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

SEVENTH SEMI-ANNUAL TECHNICAL PROGRESS REPORT

REPORT PERIOD: October 1, 2005-March 31, 2006

PRINCIPAL INVESTIGATOR: CONRAD INGRAM, Ph. D.
Co. PI MARK MITCHELL, Ph. D.

REPORT DATE: JUNE 20, 2006

GRANT NUMBER: DE- FG26-02NT41676

SUBMITTED TO: U.S. Department of Energy

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

I. ABSTRACT

Al-SBA-15 mesoporous catalysts with strong Brönsted acid sites and Al stabilized in a totally tetrahedral coordination was synthesized from the addition of hydrothermally aged zeolite Y precursor to SBA-15 synthesis mixture under mildly acidic condition of pH 5.5. The materials possessed surface areas between 690 and 850 m²/g, pore sizes ranging from 5.6 to 7.5 nm and pore volumes up to 1.03 cm³, which were comparable to parent SBA-15 synthesized under similar conditions. Up to 2 wt. % Al was present in the most aluminated sample that was investigated, and the Al remained stable in totally tetrahedral coordination, even after calcination at 550°C. The Al-SBA-15 mesoporous catalyst showed significant catalytic activity for cumene dealkylation, and activity increased as the amount of zeolite precursor added to the SBA-15 mixture was increased. The catalyst's activity was not affected by the aging time of the precursor for up to the 24 hr aging time investigated. This method of introducing Al and maintaining it in a total tetrahedral coordination is very effective, in comparison to other direct and post synthesis aluminations reported. The catalytic performance of the zeolite Y/SBA-15 composite materials will be compared with that of pure SBA-15. The catalysts will then be evaluated for the conversion of heavy petroleum feedstocks.

Table of Contents

I	ABSTRACT	2
II	DISCLAIMER	4
III	EXECUTIVE SUMMARY	5
IV	INTRODUCTION	7
	IV-1 BACKGROUND	7
V	EXPERIMENTAL DETAILS	10
VI	RESULTS AND DISCUSSION	14
VII	CONCLUSIONS	28
VIII	FUTURE WORK	29
IX	TECHNOLOGY/INFORMATION TRANSFER	30
X	REFERENCES	31

II 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 the authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

III EXECUTIVE SUMMARY

The objective of this project is to synthesis 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 catalysts deactivation and prolong catalysts life. 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: a) 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; b) synthesis of nanoporous silicate host materials of up to 30 nm pore diameter. This was conducted using poly (alkylene oxide) copolymers as template around which inorganic silicate 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; (3) Synthesis of zeolite Y/Nanoporous Host composite materials as potential catalysts, and (d) catalysts evaluation for the upgrading of heavy petroleum feedstocks.

Al-SBA-15 mesoporous catalysts with strong Brönsted acid sites and Al stabilized in a totally tetrahedral coordination was synthesized from the addition of hydrothermally aged zeolite Y precursor to SBA-15 synthesis mixture under mildly acidic condition of pH 5.5. The materials possessed surface areas between 690 and 850 m²/g, pore sizes ranging from 5.6 to 7.5 nm and pore volumes up 1.03 cm³, which were comparable to parent SBA-15 synthesized under similar conditions. Up to 2 wt. % Al was present in the most aluminated sample that was investigated, and the Al remained stable in totally tetrahedral coordination, even after calcination at 550°C. The Al-SBA-15 mesoporous catalyst showed significant catalytic activity for cumene

dealkylation, and activity increased as the amount of zeolite precursor added to the SBA-15 mixture was increased. The catalyst's activity was not affected by the aging time of the precursor for up to the 24 hr aging time. This method of introducing Al and maintaining it in a total tetrahedral coordination is very effective, in comparison to other direct and post synthesis aluminations methods reported.

IV INTRODUCTION

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 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 catalysts deactivation and prolong catalysts life. 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: a) 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; b) synthesis of nanoporous silicate host materials of up to 30 nm pore diameter. This was conducted using poly (alkylene oxide) copolymers as template around which inorganic silicate 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; (d) Synthesis of zeolite Y/Nanoporous Host composite materials as potential catalysts and (d) catalysts evaluation for the upgrading of heavy petroleum feedstocks.

