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HEAVY OIL UPGRADING

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Semi Annual Report #2

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EXECUTIVE SUMMARY

For the period April 1 to September 30, 1996, our research efforts were focussed on the synthesis and characterization of large quantities of Metal Substituted Aluminophosphate Molecular Sieves Catalysts of type 36 structure (MeAPO-36) for use in the upgrading of petroleum residuum. So far we have succeeded in synthesizing catalysts samples containing magnesium, zinc, cobalt and manganese in the frameworks of the respective molecular sieve. Preliminary characterization studies done by Infrared Spectroscopy demonstrated that these materials contains the Bronsted acid sites that we proposed will be active centers in the Mild Hydrocracking Process.

Recently, a range of interesting aluminosilicates mesoporous materials was synthesized by Mobil R & D. These materials, known as MCM-41 type materials, contain ultra large pore unidimensional channels ranging from 20 angstrom to 100 angstrom and therefore have tremendous potential for Resid Upgrading since their acid strengths are milder than zeolite. To broaden the scope of our project, MCM 41 was synthesized in our laboratory according to published procedures and the structure was confirmed by XRD. In addition, an ultra large pore high silica zeolite, UTD-1, containing a 14 angstrom tetrahedral atom pore opening was recently synthesized by Researchers at Texas A & M University. Like MCM-41, this material also have tremendous potential for Resid Upgrading since the pores are capable of accommodating larger organic molecules. We are currently characterizing samples of this zeolite that we intend to use in conjunction with the MeAPOs to form composite catalysts for use in resid upgrading.

1. Catalysts Synthesis and Characterization:

Metal substituted Aluminophosphate Molecular sieves (MeAPOs) :

Metal Substituted Aluminophosphate Molecular Sieves samples are synthesized according procedures that were optimized from US patent # 4567029 awarded to Union Carbide Oil Company, 1986. 40 g batches of MeAPO-36 are currently been synthesized in a 500 CC zipperclave. A typical synthesis procedure is outline below using MgAPO-36 as an example. Typically, 5.28 g of magnesium acetate was dissolved in 10 mL of deionized water to form solution A. Solution B was prepared by diluting 28.3 g of phosphoric acid in 68.6g of deionized water. Solution A was added to solution B with mixing. 15.8 g of psuedoboehemite alumina (Catapal B) was slowly added to the above mixture. Finally 33.8 g of tripropylamine (R) was slowly added to the mixture with continuous stirring. The molar composition of the reaction mixture is $1.9\text{R}:0.925\text{Al}_2\text{O}_3:1\text{P}_2\text{O}_5:35\text{H}_2\text{O}$. The mixture was placed in the 500 CC zipperclave for 2 days at 100°C and then at 150°C for 3 days. After cooling, the product was filtered washed with deionized water and dried at 100°C. MeAPOs containing other divalent metal such as zinc, magnesium, manganese and cobalt are currently been made according to the above procedures or slightly modifications thereof. The successful synthesis of MeAPO-36 structures were confirmed by MeAPO-36. Figure 1 shows a typical XRD pattern of MgAPO-36.

Acid sites present in these catalysts will be the essence of their catalytic activities. It is therefore important to characterize such acid sites with appropriate analytical techniques. Diffuse Reflectance Infrared Spectroscopy was used to carry out this task since the presence of OH groups in the catalysts can be observed as vibration bands in the 3600 cm^{-1} region of an infrared spectrum. Figure 2 shows a series of infrared spectra of MgAPO-36 evacuated at various temperatures in an environmental infrared cell. The presence of the Bronsted acid sites can be seen as a vibration band at 3595 cm^{-1} , whereas the vibration band at 3670 cm^{-1} is not yet assigned. This compares well with a similar vibration band at around 3608 cm^{-1} that was observed in a sample of the well known, highly acidic zeolite, H-ZSM-5 (Figure 3). Other metal containing MeAPOs that were investigated showed similar vibration bands. To confirm the Bronsted acidic nature of these OH groups, they were allowed to interact with gaseous ammonia (a strong base). In the presence of ammonia at room temperature, the vibration band at 3595 disappeared (Figure 4), but reappeared after the sample was reheated above 300°C .

