

TOWARDS A NEW CLASS OF MESOPOROUS MATERIALS FOR
APPLICATIONS IN PETROLEUM REFINING

FOURTH ANNUAL TECHNICAL PROGRESS REPORT

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I. ABSTRACT

This project focuses on the synthesis of mesoporous aluminophosphates, silicates and aluminosilicates as catalysts for applications in the conversion of large petroleum feedstock compounds to useful middle distillates and naphtha transportation fuels. Summarized herein is our research progress from September 1, 2003, to August 31, 2004. In previous reports it was demonstrated that mesoporous aluminophosphates with neutral framework (containing Al, P and O) could be synthesized, but their thermal stabilities were limited. In general, the materials' pore structure collapsed when calcined at 500-550°C in air or extracted in ethanol/HCl mixture to remove the surfactants, which were used as synthesis templates. New methods to improve the thermal stability of the materials needed to be explored. It was conceived that by adding divalent metals cations, such as Mg and Co, not only that the acid sites would be created by balancing the negatively charged framework (balanced by H^+), but the thermal stability of the materials would be improved. In addition, methods to facilitate the interaction of hydrocarbon substrates with acid sites within the mesoporous are also needed. One concept towards improving this was to incorporate organic functional groups within or attached to the otherwise purely inorganic aluminophosphate (containing Co or Mg) or aluminosilicate pore walls of the mesopores. In the last report we detailed that mesoporous organosilicates were synthesized using block copolymer under acid conditions containing silica and phenylene ($-C_6H_4-$). Materials prepared with phenylene group among the silica pore walls was found to be thermally stable up to 550 C which is almost 100°C higher than the temperature used for the mild hydrocracking of petroleum. It was also highlighted that this area was the subject of recent intense research activities by other researchers.

Building on precedence of the last report and on the results of other researchers, we investigated the synthesis of a wide range of mesoporous silicates containing different organic functionalities within the pore walls (using $-CH_2CH_2-$), simultaneously combined with additional organic functional groups extended within the mesopores and grafted through silicate linkages to the pore walls (including $(SiO)_3-CH_nSH$, $(SiO)_3-CH_nNH$ $(SiO)_3-CH_nIM$ and $(SiO)_3-CH_nC_6H_4$, X is imidazole) for use as potential acid catalysts in petroleum upgrading. Based on modifications to published procedures, we synthesized organic functionalized mesoporous organosilicates described above with surface area greater than 700 m^2/g , pore volume $> 0.73 cm^3$. The materials were stable to ethanolic extraction, but showed various degrees of thermal stability depending on the nature of the organic groups attached. We also investigated the synthesis of a wide range of mesoporous aluminophosphate containing Mg and Co in the matrix. Synthesis was also conducted on organic functionalized aluminophosphates containing similar organic functionalities described above. Syntheses of the phosphates was conducted in basic conditions with cationic surfactant, namely $C_{16}H_{33}N(CH_3)Cl$ as templates. However, the structure of all the aluminophosphates appear to collapse when the template was removed by extraction or calcination.

The catalytic testing phase of the project has commenced with the assembly of a micro-reactor interfaced with a gas chromatograph. Further research will be focused on use the micro-reactor to evaluate those potential mesoporous aluminosilicate and aluminophosphate catalyst materials which has maintained some stability, as detailed in this and previous reports, and will also be focused on investigating alternative synthesis approach to strengthen the thermal stability of the aluminophosphates.

II. DISCLAIMER

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Table of Contents

	Page No.
I ABSTRACT	2
II DISCLAIMER	3
III EXECUTIVE SUMMARY	5
IV INTRODUCTION	6
V RESEARCH PROGRESS	7
V-1 Mesoporous organosilicates	7
V-1-1 Synthesis of mesoporous organosilicates	7
V-1-2 Characterization	8
V-1-3 Results and Discussion	8
V-2 Mesoporous aluminophosphates and organoaluminophosphates	14
V-2-1 Synthesis of mesoporous aluminophosphates aluminosilicates under basic conditions using cationic surfactants	14
V-3 Research Progress on Catalysis	17
VI CONCLUSIONS	CAPut!
VII FUTURE WORK	CAPut!
VIII TECHNOLOGY/INFORMATION TRANSFER	CAPut!
IX REFERENCES	20