IV-1 BACKGROUND

The high surface area mesoporous silicate, SBA-15, which possesses well defined and large pores of 2 to 30 nm offers significant potential for the catalytic conversion of bulky organic compounds, such as those found in heavy petroleum feedstocks.¹⁻³ Its larger pore size, thicker pore walls, and the resulting high thermal stability affords it much greater potential advantages over its basic-media-synthesized counterpart, MCM-41.⁴ SBA-15 however, lacks the Brönsted acid sites that are important in many of these catalytic processes. The incorporation of Al into its

siliceous framework by direct synthesis is difficult, since it is synthesized in a strongly acidic medium in which most Al species are soluble. Its microporous aluminosilicate predecessor, zeolites, with pore sizes < 1 nm, possess a combination of strong Brönsted acid sites, thermal stability, uniform pore structures, and are widely used as heterogeneous Brönsted acid catalysts in a wide range of processes, including petroleum processing. Zeolite Y, a member of the faujasite (FAU) family of zeolites (with pore size of 0.8 nm), is a critical component in industrial fluidized cracking catalysts used in petroleum processing. Zeolites however, suffer deactivation under petroleum processing conditions due their small pores, which restrict their ability to convert large molecules. Pores and acid sites blockage often result from larger refractory compounds present in heavy feedstocks. The objective of this study is to investigate the incorporation of tetrahedrally coordinated Al, and the associated Brönsted acid sites, within the pore walls of SBA-15 using preformed zeolite Y aluminosilicate precursors (seeds) containing zeolitic nanoclustered subunits.

Past efforts to introduce Al in tetrahedral coordination by direct synthesis, post-synthesis alumination, and by the addition of seed precursors have produced mixed results.⁵ Yue *et al.* reported that incorporating Al in SBA-15 by direct synthesis resulted in materials containing high surface area, large pore size and pore volume, but the method was not successful in placing Al in totally tetrahedral coordination, and the Al was found in both tetrahedral and octahedral environments.⁶ Post synthesis alumination approaches in which Al is grafted to the pre-formed mesoporous silicate framework have resulted in formation of both tetrahedral and octahedral Al species.^{5,7} For example, Sumiya *et al.* investigated the post synthesis incorporation of Al in siliceous SBA-15 structure using tetramethylaluminum as the aluminum source.⁷ Though

Brönsted acid sites were generated, the materials were of relatively low surface areas that decreased from 600 to 400 m²/g as the Al content was increased, and Al occupied both tetrahedral and extra-framework octahedral environments upon calcination. Another approach involved coating the pre-synthesized SBA-15 with ZSM-5 zeolitic nanostructured subunits from the precursor solution of the latter under basic conditions to produce materials of high thermal stability and acidity. The resulting materials possessed significantly reduced surface areas.⁸ An effective strategy, which forms the basis for our investigation, involves the direct incorporation of zeolitic nanoclusters in mesoporous silicate during synthesis. This was first demonstrated for the synthesis of stable aluminosilicate mesostructures utilizing zeolite Y seeds to construct the walls of hexagonally ordered MCM-41 under basic conditions.⁹ The zeolite Y precursor was prepared from hydrothermal treatment of sodium silicate, sodium aluminate, and sodium hydroxide mixture. Similar results were reported by Pariente and co-workers, who synthesized the zeolite Y precursor in the presence of the tetramethylammonium (TMA⁺) ion in the synthesis mixture.^{10,11} Other studies have reported the successful assembly of stable hexagonal MCM-41 from the zeolitic nanoclusters which are present in the seed precursors of ZSM-5, TS-1(MFI with ~ 0.5 nm pore size) and zeolite beta (BEA with ~0.6 nm pore size), all synthesized under basic conditions.¹²⁻¹⁶ Under neutral conditions and with non-ionic surfactants, aluminosilicate mesostructures with wormhole pore features were also synthesized using precursor mixtures of zeolites Y, ZSM-5 and Beta.¹⁷ These materials exhibited hydrothermal stability, but showed low surface areas and small pore volumes. In addition to basic and neutral conditions, the seeding concept was extended to incorporating FAU, ZSM-5, Beta, and silicalite (an all-silica member of MFI family) structural subunits in the pore walls of SBA-15 by adding the respective zeolite precursor into SBA-15 synthesis mixtures under acidic conditions.¹⁸⁻²²

In the case of Al-SBA-15 synthesis from zeolite Y precursor, results reported by Pinnavaia and coworkers indicate that strong acidic conditions ($\text{pH} < 2$) should be avoided, and mild acid conditions ($\text{pH} 4\text{-}6.5$) was necessary to prevent the decomposition of the zeolite Y precursor and the solubilization of Al.¹⁸ The resulting materials obtained by these researchers had low surface areas ($< 650 \text{ m}^2/\text{g}$), but showed significant steam stability compared to the parent SBA-15, and good activity for acid catalyzed cumene conversion. In this communication, we report that by using an alternative strategy to synthesize the seed precursor and combining the reactants, Al-SBA-15 catalysts were produced with higher surface areas, and the Al was stabilized in total tetrahedral coordination upon high temperature calcinations. The effects of precursor quantity and aging time on the physicochemical and catalytic properties of the resulting catalysts were investigated.

