A NEW CLASS OF MESOPOROUS ALUMINOPHOSPHATES FOR APPLICATION IN PERTOLEUM REFINING

SECOND ANNUAL REPORT

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I. Disclaimer

II ABSTRACT

This project focuses on the synthesis of mesoporous aluminophosphate and aluminosilicates as catalysts for application in the conversion of large petroleum feedstock compounds to useful middle distillates and naphtha transportation fuels. Summarized herein, is our research progress for September 1, 2001 to August 31, 2002. The synthesis of aluminophosphates in the presence of nonionic surfactants and block co-polymers were explored over a wide range of synthesis variables such as temperature, Al/P ratio, pH and surfactants/polymer concentrations. In most cases, the resulting products were found to be amorphous. A partially ordered aluminophosphate mesophase was obtained in the presence of Brij 56 non-ionic surfactant. Further characterization to determine the phase type (eg hexagonal lamellar or cubic) of this product is pending. The amorphosu nature of the products obtained using these classes of surfactants are in contrast to highly ordered aluminophosphates mesophases obtained in the presence of cationic quaternary ammonium surfactants, such as cetyltrimethylammonium detailed in a previous report. The synthesis of pure- silica and aluminosilicate mesophases of different type and quality were also conducted over a wide range of variables such as temperature, Si/Al ratio, pH and surfactants/polymer concentrations. However characterization of the phase type and quality of the materials produced is pending due to a severe and extended malfunction of the X-Ray Diffractometer. Nitrogen porosimetry of selected calcined samples showed various absorption isotherm with some samples showing type IV with a large step in the mesoporous range. Surface area of the samples varied and maximized at approximately 1000 m^2/g, which is typically reported for materials of this type. Further characterization of the sample will be conducted following repair of the X-Ray Diffractometer

III INTRODUCTION

This project focuses on the synthesis of mesoporous aluminophosphate catalysts for application in the acid catalyzed conversion of large petroleum feedstock compounds to useful middle distillates and naphtha transportation fuels. Our approach utilizes large surfactant micelles as the templating agents around which "silicon and transition-metals-containing mesoporous catalysts with pores size in the 2-10 nm range are synthesized. The rationale is based on the knowledge that individual surfactant molecules are known to aggregate when they are present in solution at or above certain concentrations - the critical micellar concentration (CMC). In the case of micelle-templated mesoporous materials, the individual surfactant monomer contained in each micelle, is extended across the cross-section of the pore. The length of the surfactant molecule defines the pore size of the resulting material.

This report summarizes our research progress for September 1, 2001 to August 31, 2002. In our previous report a range of mesoporous aluminophosphates materials were prepared to increase the inventory of materials to be tested as catalysts. This reporting phase of our research was to extend, by varying the synthesis parameters, the type and quality of mesoporous aluminophosphates and aluminosilicates inventory. To that end, the synthesis of these two classes of materials in the presence of nonionic surfactants and block co-polymers were explored over a wide range of synthesis variables such as temperature, Al/P ratio, Si/Al, pH and surfactants/polymer concentrations. For the aluminophosphates in most cases, the products were found to be amorphous, whereas for the aluminosilicates, most of the are not yet characterized due to a severe and extended malfunction of the X-Ray Diffractometer.

A summary of our synthesis activities is given below showing the composition of synthesis mixtures and in some cases, a description of the products obtained.

IV RESEARCH PROGRESS

EXPERIMENTAL

Synthesis of aluminophosphates

The type of reactants, order of mixing, synthesis temperature and time were varied. In a typical synthesis procedure, 1.13 and 2.27g of phosphoric acid is mixed with 2.32 g of aluminum isopropoxide or aluminum hydroxide. A 10.0 ml aliquot of 2M HCl was added and stirred for 3 hours at room temperature (solution A). 4.0 g of surfactant (Pluronic L-64, Brij 30 and 56 was dissolved in 30 ml of water and added to 110 ml of 2M HCl (solution B). Solution A and B was then mixed and stirred for an hour at 40°C, then heated at 80°C for 48 hours. Table 1 through 3 below shows selected composition synthesis mixtures, along with other synthesis parameters such as pH, temperature and time.