The catalysts preparation phase of this project is well underway. Further catalysts characterization, such as chemical and surface area analysis as well as sorption properties is currently in progress.

New Mesoporous Materials:

Recently, a range of interesting aluminosilicates mesoporous materials was synthesized by Mobil R & D. These materials, known as MCM-41 type materials, contain ultra large pore unidimensional channels ranging from 20 angstrom to 100 angstrom. These material have

tremendous potential for resid upgrading, since their acid strengths are milder than that zeolite USY and also, their enormous channels are capable of accommodating large organic molecules. Their channel diameters are tunable and are dependent on the chain lengths of the organic surfactant molecules, the latter which functions as the templating agent during synthesis. To broaden the scope of our project, MCM 41 was synthesized in our laboratory according to published procedures and the structure was confirmed by XRD (Figure 5). This material will be used in conjunction with the MeAPOs to form composite catalysts to be used for resid upgrading.

New Ultra Large Pore Zeolite

In other developments, Balkus and fellow researchers recently reported in Nature, the synthesis of an ultra large pore high silica zeolite, UTD-1, containing a 14 tetrahedral atom pore opening of dimension 7.5 angstroms x 10 angstroms. This is the first example of an ultra large pore zeolite and this material have tremendous potential for resid upgrading since the pores are capable of accommodating larger organic molecules. Samples of this promising material was obtained from the researchers and are currently been characterized in our laboratory. So far X-ray diffraction (Figure 6), framework Infrared spectrum (Figure 7) and ^{29}Si MAS NMR (Figure 8) have been recorded. The spectra are currently being analyzed. Like zeolite MCM-41, we intend to combine the large pore size and acidic properties of this material with those of the smaller pore MeAPOs to form composite catalysts to be used for resid upgrading.

2. Other Activities

In other activities, Dr. C. Ingram presented a paper on Catalytic Hydroxylation of Phenol over MeAPO-11 Molecular Sieves at The 30th Mid-Atlantic Regional Meeting of the American Chemical Society at Vilanova University, Pennsylvania, in May, 1996 (see attached abstract). The information presented at this conference were obtained from our efforts in synthesizing and characterizing the catalytic activities of MeAPO catalysts. The full paper from this research effort will be published in Applied Catalysis and is currently in press.

3. Future Work

The next phase of this project will be involved in the investigating the catalytic activities of our catalysts samples. A 500 CC capacity reactor that is capable of attaining Mild Hydrocracking Conditions of 450°C and 1500 psig is currently being secured from Theta Enterprises Inc., in New Jersey. The reactor is equipped with a variable speed motor magnetic drive assemble, heater and other accessories. Other reactors that are currently available in our laboratory (500 CC and 4000 CC zipperclaves from autoclave Engineers) have 250°C as their maximum temperature limits. Whereas they are quite useful in the large scale synthesis of catalysts, they are not capable of reaching the desired MHC temperature conditions of 450°C.

Sample identification: KC051496C

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Figure 1: XRD pattern of MgAPO-36

Figure 2: Infrared spectra showing OH region of MgAPO-36. Vibration band at 3597cm⁻¹ is assigned to Brønsted Acidic OH groups.

Figure 3: Infrared spectra showing OH region of H-ZSM-5 zeolite before ammonia absorption and after ammonia desorption.

Figure 4: Infrared spectra showing the disappearance and reappearance of the 3597 cm⁻¹ vibration band from MgAPO-36 resulting the absorption and desorption of ammonia.