V EXPERIMENTAL DETAILS

Materials: Tetramethylammonium hydroxide $[(\text{CH}_3)_4\text{NOH}]$, TMAOH, 25 wt % in water], aluminum isopropoxide $[(\text{CH}_3)_2\text{CHO})_3\text{Al}]$, 98%, tetramethylammonium bromide $[\text{C}_4\text{H}_{12}\text{NBr}]$, TMABr, 98%, tetrapropyl ammonium hydroxide [TPAOH], isopropyl benzene $[\text{C}_9\text{H}_{12}]$, cumene, 98%] were obtained from Aldrich Chemical Co. Ammonium nitrate $[\text{NH}_4\text{NO}_3]$, sulfuric acid $[\text{H}_2\text{SO}_4]$, 98%, hydrochloric acid $[\text{HCl}]$, 37.2%, sodium hydroxide $[\text{NaOH}]$, tetraethyl orthosilicate $[(\text{C}_2\text{H}_5\text{O})_4\text{Si}]$, TEOS] were obtained from Fischer Scientific Co. Pluronic P-123 $[(\text{EO}_{20}\text{PO}_{70}\text{EO}_{20})]$, $M_{\text{av}} = 5800$) was obtained from BASF company.

Synthesis of Al-SBA-15: In general, zeolite Y seed precursor was first prepared under basic conditions and aged by a slightly modified method of Yan and coworkers.²³ SBA-15 synthesis mixture was then prepared according to the method reported by Stucky and coworkers, and aliquots of the aged precursor added.¹ Zeolite Y seed mixture with Si/Al ratio of 5 was prepared in the presence of TMA cation as follows: 76.5 g of double deionized water, 52.3 g of TMAOH, 11.0 g TMABr, 12.5 g of aluminum isopropoxide, 0.60 g of NaOH and 27 g of TEOS were mixed for 3 days at room temperature, followed by heating at 100°C for up to 24 hr. The pH of the mixture was 10.5. Aliquots (0.5 to 3.0 g) of the precursor was added to 4 g of P-123 surfactant, 10 g of TEOS and 98.8 g of water which resulted in a final mixture of molar composition of $\text{SiO}_2 : x\text{Al}_2\text{O}_3 : 0.013 \text{ P-123} : 5.0 \text{ TMA} : 70 \text{ H}_2\text{O}$, with $x = 0.0017$ to 0.010 . The pH of the mixture was adjusted to 5.5 with 1.7M of H_2SO_4 . The mixture was stirred for 12 hr at 35°C, and then heated in a sealed high-density polyethylene bottle under static conditions at 100°C for 24 hr. The solid was recovered by filtration, washed with deionized water, dried and calcined at 550°C in flowing dry air for up to 14 hr.

Synthesis of zeolite Y nanoparticles: Nanoparticles of zeolite Y were prepared by further heating unused portions of the seed precursor at 100°C for 3 days. The mixture was then cooled, centrifuged at 15000 rpm for 40 min, washed repeatedly with deionized water, and the solid recovered and dried at room temperature.

Characterization: X-ray powder diffraction (XRD) was recorded using a Philips X'PERT diffractometer fitted with Cu-K α anode. Voltage and current were maintained at 40KV and 45 mA, respectively. Diffractograms were recorded between (2 θ) angles of 1 to 40° with a step size

of 0.02 (2 θ), step time of 10 s, and, slit width of 0.5°. Samples were ground into fine powders and placed into aluminum sample holders. High Resolution Transmission Electron Micrographs were obtained with an MAS HD2000 Transmission Electron Microscope operating at 200 KV. Samples were deposited on a copper coated carbon grid from acetone solution. Multiple point BET surface area and pore size analyses were conducted on the calcined products using a Micromeritics ASAP 2020 Porosimeter. Pre-weighed samples were degassed for 2 hr at 200°C under nitrogen gas. Nitrogen sorption experiments were performed at 77 K. Fourier Transformed Infrared (FTIR) absorption measurements were conducted with a Nicolet 750 Magna FTIRTM instrument. Samples were prepared by mixing approximately 2 mg quantities of sample with approximately 50 mg of the KBr and pressed into translucent discs and 100 scans were acquired. ²⁷Al Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) measurements were performed with a Bruker DSX-300 spectrometer operating at 7.4 Tesla, with sender frequency at 78.21 MHz, and magic angle spinning at 5 kHz in a 7 mm rotor. Repetition delay between scans of 1 s and pulse length of 0.6 μ s (the 90 degree pulse length as determined in a solution of Al³⁺ ions was 10 μ s) were used. A total of 1024 scans were collected and averaged. Aluminum nitrate solution was used as an external reference. Chemical analysis was conducted using a Perkin Elmer Elan 9000 Inductively Coupled Plasma/Mass spectrometry. The samples (~5 mg) were digested in 3 ml of 40% hydrofluoric acid in covered Teflon beakers at 150°C for 30 min. The digestates were cooled and diluted with DDI water to mark in 100 ml plastic volumetric flasks. Ammonia temperature program desorption (NH₃-TPD) experiments were conducted on the proton exchanged form of the catalyst to determine the relative strength of catalysts' acid sites. A 50 mg sample was placed in a 7cm long x 1/2 cm i.d. Stainless Steel tube and was heated in a muffle furnace to 550°C at 20°C per min in helium flow, then cooled to