Synthesis of silicates and aluminosilicates

As in the case of aluminophosphates, the type of reactants, order of mixing, synthesis temperature and time were varied. In a typical synthesis, 8.5 g of tetraethylorthosilicates (TEOS) and 0.2 g and 0.5 g of aluminum t-butoxide was mixed with 10ml of 2M HCl. The solution is stirred for 3 hours (solution A). 4g of surfactant (Pluronic L64, 61,,121, F-68, P-123, Brij 30, 56,76) was dissolved in 30ml of water and added to 110ml of 2M HCl (solution B). Solution A and B were mixed and stirred for 1 hour at 40 degrees and then autoclaved for 48 hrs at 100 degrees.

Characterization

Powdered X-ray diffraction measurements were performed on a Phillips X-Pert X-Ray Diffractometer using Cu-K_{∞} radiation ($\lambda = 0.15418$ nm) between 1 and 10 two theta. Nitrogen adsorption isotherms and BET surface area measurements were obtained using a Micromeritics Gemini 2310 under liquid nitrogen temperature. The samples were preheated at 200°C in nitrogen for 3 hr, then evacuated prior to adsorption measurement. Thermogravimetric analysis was done using a TA Instrument model SD2960 Thermal Analyzer.

Table 1: Synthesis parameters for mesophase aluminophosphates using non-ionic and block copolymers surfactnants as templates under acidic conditions

Sample ID	Wt.Al hydroxide	Mol.Al. hydroxide	Wt.P acid	Mol.P acid	Wt.Water	Mol.Water	pH P,Water	pH Al, P,water	Surfactant type	Wt. Surfactant	pH Al,P,Surf&water	Time	Temp	pH after 20hrs	X-ray data
SA141301	1.67	0.02	4.25	0.04	35.00	1.94	0.53	1.69	Brij 56	4.01	2.03	20hrs	RT	2.19	None
SA241301	3.34	0.04	4.25	0.04	35.00	1.94	0.55	1.88	Brij 56	4.09	2.08	20hrs	RT	2.21	None
SA341301	1.67	0.02	4.25	0.04	35.00	1.94	0.55	1.71	Brij 76	4.07	2.01	20hrs	RT	2.11	None
SA441301	3.34	0.04	4.25	0.04	35.00	1.94	0.53	1.78	Brij 76	4.04	2.04	20hrs	RT	2.17	None
SA541301	1.67	0.02	4.24	0.04	35.00	1.94	0.55	1.64	Brij 30	4.04	2.21	20hrs	RT	2.10	Amorphous
SA641301	3.34	0.04	4.24	0.04	35.00	1.94	0.56	1.88	Brij 30	4.09	2.15	20hrs	RT	2.18	Amorphous
SA142501RT	1.67	0.02	4.23	0.04	35.00	1.94	0.52	1.96	Pluronic F68	4.00	2.17	20hrs	RT	2.13	Amorphous
SA142501HT	1.67	0.02	4.23	0.04	35.00	1.94	0.52	1.96	Pluronic F68	4.00	2.17	20hrs	100	1.74	Amorphous
SA242501RT	3.33	0.04	4.20	0.04	35.00	1.94	0.55	1.89	Pluronic F68	4.01	2.23	20hrs	RT	2.19	Amorphous
SA242501HT	3.33	0.04	4.20	0.04	35.00	1.94	0.55	1.89	Pluronic F68	4.01	2.23	20hrs	100	1.95	Amorphous
SA342501RT	1.67	0.02	4.21	0.04	35.00	1.94	0.49	1.86	Pluronic L-61	4.01	2.14	20hrs	RT	2.13	None
SA342501HT	1.67	0.02	4.21	0.04	35.00	1.94	0.49	1.86	Pluronic L-61	4.01	2.14	20hrs	100	1.86	Amorphous
SA442501RT	3.33	0.04	4.20	0.04	35.00	1.94	0.52	1.94	Pluronic L-61	4.01	2.12	20hrs	RT	2.27	Amorphous
SA442501HT	3.33	0.04	4.20	0.04	35.00	1.94	0.52	1.94	Pluronic L-62	4.01	2.12	20hrs	100	2.12	Amorphous
SA542501RT	1.66	0.02	4.20	0.04	35.00	1.94	0.52	1.97	Pluronic P-123	4.03	2.16	20hrs	RT	2.16	Amorphous
SA542501HT	1.66	0.02	4.20	0.04	35.00	1.94	0.52	1.97	Pluronic P-123	4.03	2.16	20hrs	100	1.99	Amorphous
SA642501RT	3.33	0.04	4.21	0.04	35.00	1.94	0.64	2.10	Pluronic P-123	4.01	2.18	20hrs	RT	2.30	Amorphous
SA642501HT	3.33	0.04	4.21	0.04	35.00	1.94	0.64	2.10	Pluronic P-123	4.01	2.18	20hrs	100	2.08	Amorphous

