

QUARTERLY REPORT #5

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For Period: October 30, 1995 - January 31, 1996

Project Title: ADVANCE CONCEPTS FOR THE CONVERSION
OF SYNGAS LIQUIDS

Grant #: DOE-FG22-94MT-94010

Project Director: Dr. Rosemarie Szostak
Telephone Number: (404) 880-6861

Prepared by: Dr. Rosemarie Szostak
Dr. Conrad Ingram

Date of report: February 12, 1996

Institution: Clark Atlanta University
223 James P. Brawley Drive
Atlanta, Georgia 30314

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1.0 SUMMARY:

Research efforts for the period October 30, 1995 to January 30, 1996 have been focused on the characterization of catalyst samples, mainly by ion exchange and spectroscopic techniques. Other activities included, the preparation of more variants of the MeAPO-36 family containing various types and amounts of metals in their frameworks. Characterization of these samples by x-ray diffraction analysis was delayed due to malfunction of the Diffractometer since October of 1995. The instrument was back in working condition only since the ending of January and XRD analysis has resumed since then. Efforts from our research group were also concentrated on the preparation of manuscripts for publication in Applied Catalysis Journal and Preprints of ACS National Meeting in New Orleans, March, 1996 (see attached correspondence from the editors).

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

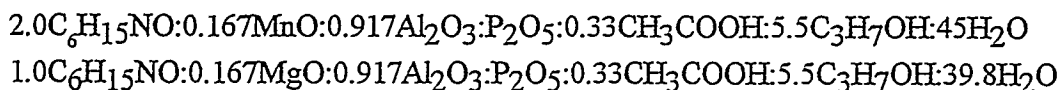
2. WORK IN PROGRESS

Introduction of divalent metals (e.g. Co, Zn, Mn or Mg) into AlPO_4 framework are expected to generate a negative framework which is balanced by a cations such as Na^+ , NH_4^+ or Ca^{2+} and therefore possess ion exchange characteristics. If the cation is H^+ , Bronsted acid sites are expected to be created. To reveal the internal distribution of Bronsted and possibly Lewis acid sites and their relative strengths, suitable probe molecules can be used. These molecules should have spectroscopic properties which are altered upon interaction with acid centres. The ion exchange properties of MeAPO samples (prepared in an earlier phase of this project) are currently being investigated using ammonium, alkaline and alkaline earth metals. The acidic properties of MeAPO samples containing different metals are also currently being investigated by Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS).

2.1 Ion exchange properties of metal substituted aluminophosphate molecular sieves

2.1.1 Synthesis of MnAPO5 and MgAPO5

Deionized water (23.4g) was slowly added to hydrated aluminum oxide (6.23 g) in a porcelain dish with thorough stirring. To this was gradually added orthophosphoric acid (11.58g). A solution prepared by dissolving metal acetate tetrahydrate (1.80g) (metal = magnesium or manganese) in water (6.28 g) was then slowly stirred into the reaction mixture. Finally diethylethanolamine (5.88 g) was added.



The reaction mixtures were placed in sealed 50 cm³ stainless steel Teflon lined parr autoclaves and heated at autogeneous pressure at 200°C for 24h for both MnAPO5 and MAPO5 and 200°C for 48h for CoAPO5. The solids were recovered from the supernatant liquid by centrifugation with successive washing with deionized water followed by drying. Calcination was performed in a muffle furnace in dry nitrogen atmosphere by slowly heating the samples to 500°C for 12 h, followed by 510°C at 6h in dry air.

2.1.2 Synthesis of CoAPO5

A solution containing cobalt acetate tetrahydrate (2.08 g) dissolved in water (25.48 g) was thoroughly and gradually stirred into aluminum isopropoxide (18.3g) in porcelain dish. The mixture was then placed in a high shear blender and processed until a thick gel was formed. To this gel was added a solution containing orthophosphoric acid (5.9 g), diethylethanolamine (9.37 g) and water (11.64 g). The molar composition of the reaction mixture was as follow:

1.0C₆H₁₅NO:0.167CoO:0.917Al₂O₃:P₂O₅:0.33CH₃COOH:5.5C₃H₇OH:45H₂O. The reaction mixture and product were subsequently treated as in section 2.1.1.

2.2 Characterization of samples

Samples were characterized by XRD and chemical analysis

2.2.1 Chemical analysis

Zeolite sample (0.0500 g) was dissolved in 0.5 mL of deionized water and 1.0 mL of concentrated HCl with heating (not boiling). The solution was then filtered into a 25 mL volumetric flask and made up to mark with deionized water. The sodium concentration was determined by flame photometry using a Corning 400 Flame Photometer. Aluminum was determined by AAS, phosphorus was determined by UV spectrophotometer using the ammonium vanadate-ammonium molybdate method.