100°C. Ammonia gas diluted in helium was allowed to flow over the catalyst for two hours through the injection port of a Gas Chromatograph that was interfaced to the furnace. The catalyst was then heated at 10°C per min under a flow of pure helium and desorbed ammonia effluent flowed through an attached stainless steel tube with its other end connected to the GC's thermal conductivity detector. The furnace temperature vs detector response was recorded. Pyridine was adsorbed onto the samples for further analysis by FTIR using the apparatus and conditions described for ammonia. A 50 mg aliquot of sample was first slowly heated to 550°C, cooled to 100°C, and microliter quantities of pyridine were repeatedly injected through the GC injection port with a microsyringe until saturation was observed. The sample was heated to 120°C to remove physisorbed pyridine, then removed and FTIR measurement done on a transparent self supporting disc.

Catalytic Evaluation: Prior to testing catalysts, the calcined materials were converted to acidic form (H^+) by twice refluxing in 0.5M NH_4NO_3 (50 ml / 0.5 g) at 70°C for 6 hr. The solid was filtered, washed, dried and calcined at 550°C for 5 h. Cumene conversion was performed at various temperatures using a tubular quartz, continuous up-flow, fix-bed microreactor with a catalyst loading of 0.12 g. The H^+ exchanged catalyst was introduced into the 1 cm internal diameter quartz reactor and held in place in the center of the tube between glass fritz and quartz wool plug. The catalyst temperature was monitored with a thermocouple centrally placed in the catalyst bed. The catalyst was pretreated inside the reactor by heating in a 30 ml/min N_2 flow at 300°C for 1 hr. The N_2 carrier flow (20 ml/min) was then saturated with cumene by passing it through a thermostated saturator at 24°C and then allowed to flow through the catalyst bed. A cumene flow rate of 9.5 $\mu\text{mol}/\text{min}$ was generated using the saturator. The reactor effluent flowed

through a Valco six-port sampling valve that was interfaced to an Agilent 5890 Gas Chromatograph that was equipped with a flame ionization detector, and a 30 meter HP-5 capillary column of 1.5 μm film thickness, and 0.53 mm inside diameter.

VI RESULTS AND DISCUSSION

Synthesis: Figure 1 shows XRD patterns of the calcined products obtained from varying the amount (0 to 3 g, Si/Al ratio = 0 to 50) of zeolite Y precursor mixture added to the SBA synthesis mixture. For each sample, a major reflection was observed at 2θ angle of 1° and two smaller peaks between 1.5° and 1.7° which can all be indexed to the hexagonal symmetry of SBA-15, and are assigned to the d(100), d(110) and d(210) lattice reflections respectively.¹ These results indicate that highly ordered SBA-15 can be synthesized at pH 5 which is much milder than the highly acidic medium (pH <2) typically utilized. In addition, the presence of zeolite Y precursor components in the amounts added had no apparent adverse effect on the long range ordering of the mesostructure. The unit cell lengths of the resulting Al-SBA-15, a_0 ($a_0 = 2 \times d(100)/\sqrt{3}$) ranged between 11 and 12.5 nm, which is consistent with values observed (Table 1), and reported for the parent SBA-15.¹ In order to investigate the possible existence of zeolite Y crystals within the Al-SBA-15 products, the diffractograms were compared with that of a fully crystalline zeolite Y nanoparticles (40 nm particle size) that was synthesis as a reference as described above (Figure 1 inset).²⁴ Low angle reflections present in the zeolite Y reference at 2θ angles of 7.1° , 10.1° , and those at higher angles are all characteristic of zeolite Y, but were undetected in the Al-SBA-15 mesostructures, thus suggesting the absence of any fully crystalline zeolite phase within the Al-SBA-15 matrix. The transmission electron micrograph of a typical sample shows well defined uniformed hexagonally arrangement pores with diameter estimated at 6 nm (Figure 2). From the micrographs also, no crystallites were observed within the vicinity of

the mesoporous structures, hence providing additional evidence for the absence of domains of fully crystalline nanoparticles of zeolite Y within the bulk phase of the mesostructures.

Nitrogen adsorption-desorption isotherms of Al-SBA-15 with varying amounts of “6 hr-aged” zeolite Y precursor are shown in Figure 3A. Their textural properties are presented in Table 1. Type IV isotherms were observed with inflection points corresponding to internal pore filling at P/P_0 above 0.7, and with hysteresis loops typical of SBA-15, were observed in all samples, therefore confirming their mesoporous characteristics. The samples showed surface areas ranging from 790-830 m^2/g , pore volume (0.7-1.0 cm^3/g), and BJH diameters between 5.5 to 6 nm. Surface areas were consistently higher than those reported by Pinnavaia and coworkers.¹⁸

Fig. 1. X-ray diffraction patterns of zeolite Y(inset), and Al-SBA-15 synthesized with the addition of varying amounts of zeolite Y precursor to SBA-15 mixture. (a) 0 g, b) 0.5 g, c) 1.5g, and d) 3.0g precursor. (The precursor was aged for 3 days at room temperature and 24 hr at 100°C).