Table 2: Synthesis parameters for mesophase aluminophosphates using non-ionic and block copolymers surfactnants as templates under neutral conditions

Wt.Al hydroxide	Mol.Al. hydroxide	Wt.P acid	Mol.P acid	Wt.Water	Mol.Water	pH P,Water	pH Al, P,water	Surfactant	Wt. Surf.	pH Al,P,Surf&water	Wt. TMAOH	Final pH	Time	Temp.	pH after 20hrs	X-ray data
1.67	0.02	4.28	0.04	35.0	1.94	0.49	1.53	Brij 30	4.08	1.82	14.75	7.58	20 hrs	RT	7.06	None
3.34	0.04	4.22	0.04	35.0	1.94	0.44	1.88	Brij 30	4.07	2.03	12.18	7.06	20 hrs	RT	6.72	Amorphous
1.67	0.02	4.22	0.04	35.0	1.94	0.45	1.72	Brij 56	4.06	1.98	12.51	7.14	20 hrs	RT	6.73	Amorphous
3.34	0.04	4.21	0.04	35.0	1.94	0.44	1.83	Brij 56	4.04	2.02	11.68	7.44	20 hrs	RT	6.94	Peak exists
1.67	0.02	4.23	0.04	35.0	1.94	0.50	1.75	Brij 76	4.05	2.02	13.51	7.13	20 hrs	RT	6.91	Amorphous
3.33	0.04	4.28	0.04	35.0	1.94	0.51	1.84	Brij 76	4.04	2.01	11.08	7.1	20 hrs	RT	6.79	None
1.67	0.02	4.20	0.04	35.0	1.94	0.68	1.68	Pluronic P-123	4.00	2.12	10.80	6.97	20hrs	RT	6.59	Pending
1.67	0.02	4.20	0.04	35.0	1.94	0.68	1.68	Pluronic P-123	4.00	2.12	10.80	6.97	20hrs	100	6.32	Pending
3.34	0.04	4.20	0.04	35.0	1.94	0.66	1.89	Pluronic P-123	4.01	2.17	9.45	6.98	20hrs	RT	6.59	Pending
3.34	0.04	4.20	0.04	35.0	1.94	0.66	1.89	Pluronic P-123	4.01	2.17	9.45	6.98	20hrs	100	6.45	Pending
1.67	0.02	4.21	0.04	35.0	1.94	0.60	1.77	Pluronic L-61	4.00	2.14	13.14	7.01	20hrs	RT	6.85	Pending
1.67	0.02	4.21	0.04	35.0	1.94	0.60	1.77	Pluronic L-61	4.00	2.14	13.14	7.01	20hrs	100	6.65	Pending
3.34	0.04	4.20	0.04	35.0	1.94	0.56	1.93	Pluronic L-61	4.00	2.18	10.86	7.01	20hrs	RT	6.76	Pending
3.34	0.04	4.20	0.04	35.0	1.94	0.56	1.93	Pluronic L-61	4.00	2.18	10.86	7.01	20hrs	100	6.72	Pending
1.66	0.02	4.21	0.04	35.0	1.94	0.54	1.81	Pluronic F-68	4.00	2.12	10.78	7	20hrs	RT	6.52	Pending
1.66	0.02	4.21	0.04	35.0	1.94	0.54	1.81	Pluronic F-68	4.00	2.12	10.78	7	20hrs	100	6.45	Pending
3.33	0.04	4.21	0.04	35.0	1.94	0.69	1.92	Pluronic F-68	4.00	2.13	9.18	6.99	20hrs	RT	6.53	Pending
3.33	0.04	4.21	0.04	35.0	1.94	0.69	1.92	Pluronic F-68	4.00	2.13	9.18	6.99	20hrs	100	6.48	Pending

Table 3: Synthesis parameters for mesophase aluminophosphates using non-ionic and block copolymers surfactnants as templates under basic conditions