2.3 Preliminary investigation of ion exchange capacities of zeolites

The calcined samples were converted to the homoionic sodium forms as follows. Samples were placed in polyethylene bottles and equilibrated twice in 1M sodium chloride (20ml/g) for 48hr at 20°C with agitation using mineralogical rollers. After equilibration samples were centrifuged at 2000 rpm, washed free of chloride (filtrate tested with AgNO₃) and then dried at 80°C. Samples were then stored over saturated sodium chloride in a dessicator.

Duplicate portions of zeolite (0.1000g) samples were weighed in 20 mL capacity polyethylene vials to which was added 20 mL of 0.1 M NH₄NO₃. The vials were then sealed with PTFE tape and were equilibrated for 2.5 days at 20°C, 40°C and 65°C. The experiments were also performed using 0.1M KNO₃ at similar temperatures and with 0.5M NH₄NO₃ at 20°C. After equilibration, samples were centrifuged at 2000 rpm for 15 minutes and the sodium concentration of the supernatant liquid determined flame photometry. For repeat exchange, the supernatant was removed from the samples and 10.0 cm³ of fresh 0.1 M solution KNO₃ added. The samples were equilibrated for a further 2.5 days at 20°C after which the sodium content in solution was determined by flame photometry.

2.4 Uptake kinetics on the Na-exchanged MnAPO5 and MAPO5 with alkali and alkali earth metals.

The kinetics of release of sodium from zeolites over many hours were monitored as follows. 0.0250 g of zeolite sample was placed in a 6 mL capacity polyethylene vial. 5.0 cm³ of 0.1M MNO₃ solution was added using a micro pipette with 5.0 mL disposable tips attached.

3. RESULTS AND DISCUSSION

3.1 Characterization

X-ray diffraction patterns (*not shown*) of the Na exchanged forms of the calcined samples showed them all to be of high crystallinity and isostructural to the AlPO₅ topology. Chemical analyses of Na exchanged MeAPOs showed the following results.

Table 1. Chemical compositions of NaMeAPOs

	CoAPO-5		MnAPO-5		MAPO-5	
	Wt % found	*Exptd values	Wt % found	*Exptd values	Wt % found	*Exptd values
Al ₂ O ₃	47.2	32.4	36.7	33.8	29.4	33.2
P ₂ O ₅	52.1	49.8	49.6	48.2	62.2	49.4
MO	2.0	4.3	1.5	4.0	2.0	2.6

M= divalent metal

* Exptd = Expected values.

Table 2. Molar Chemical composition of NaMeAPO₅ (mol %)

	Al	P	M	H ₂ O	Na	O	Al+M	Ion exchange capacities, (IEC) (mmol/g)
NaMAPO ₅	0.58	1.14	0.05	1.17	0.02	3.77	0.63	20.9
NaMnAPO ₅	0.71	0.90	0.02	1.18	0.03	3.45	0.73	33.7
NaCoAPO ₅	0.94	0.96	0.03	1.15	0.03	3.94	0.97	20.6
NaZSM-5								80.6

M=divalent cation

Table 1 shows a comparison of the chemical composition of our NaMeAPO₅ samples versus the expected values. NaMnAPO-5 and NaCoAPO₅ samples show a higher Al content than the expected values, while the NaMAPO₅ sample shows a lower value. With respect to phosphorus, only NaMAPO₅ gave a value higher than expected. With respect to the divalent

ions, all three catalysts show a M^{2+} content lower than the expected values. The molar chemical composition of NaMeAPO5 samples are presented in Table 2. The order of aluminum concentration (mol %) found in the samples is NaMAPO5 < NaMnAPO5 < NaCoAPO5, while the order of phosphorus concentration found was NaMAPO5 > NaMnAPO5 = NaCoAPO5. The order of the concentration of divalent cations found was Mg in NaMAPO5 > Co in NaCoAPO5 > Mn in NaCoAPO5. In MeAPOs, the divalent ions substitute for aluminum in the framework and the number of moles of Al+M (M=divalent cation) should be equivalent to the number of moles of P. This relationship was observed only for NaCoAPO5. For NaMnAPO5 and NaMAPO5, the P/(Al+M) was 1.3 and 1.8 respectively. It is not clear why a ratio of > 1 was observed in the latter cases. Another important consideration is that if all negative charges are balanced by Na^+ cations then the number of moles of M should be equivalent to the number of moles of Na^+ , since the introduction of each M in the framework produces one negative charge. The ion exchange capacities (mmol Na/100 g) of each sample are compared with that of NaZSM-5 sample in Table 2. It can be observed that the order of exchange capacities are ZSM-5 > MnAPO5 > MAPO5 > CoAPO5. NaCoAPO5 possessed this 1:1 relationship suggesting that cobalt is present in the framework of the sample while sodium existed as balancing cations. However, NaMAPO5 had a Mg/Na ratio of 2.4 suggesting that (1) some Mg ion may exist as nonframework species (possibly as balancing cations) or (2) incomplete ion exchange during conversion to the sodium form. NaMnAPO-5 had a M/Na ratio of 0.6. Reasons for this excess of Na^+ is not quite clear but may be due to incomplete removal of the NaCl solution used in preparing the sodium form, even though the sample was washed until it tested negative for free chloride ions.