Fig. 2. TEM of SBA-15 synthesized with 3.0 g of zeolite precursor added to SBA-15 mixture showing. (The precursor was aged for 3 days at room temperature and 24 hr at 100°C)

Fig. 3A. Adsorption-desorption isotherms of Al-SBA-15 synthesized with the addition of varying amounts of zeolite precursor to SBA-15 mixture: a) 0.5g b) 1.5g and c) 3.0g precursor. (The precursor was aged for 3 days room temperature and 6 hr at 100°C).

Type IV adsorption-desorption isotherms for mesostructures containing varying amounts of 10 hr (not shown) and “24 hr-aged”(Figure 3B) zeolite Y seeds were observed in all samples, again confirming their mesoporous nature. Hysteresis loop, typical of these materials, were also observed at P/P_0 values between 0.5 and 0.9. The samples show varying surface areas between 690 to 840 m^2/g , pore volumes of 0.74 to 0.96 cm^3/g , and BJH diameters between 5.6 to 6.9 nm (Table 1).

Fig. 3B. Adsorption-desorption isotherms of mesoporous SBA-15 synthesized with the addition of varying amounts of zeolite precursor to SBA-15 mixture.: a) 0.5g b) 1.5g and c) 3.0g precursor. (The precursor was aged for 3 days at room temperature and 10 hr at 100°C)

Table 1. Textural properties of SBA-15 products and crystalline zeolite Y

Sample ID	Zeolite precursor aging time at 100°C (hr)	Amt. of zeolite seeds added to SBA-15 mixture (g)	Surface area (m ² /g)	*Unit cell size a ₀ (nm)	#BJH Pore size (nm)	**Wall thickness (nm)	Pore volume (cm ³ /g)	Percent Al in calcined products
SBA-15	n/a	none	828	11.0	7.5	3.5	0.83	none
Al-SBA15A	6	0.5	700	12.3	5.9	-	0.60-	0.50
Al-SBA15B	6	1.5	798	11.0	5.8	5.2	1.03	1.20
Al-SBA15C	10	0.5	839	11.0	5.6	5.4	0.87	0.48
Al-SBA15D	10	1.5	689	11.3	6.2	4.9	0.81	1.10
Al-SBA15E	10	3.0	690	11.5	6.9	4.9	0.75	2.10
Al-SBA15F	24	1.5	836	12.5	6.1	5.3	0.74	1.20
Al-SBA15G	24	3.0	728	11.3	7.5	4.3	0.96	2.10
Zeolite Y	72	none	400	nd	n/a	nd	0.43	4.75

* $a_0 = 2 \times d(100)/\sqrt{3}$, ** Wall thickness = $a_0 - \text{pore size}$. #Pore size was calculated from the adsorption branch of the isotherms.

No correlation was observed between the amounts of seed precursor added and the pore sizes or wall thicknesses of the resulting mesostructures within the range investigated. Pore sizes ranged between 5.6 and 7.5 nm and were close to the value observed for the parent SBA-15. Pore wall thickness in the samples ranged between 4.3 and 5.4 nm which are also close to the value observed above and reported for the parent SBA-15.¹⁸ The sizes of subunits in zeolite precursors are reported to be in the range of 1-3 nm. It is therefore conceivable that these subunits can be accommodated within the SBA-15 porewalls of the dimensions observed.²⁵⁻²⁷

Figure 4 shows IR adsorption spectra of SBA-15 treated with 3 g of zeolite precursor, a parent “all-silica” SBA-15, and zeolite Y nanoparticles obtained from precursor crystallized for 3 days at 100°C. A band at 470 cm^{-1} is present in all three samples, and is assigned to the structure insensitive T-O bending modes for tetrahedral TO_4 units ($\text{T} = \text{Si}$ or Al).²⁸ The IR band observed at 570 cm^{-1} in the spectrum of zeolite Y nanoparticles is attributed to the double six membered rings associated with the FAU structure.²⁹ This band is absent from both the parent and the precursor treated SBA-15 materials, suggesting the absence of the double ring, and hence further suggesting the absence of fully formed zeolite Y crystals within the bulk phase of the precursor-derived SBA-15 products. This implies that any zeolitic precursor species present in the mesostructures must be in the form of the zeolite subunits.

Fig. 4. FTIR spectra of (a) zeolite Y nanoparticles, (b) Al-SBA-15 from 3.0 g zeolite precursor added, and (c) all-silica SBA-15

Fig. 5. Al content in SBA-15 mesostructures vs amount of zeolite precursor added.