Sample ID	Wt.Al hydroxide	Mol.Al. hydroxide	Wt.P acid	Mol.P acid	Wt.Water	Mol.Water	pH P,Water	pH Al, P,water	Surfactant	Wt. Surfactant	pH Al,P,Surf&water	Wt. TMAOH	Final pH	Time	Temp.	pH after 20hrs
SA141701	1.67	0.02	4.25	0.04	35.0	1.94	0.44	1.82	Brij 30	4.05	2.08	28.21	11.44	20 hrs	RT	11.43
SA241701	3.33	0.04	4.23	0.04	35.0	1.94	0.47	1.94	Brij 30	4.05	2.09	23.09	10.81	20 hrs	RT	10.69
SA341701	1.67	0.02	4.27	0.04	35.0	1.94	0.43	1.77	Brij 56	4.04	2.05	27.37	10.39	20 hrs	RT	8.46
SA441701	3.33	0.04	4.23	0.04	35.0	1.94	0.47	2.18	Brij 56	4.05	2.06	27.31	9.48	20 hrs	RT	10.02
SA541701	1.67	0.02	4.28	0.04	35.0	1.94	0.47	2.25	Brij 76	4.05	2.47	22.05	10.15	20 hrs	RT	10.15
SA641701	3.33	0.04	4.26	0.04	35.0	1.94	0.46	1.89	Brij 76	4.05	2.11	20.24	9.74	20 hrs	RT	10.05
SA243001	1.67	0.02	4.21	0.04	35.0	1.94	0.34	1.61	Pluronic F-68	4.03	2.01	19.73	9.43	20 hrs	RT	
SA243001	1.67	0.02	4.21	0.04	35.0	1.94	0.34	1.61	Pluronic F-68	4.03	2.01	19.73	9.43	20 hrs	HT	
SA343001	3.34	0.04	4.21	0.04	35.0	1.94	0.41	1.95	Pluronic F-68	4.02	2.06	18.53	9.13	20hrs	RT	
SA343001	3.34	0.04	4.21	0.04	35.0	1.94	0.41	1.95	Pluronic F-68	4.02	2.06	18.53	9.13	20hrs	HT	
SA443001	1.66	0.02	4.20	0.04	35.0	1.94	0.49	1.67	Pluronic L-61	4.02	2.03	22.31	9.52	20hrs	RT	
SA443001	1.66	0.02	4.20	0.04	35.0	1.94	0.49	1.67	Pluronic L-61	4.02	2.03	22.31	9.52	20hrs	HT	
SA543001	3.34	0.04	4.21	0.04	35.0	1.94	0.45	1.92	Pluronic L-61	4.00	2.08	22.09	9.33	20hrs	RT	
SA543001	3.34	0.04	4.21	0.04	35.0	1.94	0.45	1.92	Pluronic L-61	4.00	2.08	22.09	9.33	20hrs	HT	
SA643001	1.66	0.02	4.20	0.04	35.0	1.94	0.43	1.70	Pluronic P-123	4.06	2	20.24	9.29	20hrs	RT	
SA643001	1.66	0.02	4.20	0.04	35.0	1.94	0.43	1.70	Pluronic P-123	4.06	2	20.24	9.29	20hrs	HT	

Table 4: Synthesis parameters for mesophase silicates and aluminosilicates using non-ionic and block copolymers surfactnants as templates under basic conditions

Si/Al =50

Sample ID	Wt.Al-t-butoxide(g)	Wt. 2M HCL(ml)	Wt.TEOS	Mol.TEOS	Wt.Water	Wt. Surfactant	pH(Al,TEOS,HCl)	Final pH	Temp.	Time	X-Ray
Al-SBA06	0.20	120.00	8.50	0.04	30.0	4.00g(Pluronic F-68)	1.35	0.66	100	48hrs	Pending
A-SBA07	0.20	120.00	8.51	0.04	30.0	4.03g(Pluronic L-61)	1.11	0.62	100	48hrs	Pending
Al-SBA08	0.20	120.00	8.51	0.04	30.0	4.03g(Pluronic P123)	0.64	0.62	100	48hrs	Pending
Al-SBA09	0.20	120.00	8.50	0.04	30.0	4.02g(pluronic L121)	0.66	0.63	100	48hrs	Pending
Al-SBA10	0.20	120.00	8.50	0.04	30.0	4.06g(Pluronic L-64)	1.28	0.63	100	48hrs	Pending
WA Al-SBA22601A	0.20	120.00	8.51	0.04	30.0	4.00g(Brij30)	0.14	0.09	100	48hrs	Pending
WA Al-SBA226001B	0.20	120.00	8.51	0.04	30.0	4.00g(Brij76)	0.11	0.07	100	48hrs	Pending
WA Al-SBA22601C	0.20	120.00	8.51	0.04	30.0	4.00g(Brij56)	0.09	0.06	100	48hrs	Pending