III EXECUTIVE SUMMARY

This project focuses on the synthesis of mesoporous aluminophosphates, silicates and aluminosilicates as catalysts for applications in the conversion of large petroleum feedstock compounds to useful middle distillates and naphtha transportation fuels. In previous reports it was demonstrated that mesoporous aluminophosphates with neutral framework (containing Al, P and O) could be synthesized, but their thermal stabilities were limited. In general, the materials' pore structure collapsed when calcined at 500-550°C in air or extracted in ethanol/HCl mixture to remove the surfactants which were used as synthesis templates. New methods to improve the thermal stability of the materials needed to be explored. It was conceived that by adding divalent metals cations, such as Mg and Co, not only that the acid sites would be created by balancing the negatively charged framework (balanced by H⁺), but the thermal stability of the materials would be improved. In addition, methods to facilitate the interaction of hydrocarbon substrates with acid sites within the mesoporous are also needed. One concept towards improving this was to incorporate organic functional groups within or attached to the otherwise purely inorganic aluminophosphate (containing Co or Mg) or aluminosilicate pore walls. In the last report we detailed that mesoporous organosilicates were synthesized using block copolymer under acid conditions containing silica and phenylene (-C₆H₄-). Materials prepared with phenylene group among the silica pore walls was found to be thermally stable up to 550 C which is almost 100°C higher than the temperature used for the mild hydrocracking of petroleum. It was also highlighted that this area was the subject of recent intense research activities by other researchers.

Building on precedence of the last report and on the results of other researchers, we investigated the synthesis of a wide range of mesoporous silicates containing different organic functionalities within the pore walls (using -CH₂CH₂-), simultaneously combined with additional organic functional groups extended within the mesopores and grafted through silicate linkages to the pore walls (including (SiO)₃-CH_nSH, (SiO)₃-CH_nNH (SiO)₃-CH_nIM and (SiO)₃-CH_nC₆H₄, X is imidazole) for use as potential acid catalysts in petroleum upgrading. Based on modifications to published procedures, we synthesized organic functionalized mesoporous organosilicates described above with surface area greater than 700 m²/g, pore volume > 0.73 cm³. The materials were stable to ethanolic extraction, but showed various degrees of thermal stability depending on the nature of the organic groups attached. We also investigated the synthesis of a wide range of mesoporous aluminophosphate containing Mg and Co in the matrix. Synthesis was also conducted on organic functionalized aluminophosphates containing similar organic functionalities described above. Syntheses of the phosphates we conducted in basic conditions with cationic surfactant, namely C₁₆H₃₃N(CH₃)Cl as templates. The structure of all the aluminophosphates appear to collapse when the template was removed by extraction or calcinations. The catalytic testing phase of the project has commenced with the assembly of a micro-reactor interfaced with a gas chromatograph. Further research will be focused on use the micro-reactor to evaluate those potential catalysts materials which has maintained some stability, as detailed in this and previous reports and will also be focused on investigating alternative synthesis approach to strengthen the thermal stability of the aluminophosphates.

IV INTRODUCTION

This project focuses on the synthesis of mesoporous aluminophosphates, silicates and aluminosilicates as catalysts for applications in the conversion of large petroleum feedstock compounds to useful middle distillates and naphtha transportation fuels. In previous reports it was demonstrated that mesoporous aluminophosphates with neutral framework (containing Al, P and O) could be synthesized, but their thermal stabilities were limited. In general, the materials' pore structure collapsed when calcined at 500-550°C in air or extracted in ethanol/HCl mixture to remove the surfactants which was used as synthesis templates. New methods to improve the thermal stability of the materials needed to be explored. It was conceived that by adding divalent metals cations, such as Mg and Co, not only that the acid sites would be created by balancing the negatively charged framework (balanced by H⁺), but the thermal stability of the materials would be improved.

In addition, methods to facilitate the interaction of hydrocarbon substrates with acid sites within the mesoporous is also needed. One concept towards improving this was to incorporate organic functional groups within or attached to the otherwise purely inorganic aluminophosphate (containing Co or Mg) or aluminosilicate pore walls. In the last report we detailed that mesoporous organosilicates were synthesized using block copolymer under acid conditions containing silica and phenylene (-C₆H₄-). Materials prepared with phenylene group among the silica pore walls was found to be thermally stable up to 550 C which is almost 100°C higher than the temperature used for the mild hydrocracking of petroleum. It was also highlighted that this area was the subject of recent intense research activities by other researchers.

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investigated the synthesis of a wide range of mesoporous organic functionalized aluminophosphates containing similar organic functionalities for use as potential acid catalysts in petroleum upgrading. Syntheses were also conducted in basic conditions with cationic surfactant, namely $C_{16}H_{33}N(CH_3)Cl$ as templates.