Aluminum analysis was conducted to investigate the relationship between the amount of precursor added, or the precursor aging time, and the Al content of the Al-SBA-15 products. The aluminum content in the products remained constant regardless of the zeolite Y aging time. For example, product obtained from the addition of 1.5 g of zeolite seed that was aged for 6, 10 and 24 hr showed 1.2, 1.1 and 1.2 %Al, respectively (Table 1). The Al content in the product was directly proportional to the amount of seeds added from 0.5 to 3.0 gm, for all aging time of the latter (Table 1 and Figure 5).

The coordination environment of Al in the calcined mesostructures was determined by ^{27}Al SS MAS/NMR. Figures 6A shows a single peak at 55 ppm in each spectrum of SBA-15 containing zeolite precursor that was aged for 6, 10, and 24 hr. This peak is assigned to tetrahedrally coordinated Al, thus demonstrating that the zeolitic connectivity that was formed in the precursor

has survived the mildly acidic synthesis condition, as well as the high temperature calcination. The absence of an NMR peak at 0 ppm indicates the nonexistence of octahedral coordinated Al. As expected, the spectrum of all-silica SBA-15 (Figures 6A(a)) shows no peaks.

Fig. 6A. ^{27}Al MAS NMR spectrum of a) pure SBA-15, and Al-SBA-15 from 3 g of zeolite precursor added after aging for (b) 6, (c) 10, and (d) 24 hr at 100°C.

Al-SBA-15 samples from zeolite precursor that was aged for 10 hr at 100°C, shows a single peak at 55 ppm in the ^{27}Al NMR spectrum that is assigned to tetrahedrally coordinated Al, the peak height of which increased with increase in the amount of seed added (Figure 6B). A similar

situation was observed for the sample synthesized in the presence of precursor that was aged for 24 hr.

Fig. 6B. ^{27}Al MAS NMR spectra of Al-SBA-15 with varying amounts of 100°C, 10 hr-aged zeolite precursor added. (a) 0.5, b) 1.5, and, c) 3.0 g.

The remarkable stability of Al in tetrahedral coordination during calcination is unprecedented. In previously reported cases by other researchers, some significant quantities of Al is observed to occupy octahedral arrangement either before or after thermal treatment.⁵⁷ Reasons for this could be due to the this use of TEOS rather than sodium silicate as the source of silica for both the precursor and for SBA-15 syntheses. In addition, aluminum isopropoxide, rather than sodium aluminate was the aluminum source. It is plausible therefore, that similar hydrolysis and condensation rates of the silicate and aluminate species from these sources could result in very

homogeneous distribution of the aluminosilicates bonds within the porewalls, hence stabilizing the Al in tetrahedral coordination.

The nature of the acid sites in a representative seeds-treated SBA-15 was evaluated from the IR spectrum after pyridine was adsorbed on the surface. Figure 7 shows the IR spectrum of a sample that was synthesized with 3 g of zeolite precursor added to the mixture. Strong absorbance bands were observed for Brønsted acid sites-bound pyridine at 1545 cm^{-1} , and Lewis sites-bound pyridine at 1448 cm^{-1} . The peak at 1494 cm^{-1} is assigned to pyridine associated with both Brønsted and Lewis acidic sites. These peaks were absent in SBA-15. The origin of Lewis acid site(s) is unclear but is commonly observed in fully crystalline zeolite Y and other zeolites.³⁰

Fig. 7. FTIR spectrum of pyridine adsorbed on a) zeolite seeds treated SBA-15, b) all silica SBA-15.

The relative strength of acid sites of zeolite precursor derived Al-SBA-15 was compared with the parent “all-silica” SBA-15, and a physical mixture of the parent “all-silica” SBA-15 and commercial zeolite Y using NH_3 -TPD measurements (Figure 8). The precursor derived Al-SBA-15 and physically mixed composite both showed ammonia desorption maxima at 350°C which is consistent with the presence of strong Brønsted acid sites.¹⁴ The desorption maximum occurs at higher temperature than that reported for Al-MCM-41(320°C).¹⁴ The NH_3 -TPD profile of the pure SBA-15 as expected, shows significantly less response, which is indicative of little or no acidic sites present.

Fig. 8. NH_3 -TPD profile of (a) physically mixture of commercial zeolite Y plus SBA-15, (b) Precursor derived Al-SBA-15 (3 g of zeolite precursor), and (c) All silica SBA-15.

Catalysis: Precursor derived Al-SBA-15 samples were evaluated for the dealkylation of cumene. The products, benzene and propene, were identified by GC/MS. Figure 9 shows the percent conversion of cumene on various Al- SBA-15 samples. An increase in the percentage cumene conversion with increase in amount of “6 hr-aged” precursor added was observed. Initial catalytic activity ranged from ~10-15% for sample with 0.5 g precursor added, to 30% for sample with 1.5 g precursor added, to ~ 40-60% for sample with 3.0 g precursor added after 30 min on stream. For catalyst showing 30% conversion, the activity remained constant for 12 hr. For catalyst showing 60% conversion, rapid decline in catalytic activity was observed. This is possibly due to the presence of larger percentage of acidic sites resulting in higher catalytic activity, and more rapid generation of deactivating species. Similar trends were observed for Al-SBA-15 products derived from the precursor that was aged at 100°C for 10 hr and 24 hr (Figure 10). No catalytic activity was observed with the all-silica SBA-15 which is consistent with the absence of Brønsted acid sites.