All silica

Sample ID	Wt.TEOS	Mol.TEOS	Wt. 2M HCl (ml)	Wt.Water	Mol.water	Wt. Surfactant	pH(water,Surf.,HCl,)	Final pH	Temp.	Time	X-Ray
Si-SBA01	8.50	0.04	120	30	1.67	4.0061g(L-64)	0.23	0.25	80 & 110	Overnight	Pending
Si-SBA02	8.51	0.04	120	30	1.67	4.0118g(L-61)	0.21	0.19	80 & 110	Overnight	Pending
Si-SBA03	8.51	0.04	120	30	1.67	4.0080g(L-121)	0.23	0.05	80 & 110	Overnight	Pending
Si-SBA04	8.51	0.04	120	30	1.67	4.0061g(F-68)	0.33	0.31	80 & 110	Overnight	Pending
Si-SBA05	8.50	0.04	120	30	1.67	4.0964g(P-123)	0.42	0.46	80 & 110	Overnight	Pending
WA Si-SBA 22101A	8.51	0.04	120	30	1.67	4.0158g(Brij30)	0.50	0.57	80 & 110	Overnight	Pending
WA Si-SBA 22101B	8.50	0.04	120	30	1.67	4.0079g(Brij76)	0.50	0.48	80 & 110	Overnight	Pending
WASi-SBA22301A	8.51	0.04	120	30	1.67	4.0114g(Brij56)	0.15	0.08	80 & 110	Overnight	Pending

RESULTS

Aluminophosphates synthesis

It was envisaged that the use of nonionic surfactants and block copolymers in synthesizing aluminophosphates can produce materials with thicker walls and hence increased thermal stability. Within the synthesis mixtures of P/Al ratio of 1.0 and 2.0, and using Brij 56 and Brij 76 as surfactants, no solid product was formed, while in the presence of Brij 30 a solid product which was found to be amorphous synthesis using to X-Ray. White solids were precipitated from synthesis mixtures containing block copolymers Pluronic F68 and P123 both formed products in the synthesis at high and room temperature. Pluronic L-61 formed precipitates at high temperature only. However, all solid products were amorphous to X-ray.

For samples synthesized under neutral conditions, at P/Al ratio of 1.0 and using Brij 30 and Brij 56 as surfactants, the XRD show a low diffraction peak, signaling somewhat ordering within the product. Synthesis at P/Al ratio of 2 in the presence of the Pluronic series of block copolymers (P123, L-61and F-68) yielded no solid product at room temperature synthesis, and amorphous white solids at 100°C synthesis temperature. Formation of SBA type aluminophosphates in basic condition: At higher pH's synthesis at P/Al ratio of and in the presence of Brij 76 and Brij 56 only amorphous white solids were obtained, and at higher P/Al ratio (2), while Brij 30 and Brij 56 formed no solid product.