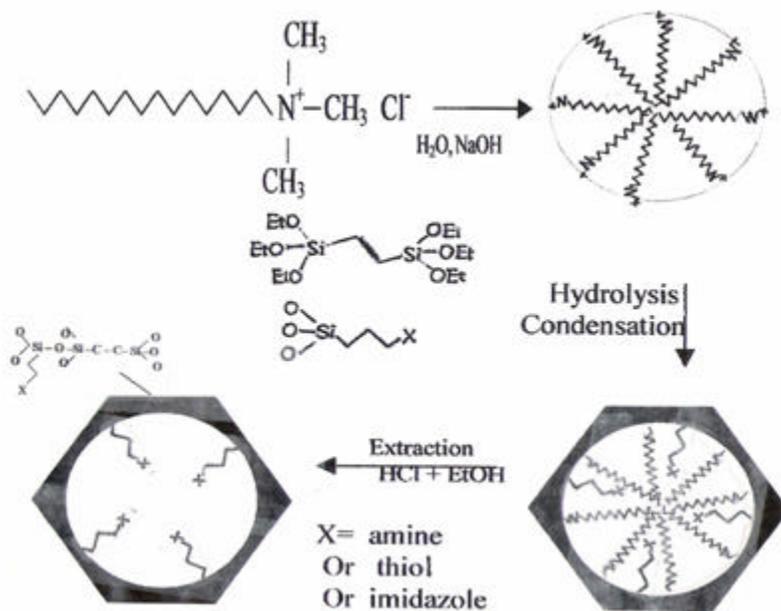


Figure 1. Illustrating synthesis of mesoporous organosilicate containing dual organic functionalities

V RESEARCH PROGRESS

V-1 Mesoporous organosilicates

V-1-1 Synthesis of mesoporous organosilicates

Cationic Surfactants cetyltrimethylammonium chloride formed micelles in basic solution, the hydrolysis and condensation of BTSE (bis tri ethoxy silyl ethane) and functional siloxane formed the walls of the mesoporous structure. After ethanolic extraction, the surfactant is removed, and the mesoporous organosilicates with two functional organic groups result with the precursor $-Si-CH_2-Si-$ in the wall, and functional siloxane, one side with siloxane group attached to the pore wall through $Si-O$ bond, and the other side with organic functional group extended into the pore. Four organosilicates were synthesized based upon modification to published procedures and with reaction mixtures of molar compositions and synthesis conditions shown in Table 1.

Table 1. Synthesis Conditions for Organosilicates

Material	Organic	Molar composition
CB	1. BTSE (1,2-Bistrimethoxysilylethane)	0.12 CTAC: 1.0BTSE: 1.0 NaOH:230 H ₂ O
CBNH	1. BTSE 2. (3-aminopropyl-triethoxysilane)	0.12 CTAC: 0.75BTSE: 0.25NH ₂ (CH ₃) ₃ Si(OC ₂ H ₅) ₃ :1.0 NaOH:230 H ₂ O
CBIM	1. BTSE 2. (n-(3-triethoxysilylpropyl)-4,5-dihydroimidazole)	0.12 CTAC: 0.75BTSE: 0.25N ₂ CH ₅ (CH ₃) ₃ Si(OC ₂ H ₅) ₃ :1.0 NaOH:230 H ₂ O
CBSH	1. BTSE 2. (3-mercaptopropyltriethoxysilane)	0.12 CTAC: 0.75BTSE: 0.25SH(CH ₃) ₃ Si(OC ₂ H ₅) ₃ :1.0 NaOH:230 H ₂ O
MCM-41	None (Si from Tetraethylorthosilicate)	5.4 CTABr: 10SiO ₂ : 4.25 Na ₂ O: 1.3H ₂ SO ₄ : 480 H ₂ O

Surfactant: Cetyltrimethyl ammonium cationic surfactant (CTAC) - C₁₆H₃₃N(CH₃)₃Cl

Synthesis Conditions: 308K for 12 h; Post synthesis treatment: ethanol/acid 343K for 6 h

V-1-2 Characterization

Powdered X-ray diffraction (XRD) patterns were recorded on a Phillips X'Pert diffractometer equipped with curved Cu Monochromator and Cu K x radiation source as detailed in Report No. 3. Multipoint Brauner-Emmett-Teller (BET) surface area was measured with a micromeritics Gemini 2360 surface area analyzer. Adsorption-desorption isotherms were measured at 77K using a micromeritics ASAP 2020 system and nitrogen as the adsorbate per procedure detailed in report No.2. Transmission Electron micrographs were recorded on a 200 kev TEM instrument.

