A New Class of Mesoporous Catalysts for Use in Petroleum Refining

Author	Dr. Conrad W. Ingram (Principal Investigator)
Students:	Sitra Abukekar (Graduate), Wren Amos (Undergraduate)
Address:	Clark Atlanta University, 223 James P. Brawley Drive, Atlanta GA 30314
Phone:	404 880-6898
Fax:	404-880-6890
E-mail:	cingram@cau.edu
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Objectives: This research project seeks to synthesize and test a new class of mesoporous aluminophosphate molecular sieves catalysts to address the growing demands for improved catalysts for the upgrading of heavy petroleum feedstocks, to produce useful middle distillates and naphtha transportation fuels.

Approach: Our research will focus on the use of large surfactant micelles, such as cetyltrimethylammonium cation (CTA), as the liquid crystalline templating agents around which to synthesize silicon, aluminum, phosphorus and transition metals containing mesoporous catalysts with pores size in the 1-10 nm range. Our initial approach will be to synthesize mesoporous materials of varying topologies, by choosing different surfactants as the templating agents. Each surfactant will be added to the synthesis mixtures based on their critical micellar concentration (CMC). Concentrations will range from less than 0.5 x CMC values to as high as 10 x CMC for each surfactant. We will also investigate the synthesis of materials containing varying channel diameters, by adjusting the length (number of carbons) of the hydrophobic hydrocarbon chain of each surfactant molecule (C6 through C16.)

The isomorphous substitution of various heteroelements inside the framework structures will be investigated. In addition to the standard aluminum and phosphorous sources, different salts from the metal ions of interest will be added to the synthesis mixtures. Metal ions will include Si, Mg, Mn, V and Co, to form mesoporous SAPO, MgAPO, VAPO and CoAPO respectively.

Extensive characterization will be conducted to discern the physicochemical characteristics of mesophases produced. X-ray diffraction will be used to identify the presence of ordered phases in all synthesis products. Mesoporous materials typically show strong X-ray diffraction intensities between 1 and 10 two theta. The identification of the structural arrangement of the metal oxide (e.g. lamellar, cubic or hexagonal) will be done by indexing with the appropriate spaces groups. Crystal morphologies will be investigated using Scanning Electron Microscopy. This will provide information on the crystal habits of the product, such as crystal sizes, shapes, surface defects and aggregation characteristics. Pores size, pore distribution and phase purity will be characterized by nitrogen porosimetry. Surface area will be determined by nitrogen BET. Channel arrangement will be investigated using High Resolution Transmission Electron Microscopy. Chemical composition will be determined by Inductively Coupled Plasma/Mass

Spectrometry (ICP/MS) of the acid digested material. Diffuse Reflectance Infrared Spectroscopy will be used to determine the acid characteristics of these materials and to identify the presence and strength of any Bronsted or Lewis acid sites. The number and strength of any acid sites present will be determined by temperature program desorption of ammonia (Ammonia TPD). Thermal stabilities will be studied using thermogravimetric analysis. This will provide information on both the temperatures required to remove the surfactants from the channels of the materials, as well as the ability of the structures to withstand elevated thermal and hydrothermal conditions.

The materials will be evaluated in applications as acid catalysts, using selected probe reactions. N-hexane cracking will be conducted in a fixed bed open tubular reactor. N-hexane cracking constants will be compared with that of zeolite, MeAPO-36 and MCM-41. The hydrocracking and alkylation of naphthalene are two other probe reactions to be tested. These reactions will be performed in a batch reactor (Parr-500 CC) using the pure, calcined forms of MeAPOs. The products will be characterized by GC and GC/MS. Catalysts performance will be compared against a) zeolite (USY), b) microporous MeAPO-36 and c) mesoporous-MCM-41. Catalyst performance will be evaluated in terms of percentage and rate of conversion of the feedstock, product selectivities, structural stabilities and rate of deactivation.

Research Status: Various synthesis procedures were conducted several products formed were found to yield X-Ray diffractograms with peaks in the 1- 10 two theta region, indicating the formation of mesoporous materials. The peak positions and intensities were fond to be sensitive to reaction pH, temperature and time, surfactant type and concentration, and mole ratio of the reactants. Preliminary thermogravimetric analyses yield desorption/decomposition patterns which are characteristic of organics encapsulated within the pores of porous inorganic materials.