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Figure 5. XRD pattern of MCM-41

Figure 6: XRD pattern of UTD-1

Figure 7: Infrared spectrum showing the framework vibrations region of zeolite UTD-1

Figure 8: ^{29}Si MAS/NMR of UTD-1

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in 5123 vft1a f1
nt 0.882 proc f1
np 27772 fn 0182
av 14888.7 math 1
tb 7808
bs 1c wfr
kpw 88 wdrp wft
pw 5.8 wdr wft
p2 2588.8 wdr
d1 5.808 wdr
xpol 9p 01241v
xrela 4804 9p -15214.5
toss n vt 14808.7
pdp 4 253 10988
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The 30th Middle Atlantic Regional Meeting of the American Chemical Society

May 22-24, 1996

Villanova University

Hosted by the Philadelphia Section

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SOL-GEL SYNTHESIS OF MICROPOROUS MANGANESE OXIDES WITH LAYERED AND TUNNELED STRUCTURES. Stanton Ching, Jenna A. Landrigan, Matthew L. Jorgensen, Diana J. Petrovay, and Jayme L. Roark, Department of Chemistry, Connecticut College, New London, CT 06320. Steven L. Suib and Niangao Duan, Department of Chemistry, University of Connecticut, Storrs, CT 06269.

We have developed new synthetic routes to microporous manganese oxides that have potential applications in heterogeneous catalysis. Layered and tunneled structure materials with near-MnO₂ stoichiometry have been prepared by non-classical sol-gel reactions. Layered birnessite is produced from gels obtained by aqueous reactions between simple sugars and permanganate. Tunneled cryptomelane is formed from gels obtained by aqueous reactions between KMnO₄ and fumaric acid. Synthetic procedures for these materials and their characterization will be presented. Properties of sol-gel-prepared birnessite and cryptomelane will also be compared to their analogs from more traditional manganese oxide syntheses.

gel -> xerogel

birnessite

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NEW APPROACHES TO THE RATIONAL AND IRRATIONAL SYNTHESIS OF NANOCOMPOSITE MATERIALS AND CATALYSTS. Stacy A. Johnson, David M. Kaschak, Geoffrey B. Saupe, Erik Reddington, Elaine S. Brigham, and Thomas E. Mallouk*, Department of Chemistry, The Pennsylvania State University, University Park, PA 16802.

Three new strategies for preparing nanocomposite materials with possible applications in thermal, photochemical, and electrochemical catalysis will be described. One of these involves the assembly of lamellar organic/inorganic heterostructures, through sequential adsorption reactions of organic polycations and colloidal inorganic polyanions. Thin films grown by this method are aperiodic surface analogs of bulk intercalation compounds. This approach has been used to make biomimetic photosynthetic assemblies that combine the photon harvesting, charge separation, and catalytic functions of natural systems. Intercalation and polymerization reactions have also been used to make high surface area, microporous polymers that are essentially "wax impressions" of inorganic molecular sieve structures. A third new strategy in the synthesis of inorganic materials is a combinatorial alternative to these rational methods, which involves parallel screening of large arrays of catalytic materials. Preliminary applications of the combinatorial method to problems in electrocatalysis will be described.

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METAL-ALUMINOPHOSPHATE MOLECULAR SIEVES FOR CATALYTIC HYDROXYLATION OF PHENOL. C. Ingram, E. Dai*, R. Szostak, Department of Chemistry, Clark Atlanta University,

Atlanta, GA; Texaco, Inc., Port Arthur, TX

The aluminophosphate based molecular sieves represents a diverse family of materials. Many are structurally related to the well known commercial zeolites. Unlike substitution of elements into the aluminosilicate zeolites, substitution of catalytically interesting elements for either aluminum and/or phosphorous in the aluminophosphate molecular sieve framework occurs readily. Transition metal containing aluminophosphate compositions therefore may be used to produce novel heterogeneous catalysts for oxidation processes used in the manufacture of fine chemicals. The liquid phase hydroxylation of phenol with hydrogen peroxide represent one important fine chemical oxidation process. Manganese aluminophosphates (MnAlPO₄s) and cobalt aluminophosphates (CoAlPO₄s) seem to favor the production of catechol, particularly at low conversions. Iron aluminophosphates (FeAlPO₄s) and the mixed iron, manganese aluminophosphates (FeMnAlPO₄s) give similar product selectivity of about 1:1 hydroquinone to catechol. Thus, these materials appear to be complimentary to the presently used titanium based catalysts.

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Monday, August 19, 1996

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