V-1-3 Results and Discussion

XRD analysis: Figures 2A-D shows XRD patterns of mesoporous organosilicates synthesized according to Table 1. Characteristic low angle diffraction peaks were observed in all samples. Peaks were broad thus indicating a high degree of disorder in the mesopores

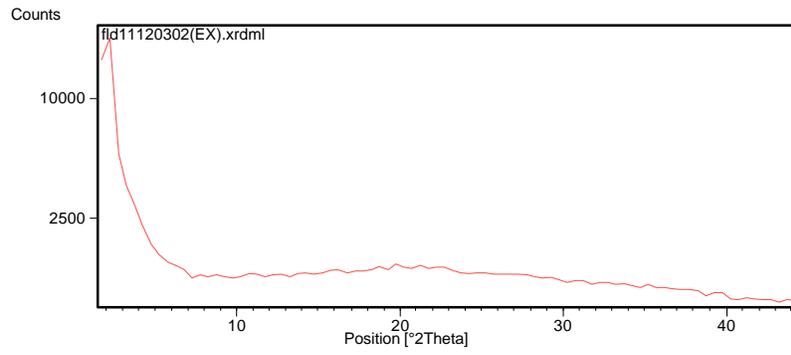


Figure 2A. XRD pattern of CB

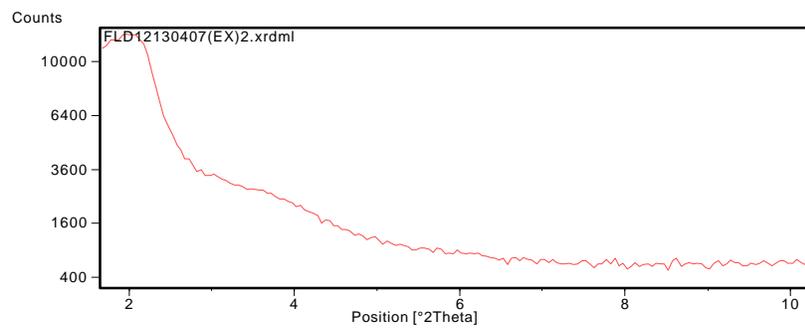


Figure 2B. XRD pattern of CBNH

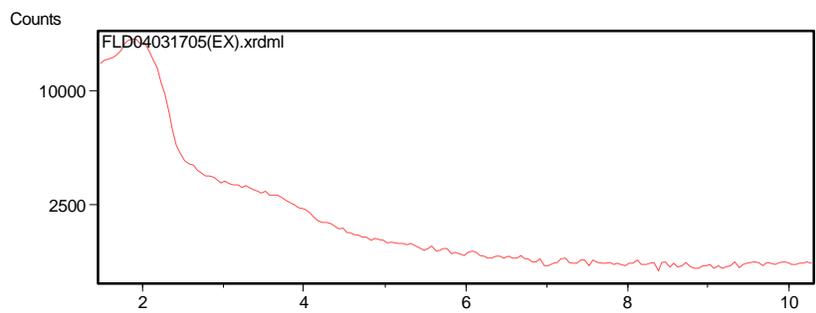


Figure 2C. XRD pattern of CBSH

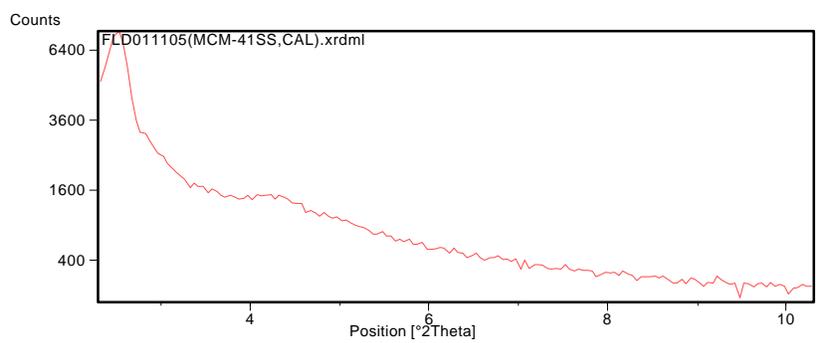


Figure 2C. XRD pattern of CBIM

Adsorption isotherms: Figures 3A-D shows nitrogen adsorption isotherms of the extracted samples. All samples show inflection point at relative pressure of P/P_0 between 0.2 to 0.4. The extracted materials show high pore volumes and high surface areas, characteristic of their all-silica parent, MCM-41 (Table 2).