Fig. 9. Cumene conversion vs time on Al-SBA-15 derived from different weights of “6 hr-aged” zeolite precursor; a) 0.5, b) 1.5, and c) 3.0 g of precursor.

The catalytic conversion results are consistent with the chemical analysis and the NMR results and confirms that catalysts that were synthesized with increasing amount of zeolite precursor posses larger amounts tetrahedral Al that are suitably positioned to generate higher concentrations of Brönsted acidic sites.

Fig. 10. Cumene conversion vs time on Al-SBA-15 synthesized with the addition of a) 0.5g, b) 1.5g, and c) 3.0 g of zeolite Y precursor that was heated for 24 hr at 100°C.

The rate of cumene conversion with temperature on SBA-15 was compared with a sample pure proton exchanged zeolite Y nanoparticles of 400 cm²/g surface area, and 0.43 cm³/g pore volume that was synthesized by allowing the zeolite mixture to crystallize for 3 days (Table 1). The catalytic activity of Al-SBA-15 after 15 min on stream was higher than that of zeolite Y at all temperatures investigated (Figure 11). The Al-SBA-15 evaluated contained 2 wt %Al, which is less than half of that of the zeolite Y (5 wt %Al). Its higher activity therefore suggests the

presence of stronger acid sites within the former. This is not unusual since it is standard practice to dealuminate zeolite Y in order to increase acid strength.

Fig.11. Cumene conversion at various reaction temperatures on Al-SBA-15 (□) and zeolite Y nanoparticles of 40 nm size and 4.7 % Al (●).

VII CONCLUSIONS

Al-SBA-15 mesoporous catalysts with Brönsted acid sites and Al in totally tetrahedral coordination were synthesized from the addition of zeolite Y precursor to SBA-15 synthesis mixture under a mild acidic condition of pH 5.5. Pore sizes of the products ranged from 5.6 to 7.5 nm, surface areas ranged between 690 and 850 m²/g, and pore volumes were up to 1.03 cm³, which are all comparable to the parent all-silica SBA-15 synthesized under similar conditions. Up to the 2 wt % Al was present in the most aluminated sample that was investigated, and all Al

remained stable in totally tetrahedral coordination, even after calcination at 550° C. Brønsted and Lewis acid sites are both present in the Al-BSA-15 products, which showed significant catalytic activities for the dealkylation of cumene to form benzene and propene. The catalytic activity increased as the amount of zeolite precursor added to the SBA-15 mixture was increased, and was not affected by the aging time of the precursor up to the 24 hr. This method of introducing Al and maintaining Al in a total tetrahedral coordination is very effective in comparison to other direct and post synthesis aluminations reported. Studies are underway to evaluate the nature of the zeolite Y precursor, to further characterize and locate the acid sites in the composites, and to investigate the catalysts' performance in the conversion of heavy petroleum gas oil.

VIII FUTURE WORK

Studies are underway to evaluate the nature of the zeolite Y precursor, to further characterize and locate the acid sites in the composites, and to investigate the catalysts' performance in the conversion of heavy petroleum gas oil. First the catalysts will be formed into pellets by combining portions of the Al-SBA-15 catalysts with pseudoboemite Catapal B alumina and kneading the mixture with the addition of acid. The paste will be extruded using a garlic press and the extrudates will be dried and calcined. Ni and Mo will be impregnated and the catalysts recalcined. The catalytic reactor will be a 500 ml batch high temperature high pressure Parr autoclave shown below in Figure 11. The catalysts will first be sulfided with 5% H₂S. The gas oil feedstock to be tested is metal free, low sulfur gas oil containing 79% heavy fraction. Reaction conditions will be 400-500°C and 5.5 MPa H₂ pressure. 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 catalysts concentration on conversion and products distribution will be assessed.

IX TECHNOLOGY/INFORMATION TRANSFER

Students:

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

Tefa 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. Submitted to *Journal of Porous Materials*, June 2006.
- 2) "On the Incorporation of Tetrahedral Aluminum in SBA-15 from Zeolitic Seeds" Conrad W. Ingram, Yohannes Ghirmazion and Tesfa Mehreteab accepted for presentation 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, Pennsylvania.
- 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 Pacificchem 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 II 57th Southeast / 61st Southwest, Joint Regional Meeting of the American Chemical Society, November 1 - 4, 2005, Memphis, Tennessee.
- 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, presented 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 Nonionic 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, presented 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.

X REFERENCES

-
- 1 D. Zhou, J. Feng, Q.Hou, N. Melosh, G. Frederickson, B. Chmelka, and G. Stucky, *Science*, **279**, 549(1998).

