Ingram* and Yohannes Ghirmazion, accepted for presentation at the 4th International Mesostructured Material Symposium, May 1st -4, 2004, Cape Tow, South Africa.
- 7) Synthesis of Aromatic Bridged Ordered Mesoporous Organosilicate with Cetyltrimethylammonium Cation as Templating Agent has been accepted for a poster presentation at the 4th International Mesostructured Material Symposium, May 1st -4, 2004, Cape Tow, South Africa.
- 8) Catalytic and selective behavior of MeAPO36 in the mild hydrocracking of heavy gas oil", Kesete Ghebreyessus and Conrad Ingram presented at the 227th ACS National Meeting, Anaheim, CA, March 28-April 1, 2004.

X REFERENCES

-
- 1 G. Zhu, S. Qiu, J. Yu, Y. Sakamoto, F. Xiao, R. Xu, O Terasaki, *Chem. Mat.*, 1998 10, 1483-1486.
 - 2 B.A. Holmberg; H. Wang; J. M. Norbeck ; Y. Yan, Controlling size and yield of zeolite Y nanocrystals using tetramethylammonium bromide, *Microporous and Mesoporous Materials*. 59 (2003)13-28.
 - 3 D. Zhao, J. Fing, Q. Huo, N. Melosh, G. Fredrickson, B. Chmelka, G. Stucky, *Science*, 279 (1998) 548-552; D. Zhao, Q. Huo, J Feng, B. F. Chmelka, G. Stucky, *J. Am. Chem. Soc.*, 120, (1988) 6024-6036
 - 4 D. Ginter in **Verified Synthesis of Zeolitic Materials**, H. Robson, ed. Elsevier: Amsterdam, (2001), 156.
 - 5 M.M.J. Tracey, J. B. Higgins; *Collection of Simulated XRD Powder Patterns for Zeolites*, 4th ed. Elsevier: Amsterdam, 2001.