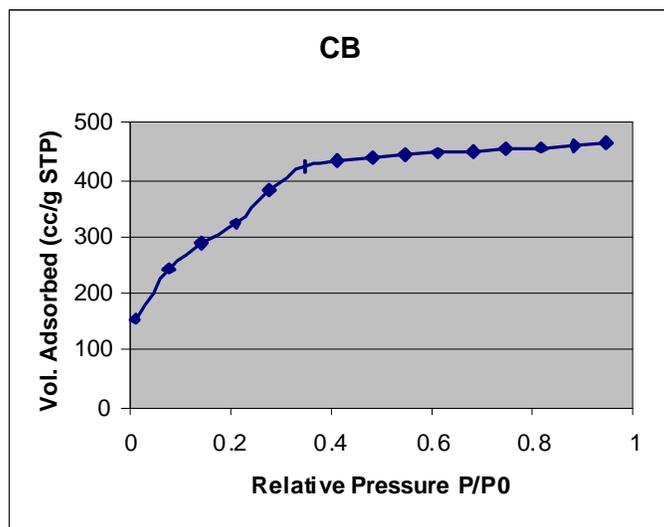


Figure 3A. N₂ Adsorption Isotherm of CB

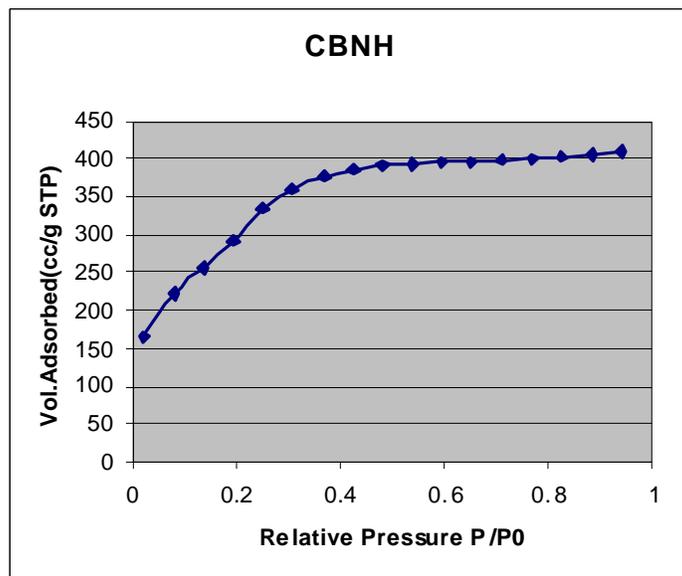


Figure 3B. N₂ Adsorption Isotherm of CBNH

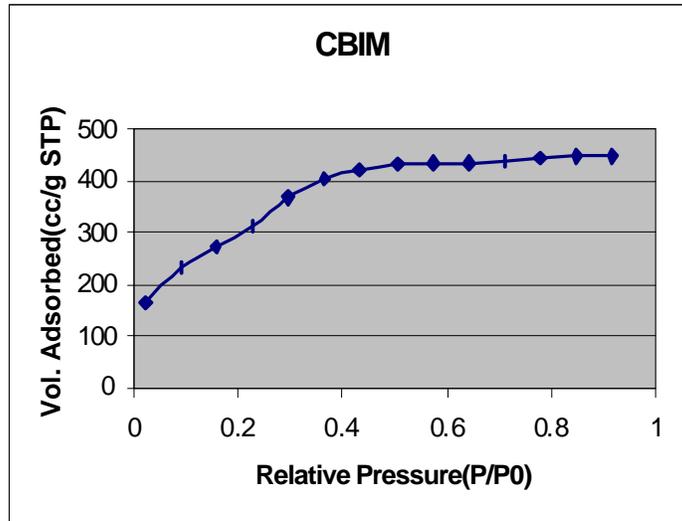


Figure 3C. N₂ Absorption Isotherm of CBIM

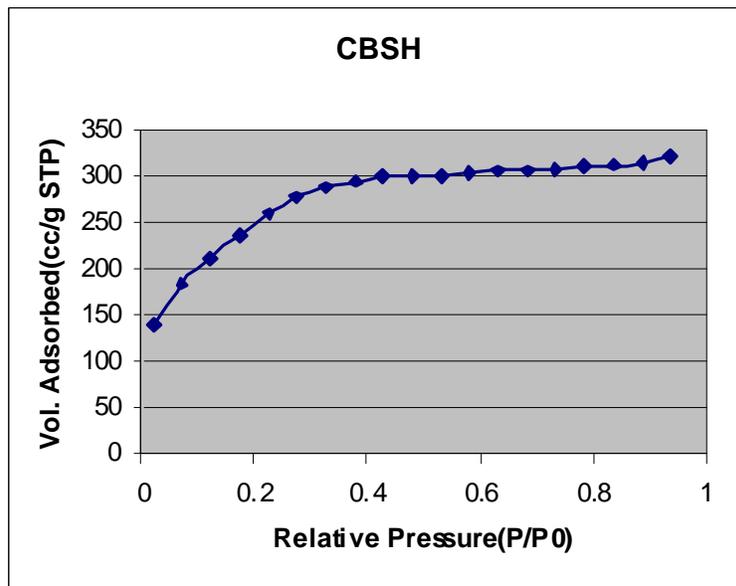


Figure 3C. N₂ Absorption Isotherm of CBSH

Table 4. Surface Area and Total Pore Vol. of the Materials

Materials	Surface Area (m²/g)	Total Pore Vol.(cc/g)
CB	1332	0.73
CBNH	1248	0.78
CBSH	928	0.50
CBIM	1002	1.12
MCM-41	1756	0.96