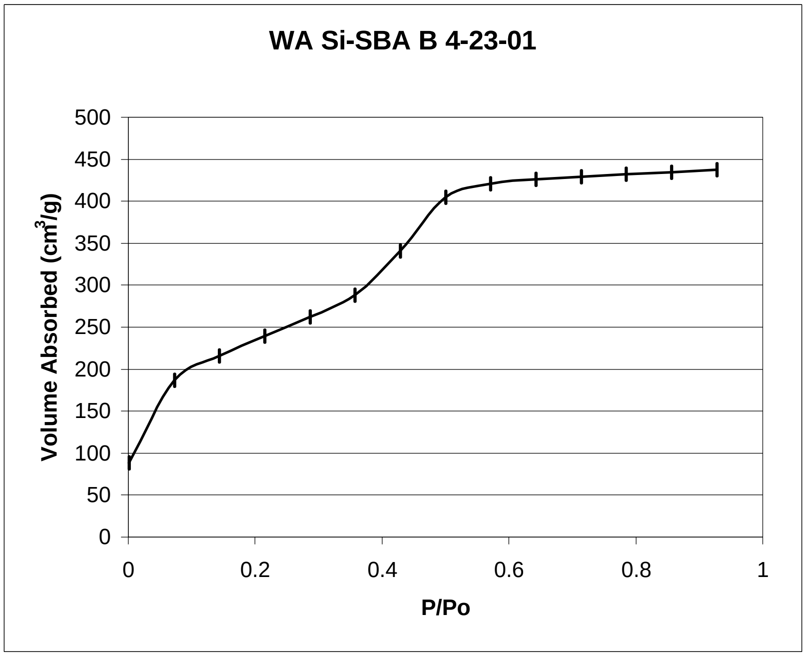
In general therefore, either no solids product was formed or in cases where a solid was obtained, they were all amorphous. The amorphous nature of the products obtained using these classes of surfactants are in contrast to highly ordered aluminophosphates mesophases obtained in the presence of cationic quaternary ammonium surfactants, such as cetyltrimethylammonium detailed in a previous report.

Silicates and aluminophosphates synthesis

A large inventory of all-silica and aluminosilicates were prepared, a selection of which is presented in Table 4. However characterization of the phase type and quality of the materials produced is pending due to a severe and extended malfunction of the X-Ray Diffractometer.

Nitrogen porosimetry of selected calcined samples showed various absorption isotherms with some samples showing type IV with a large step in the mesoporous range. Surface area of the samples varied and maximized at approximately 1000 m^2/g, which is typically reported for materials of this type. Further characterization of the samples will be conducted following repair of the X-Ray Diffractometer**.**

Figure 1. Absorption Isotherm of a typical all-silica mesoporous sample.



VI CHALLENGES

It was also reported that catalysts characterization was significantly hampered by malfunction of our Panalytical Inc X'Pert X Ray Diffraction instrument. This instrument is critical to the research project as it is used to identify the type and quality of materials synthesized. Other analytical techniques provide only secondary supporting information and sending samples elsewhere for analysis is extremely costly. I am pleased to report however, that we have since procured funds from other sources to repair the instrument. New software was ordered and the instrument is also currently undergoing hardware servicing by field engineers from Panalytical Inc. Nevertheless, we have continued to performed synthesis activities and have been using indirect methods of characterization to assess products. Full catalysts characterization will resume after instrument repair is completed. In the meantime, we have also begun to assemble a High Temperature, High Pressure Reactor for catalysts testing.

VII FUTURE WORK

Work in the immediate future will focus on characterizing the physicochemical characteristics of the materials that are pending. Samples most suitable for catalytic testing will evaluated as catalysts to upgrade petroleum feedstocks.

VII TECHNOLOGY/INFORMATION TRANSFER

1. Sitra Abubeker presented her research in defense of her Master of Science to the School of Art and Sciences, Clark Atlanta University, February, 2002

2. Research paper by Sitra Abubeker, Conrad Ingram and Andrew J. Eckles entitled "Aluminophosphate Mesostructures From the Hydrolysis and Condensation of Inorganic Precursors" was presented at the Annual National Organization of Black Chemists and Chemical Engineers (NOBCCHE) conference in March, 2002, New Orleans.

3. Research progress entitled "Studies on the Synthesis of Mesoporous Materials as Potential Petroleum Upgrading Catalysts" was presented by Dr. Conrad Ingram at University Coal Research/ Historically Black Colleges and Universities and Other Minority Institutions Program Review Meeting, Pittsburgh, June 2-5, 2002.

4. Research paper by Sitra Abubeker, Conrad Ingram entitled " The Effects of Synthesis Parameters on Mesostructured Aluminophosphates Synthesis" accepted at the 3rd International Mesostructured Materials Symposium in July Korea, 2002, **was not presented since travel was not authorized by DOE**.

5. Research paper by Sitra Abubeker, Conrad Ingram entitled: "Studies on the Synthesis of Ordered Mesostructured Aluminophosphates Using Cetyltrimethylammonium Cations as Structure Directing Agent", C. W. Ingram, S. Abubeker will be presented at the 224 ACS National Meeting, Boston, MA, August 18-22, 2002

VIII REFERENCES