-
- 2 E. L. Byambajav, and Y. Ohtsuka,. *Applied Catalysis, A: General*, **252** (1), 193-204, (2003).
 - 3 G. Kumaran, G. Muthu; S.I. Shelu, K. Kapil; K.S. Manoj; S., G. Dhar, R. K. Murali; and S. Rama,. *Applied Catalysis, A: General*, **305** (2), 123-129 (2006).
 - 4 C. T. Kresge, M.E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, *Nature*, **359**, 710-712 (1992).
 - 5 R. Mokaya. in Nanoporous Materials Science and Engineering, edited by G. Q. Lu, and X.S. Zhao (Imperial College Press, London, 2004), p.427-463.
 - 6 Y. H Yue, A Gedeon, J. L. Bonardet, N. Melosh, J. B D'Espinose, and J. Fraissard, *Chemical Communications*, 1967–1968 (1999)
 - 7 S. Sadanobu, O. Yasunori, U. Toshiya, and S. Tsuneji, *Journal of Materials Chemistry*, **11**, 1111–1115, (2001)
 - 8 D. T. On and S. Kaliaguine, *Angewandte Chemie International Edition*, **41**, 1036-1040 (2002).
 - 9 Y. Liu, W. Zhang and T. J. Pinnavaia, *Journal of the American Chemical Society*, **122**, 8791-8792 (2000).
 - 10 J. Agundez, I. Diaz, C. Marquez-Alvarez, E. Sastre, and J. Perez-Pariente, *Studies in Surface Science and Catalysis*, **142**, 1267-1274 (2002).
 - 11 J. Agundez, I. Diaz, C. Marquez-Alvarez, J. Perez-Pariente, E. Sastre, *Chemical Communications*, 150-151(2003).
 - 12 Y. Liu, W. Zhang, and T. J. Pinnavaia, *Angewandte Chemie International Edition*, **40**, 1255 (2001).
 - 13 Z. Zhang, Y. Han, L. Zhu, R. Wang, Y. Yu., S. Qiu., D. Zhao, and F. S. Xiao, *Angewandte Chemie International Edition*, **40**, 1258-1262 (2001).
 - 14 Z. T. Zhang, Y. Han, F.-S. Xiao, S. L. Qiu, L. Zhu, R. W.Wang, Y. Yu, Z Zhang, B.S. Zou, Y.Q. Wang, H.P. Sun, and D. Zhao, Y.Wei, Y. *Journal of the American Chemical Society*, **123**, 5014 (2001).
 - 15 F.-S.Xiao, Y. Han, Y. Yu, X. Meng, M. Yang, and S. Wu, *Journal of the American Chemical Society*, **124**, 888-889 (2002).
 - 16 H. Wang, Y. Liu, and T. J. Pinnavaia, *Journal of Physical Chemistry, B*, **110**, 4524-4526, (2006)
 - 17 Y. Liu and T. J. Pinnavaia, *Journal of Materials Chemistry*, **14** (7),1099-1103 (2004).

-
- 18 Y. Liu, T. Thomas, *Chemistry of Materials*, **14**, 3-5 (2002).
 - 19 Y. Han, N. Li, L. Zhao, D. Li, X. Xu, S. Wu, Y. Di, C. Li, Y. Zou, Y. Yu, and F.-S. Zhao, *Journal of Physical Chemistry, B*, **197**, 7551 (2003).
 - 20 J. Liu, X. Zhang, Y. Han, and F.-S. Xiao, *Chemistry of Materials*, **14**, 2536. (2002)
 - 21 C. Shane Carr, S. Kasfel, D. F. Shantz, *Chemistry of Materials*, **16**, 3139-3146 (2004).
 - 22 S. Zheng, D. Zhai, Y. Wu, and Y. Sun, *Journal of Solid State Chemistry*, 1630-1636 (2005)
 - 23 P. Y. Sun, Y. Yan, *Journal of Materials Chemistry, B*, **7**, 8153-1857 (2003).
 - 24 D. Ginter in *Verified Synthesis of Zeolitic Materials*, edited by H. Robson, (Elsevier: Amsterdam, 2001), p 156.
 - 25 A. E. Pearson, B. J. Schoeman, J. Sterte, J. E. Otterstedt, *Zeolites*, **14**, 557-567 (1994).
 - 26 P.P.E.A. de Moor, T. P.M Beelen, B. U. Komanschek, L. W. Beck, P. Wagner, M. E. Davis, R. A. van Santen, *Chemistry A European Journal*, **5**, 2083-2088 (1999).
 - 27 C. T. G. Knight and S. D. Kinrade, *Journal of Materials Chemistry, B* **106**, 3329-3332. (2002)
 - 28 D. W. Breck, *Zeolite Molecular Sieves*; (Wiley, New York 1974) p152.
 - 29 P.A. Jacobs, P.A., E.G. Derouane, and J. Weikamp, *Chemical Communication*, 91 (1981).
 - 30 A. Corma, *Chemical Reviews*, **95**, 559-614 (1995)