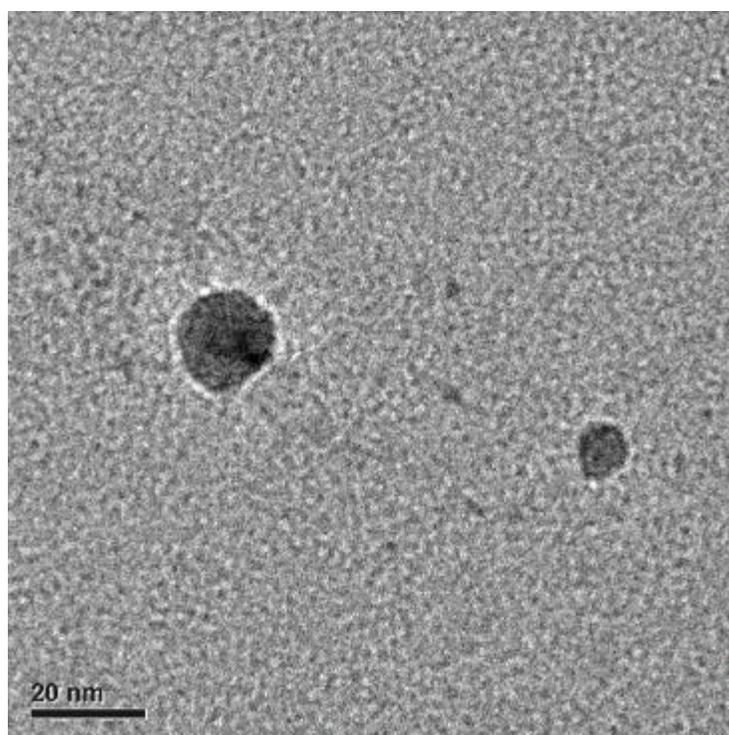


Figure 4. High Resolution Transmission Electron Micrograph of a Typical Mesoporous Organosilicate Synthesize Above

TEM and TGA: The organosilicate samples also showed pore size of approximately 2 nm which was estimated from transmission electron micrograph (Figure 4), and is typical of their all-silica parent MCM-41. The onset of decomposition of the organic groups or residual template in the samples appears to commence around 200 C based on thermal analysis. The decomposition temperature appears to depend on the type of organic functionality grafted to the pore wall. The

nature of the decomposing species (organic functional groups vs residual template) needs to be delineated in further experiments.

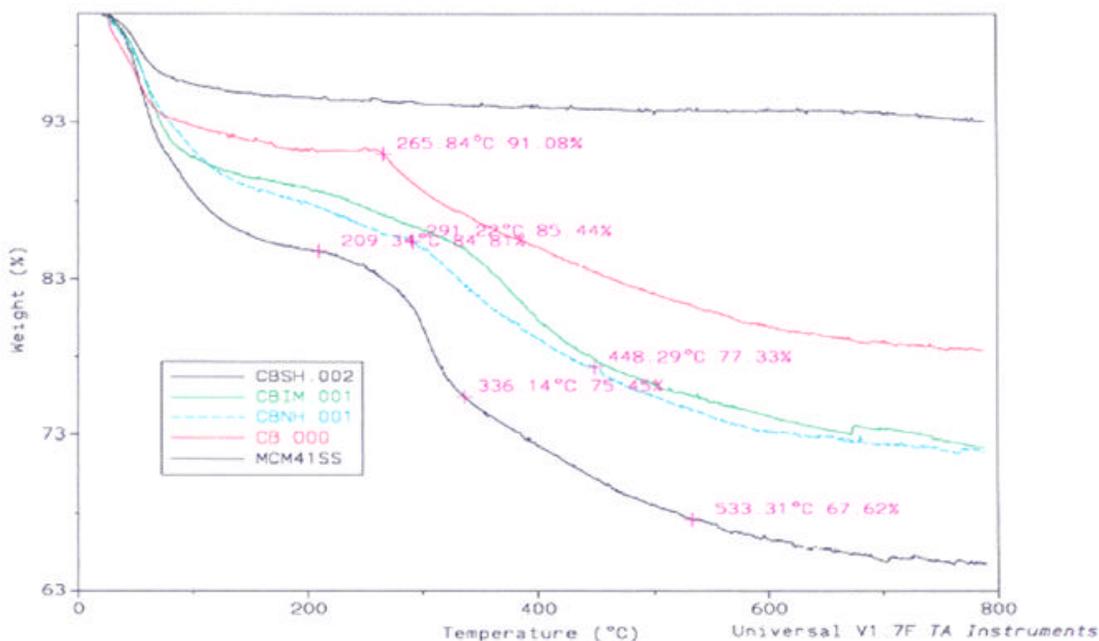


Figure 5. Thermogravimetric Analysis of Mesoporous Organosilicates

V-2 Mesoporous aluminophosphates and organoaluminophosphates

V-2-1 Synthesis of mesoporous aluminophosphates aluminosilicates under basic conditions using cationic surfactants

