TITLE: STUDIES ON THE SYNTHESIS OF MESOPOROUS MATERIALS AS POTENTIAL PETROLEUM UPGRADING CATALYSTS

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ABSTRACT

OBJECTIVES

The project objectives are to synthesize and test inorganic mesoporous catalysts to address the growing demands for improved catalysts for the upgrading of heavy feed stocks such as heavy crudes and petroleum residuum. Studies on the synthesis of all-silica, aluminosilicates, aluminophosphates ($AlPO_4$) and metal containing aluminophoshates (MeAPO) mesoporous materials will be conducted to identify ways of producing high surface area, thermally stable materials, with well defined mesopores and suitable distributions of catalytically active sites. Such materials will be evaluated for improving the conversion of heavy petroleum feedstocks to middle distillates and naphtha.

ACCOMPLISHMENTS TO DATE AND FUTURE PLANS

1. Our initial approach was to establish techniques for the synthesis of mesoporous materials in our laboratory. Several all-silica and aluminosilcate mesoporous materials were synthesis using a wide range published procedures. The materials were identified as MCM-41 type by X-Ray Diffraction, surface area and porousimetry measurements. Research efforts to identify ways of improving the crystallinity of the pore walls and the acid strength of the materials are ongoing.

2. An extensive synthesis matrix was conducted to delineate the synthetic conditions for aluminophosphate mesoporous materials. Cetyltrimethylammonium chloride surfactant was used as structure directing template. Tetramethylammonium hydroxide (TMAOH) was employed as charge compensating and/or mineralizer. Synthesis was conducted with reaction mixtures over a range of molar chemical compositions as follows: $xAl_2O_3:P_2O_5:yC_{16}TACl:zTMAOH:351H_2O$, where x = 0.29-

2.34, y = 0.12-0.50, and z = 0.34-1.82. Aluminum hydroxide and phosphoric acid were the inorganic precursors. The product type and quality were heavily dependent on synthesis variables. Lamellar (layered) phase was favored by extremely low Al/P ratios (<0.33), low TMAOH content, high C_{16}TACl concentrations and a high synthesis temperature (110°C). The hexagonal (tubular) phase was favored by higher Al/P ratios and TMAOH content; pH range between 8-10; low C_{16}TACl concentration and ambient temperature. The hexagonal phase demonstrated highest lattice ordering at Al/P ratios 0.47-1.25, above which increasingly disordered products were observed. Aluminum and phosphorus were observed in tetrahedral coordination in the lamellar phase. By Magic Angle Spinning NMR. Aluminum was observed in both tetrahedral and octahedral coordination in the hexagonal phase. No mesostructured products were observed under TMAOH-free conditions. Materials with pore size as high as 4 nm were observed. Studies on the thermal stability of the materials are ongoing.

The plan for the future work includes exploring synthesis routes to increase the crystallinity of the pore walls and the acid strengths of the mesoporous aluminosilicates and aluminophosphates. With respect to the aluminophosphates, the most stable materials will be used as the basis for introducing additional metals such as Mg, Fe, and Co in stucture to create the desired acid sites. Subsequently, catalytic testing will be conducted to evaluate the materials for heavy oil hydrocracking.

ARTICLES PRESENTATION AND STUDENTS SUPPORT

Article (Peer Reviewed)

- C. W.Ingram and K. Ghebreyessus, "Catalytic and Shape Selective Activity of MeAPO-36 in the Mild Hydrocracking of Gas Oil", Recent Research Reports, 13th International Zeolite Conference, Montpellier, France, July 8-13, 2001,ed. Groupe Francias des Zeolithes, pg. 26-R-03.

Conference Presentations

- C. W.Ingram and K. Ghebreyessus, "Catalytic and Shape Selective Activity of MeAPO-36 in the Mild Hydrocracking of Gas Oil", presentation at the 13th International Zeolite Conference, Montpellier, France, July 8-13, 2001.
- C. W. Ingram, S. Abubeker, and Jack Eckles, "Aluminophosphate Mesostruictures from the Hydrolysis and Condensation of Inorganic Precursors, presented at the Annual Conference of the National Organization of Black Chemist and Chemical Engineers, New Orleans March, 24-29, 2002.
- C. W. Ingram, S. Abubeker, Studies on the Synthesis of Ordered Mesostructured Aluminophosphates Using Cetyltrimethylammonium Cations as Structure Directing Agent, Accepted for presentation at the 224 ACS National Meeting, Boston, MA, August 18-22, 2002.
- C. W. Ingram, S. Abubeker The Effects of Synthesis Parameters on Mesoporous Aluminophosphates submitted for publication at the 3rd International Mesoporous Materials Symposium, Korea, July, 2002.

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