Experimental: An aliquot of 0.46g $\text{Al}(\text{OH})_3 \cdot x\text{H}_2\text{O}$ was added slowly to a solution A (containing 2.5 ml phosphoric acid dispersed in 25 g water) under stirring for 3 h. The mixture was then combined with solution B (containing 4.04 g CTABr and 30 ml water) and stirred another 3 h. A solution of metal salt was then added into the above mixture. Appropriate amounts of TMAOH were added slowly to above mixture until appropriate pH value was attained. The resulting mixture was stirred for 72 h at room temperature. The white precipitate was recovered by filtration, washed with distilled water, dried in an oven. Finally, the material was calcined in a

muffle furnace at 773K for 10 h. To synthesize mesoporous organo alumiophosphate, reaction conditions were similar to above, except that BTSE (bis tri ethoxy silyl ethane) was added.

Results and Discussion: X-ray patterns of AlPO, MgAPO and CoAPO samples indicated low-angle but broad peaks at 2θ of approximately 2° , which are characteristic of mesoporous materials that are reportedly synthesized under similar conditions (Figure 6A-C). The presence of Mg and Co within the porewalls will be characterized by elemental analysis. In the case of Co, efforts will be made to characterize the Co by XPS. To remove the organic template from the pores, both extraction in ethanol/HCl solution or calcination at 550°C were attempted. From XRD results (not shown) it was observed that in most cases the low angle peak was absent in the calcined or extracted materials, this suggesting that the materials were unstable when the templates are removed.

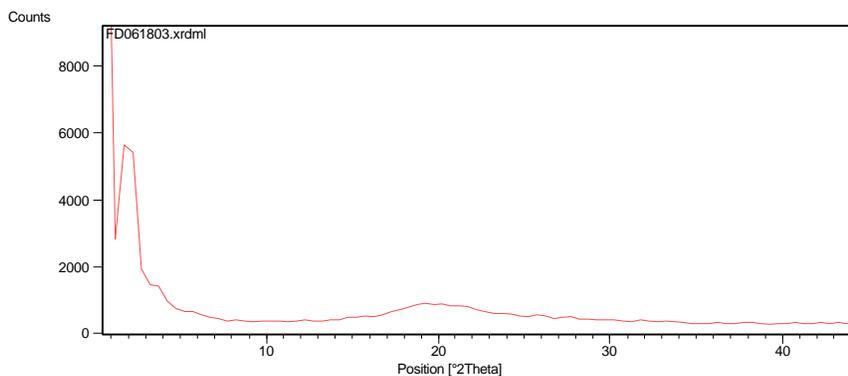


Figure 6A. XRD Pattern of AlPO synthesized at pH 9.55

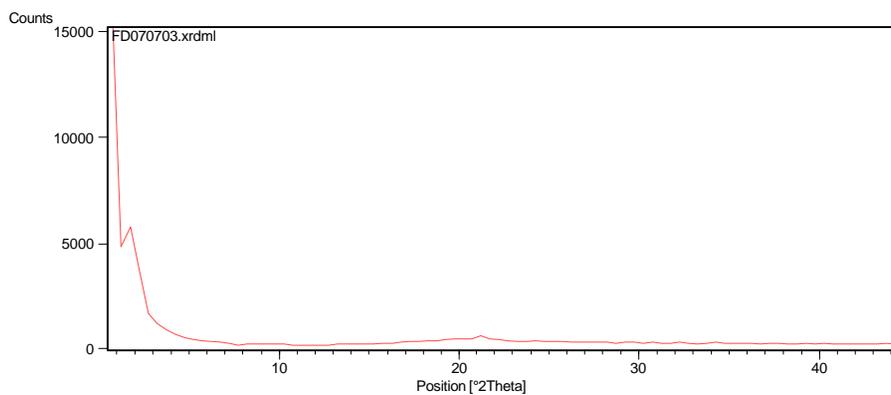


Figure 6B. XRD Pattern of CoAPO synthesized at pH 10.16

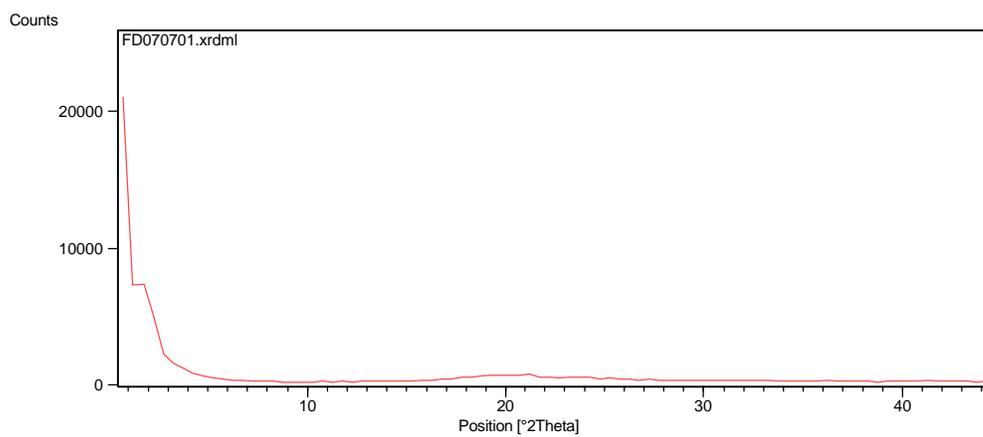


Figure 6C XRD Pattern of MgAPO synthesized at pH 10.11

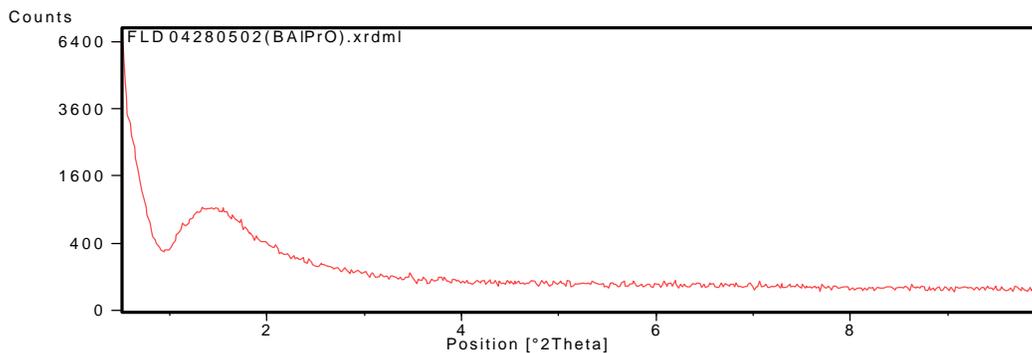


Figure 7. XRD Patterns of Organoaluminophosphate with -O-Si-CH₂-Si-O-

The organoaluminophosphate also indicated a low-angle but broad peak at 2θ of approximately 2, which is characteristic of mesoporous materials observed in Figure 6 above, thus suggesting the potential mesoporous nature of the materials. Further characterization on its the stability and chemical composition is pending.

V-3 Research Progress on Catalysis:

A single pass fixed bed continuous flow reactor catalytic reactor interfaced with a Gas Chromatograph was set up for evaluating cumene cracking (Figure 7). The instrument is currently undergoing calibration prior to catalyst evaluation. For cumene cracking, a nitrogen stream will be saturated with cumene which is placed in a saturator, and subsequently carried at various space velocities over a catalyst bed (~0.5 gm) in a tube reactor which will be heated at a predetermined temperature and space velocity. The catalytic products will be sampled on-line using a 6 port sampling valve and injected onto the GC for analysis. Product distribution will be assessed for zeolite Y/Nnaocomposite host of various physicochemical characteristics.



Figure 7. Pictorial of the single pass fixed bed continuous flow reactor catalytic reactor interfaced with for evaluating cumene cracking

VI CONCLUSIONS

Mesoporous silicates and aluminosilicates were synthesized and will be evaluated as potential catalysts for the conversion of heavy hydrocarbon substrates. Mesostructured aluminophosphates and organoaluminophosphates can be successfully synthesized, but the materials appeared structural unstable when the synthesis templates are removed. Further research on new approaches to improving the thermal stability of these materials are needed. A catalytic reactor was assembled for catalytic testing.

VII FUTURE WORK

Further research on alternative approaches to strengthen the thermal stability of the aluminophosphates will be conducted. The catalytic performance of the mesoporous aluminophosphate and other related materials synthesis according to this and previous reports will commence.

VIII TECHNOLOGY/INFORMATION TRANSFER

Students:

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

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:

- 1) Synthesis of Mesoporous Solids Containing Zeolitic Phase from Hydrothermal Treatment of Colloidal Zeolite Y Precursors submitted, by Yohannes Ghirmazion and Conrad W. Ingram, to be presented in the *Materials Chemistry and Nanotechnology Symposium* at **PACIFICHEM 2005**, Honolulu, December 15-20, 2005
- 2) 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 .

- 3) 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 .
- 4) 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-CAPut!', 2003.
- 5) 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-CAPut!', 2003.
- 6) 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.
- 7) 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.

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