3.2 Preliminary ion exchange of NaMeAPOs with NH_4NO_3

Figure 1 shows that the percentages of sodium ions released from each NaMeAPOs using 0.1M ammonium solution at 20°C was less than 40%. With a fivefold increase in the concentration of ammonium solution (0.5 M) at the same temperature (Figure 1), little or no increase in the percentage release of sodium was observed. It was concluded that increasing the concentration of the ammonium exchange solution was ineffective in bringing about exchange of the sodium ions from the samples. Ion exchange experiments done using 0.1 M ammonium solution at 40°C showed (Figure 1) an increase in the percentages of sodium released for all samples compared to the values at 20°C. For example, NaMAPO5 showed an increase from 36.6% release at 20°C to 61.1% release at 40°C. When samples which were originally ammonium exchanged at 40°C were re-exchanged with a fresh addition of 0.1 M ammonium solution (after the first solution was removed from the solid), no further exchange was observed (Figure 1). This suggested that repeated exchange, even at elevated temperatures was not effective in the release of sodium ions. Increase in the temperature of the ion exchange reaction to 65°C showed the most desirable trend in releasing the sodium ions. NaMAPO5 gave almost 100% release of sodium at 65°C. Though 100% exchange were not observed for NaCoAPO5 and NaMnAPO5, exchange at higher temperatures was not performed because of the possible hydrothermal instability of the samples. It should be noted

that ion exchange with these MeAPOs was significantly more difficult than the NaZSM-5, since greater than 90% release was obtained with the latter, even at 20°C.

3.3 Preliminary ion exchange of NaMeAPOs with K^+ and Ca^{2+}

Ion exchange experiments were done using 0.1M KNO_3 at two temperatures, 40 and 65 °C. As for the case of NH_4 , the Na/K exchange process (Figure 2) showed similar trends with increase in temperature. NaCoAPO5 and NaMAPO5 showed 100% exchange of Na^+ . Much lower uptake was observed for Ca^{2+} and this may be related to the divalent nature of Ca^{2+} , which needs two adjacent negative charge on the framework for successful ion exchange.

3.4 Uptake kinetics on MeAPOs

3.4.1 NaMAPO5

Kinetic studies for monovalent exchanges on NaMAPO-5 (Figure 3) suggested that for replacement of Na by K, Rb, Li, NH_4 and Cs, equilibrium was reached within 10 h and were temperature dependent in that an increase in temperature increases the rate and maximum uptake of cations. The order of maximum uptake at 20°C was $K > NH_4 = Rb = Li > Cs$ (bottom graphs). At 65°C (top graphs) the order was $NH_4 = Rb > K > Cs$. For divalent cations at 20°C the order was $Ca = Sr = Ba > Mg$ (bottom graphs). The behavior of are similar at 20°C. The failure Ca, Sr and Ba to show any difference in behavior may be due to the fact the hydrated radii of the cations are greater 0.4 nm above which size exclusion occurs. The much lower uptakes which were observed for the Cs^+ and the divalent cations may be related to the large hydrated cationic size of Cs^+ and divalent nature of the other cations, which requires two adjacent negative charge on the framework for successful ion exchange. The anomalous behavior of Mg is consistent with this hydrated cation having the largest cationic radius. At elevated temperature however, 65°C, much higher uptake was observed and the order was $Sr > Ca > Ba > Mg$. Since Mg possess the smallest bare cationic radii, this anomalous behavior is most likely due to it having highest hydration energy.

3.4.2 NaMnAPO5

Kinetic studies for monovalent exchanges on NaMnAPO5 (Figure 4) show similar behavior to that of NaMAPO5. It should be noted that when the ion exchange experiments were performed with pure deionized water as the exchange solution, the percent release of Na^+ was less than 5%, most likely as a result of Na^+/H^+ exchange (hydrolysis). This helps to confirm that in the other experiments genuine ion exchange processes were occurring and that the MeAPO samples indeed contained cationic sites.

4.0 Conclusion

Results from ion exchange experiments confirm the substitution of divalent ions in the framework structure of the respective MeAPOs and the resulting generation of cationic sites.

5. Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS) studies of the acidic properties of MeAPOs

Experiments are in progress to conduct Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS) studies on the acidic properties of MeAPOs (Me = Co, Mg, Mn and Zn) using adsorption of basic probe molecules such as CO, NH₃ and pyridine. These experiments are expected to give information on the strengths and distribution of acid sites in MeAPOs. Experiments are so far, incomplete and results will therefore be presented in the next quarterly report.

6. Other activities:

Efforts from our research group were also concentrated on the preparation of manuscripts for publication in Applied Catalysis Journal and Preprints of ACS National Meeting in New Orleans, March, 1996 (see attached correspondence from the editors).

Figure 1

Percentage Na⁺ released from MEAPOS by NH₄⁺

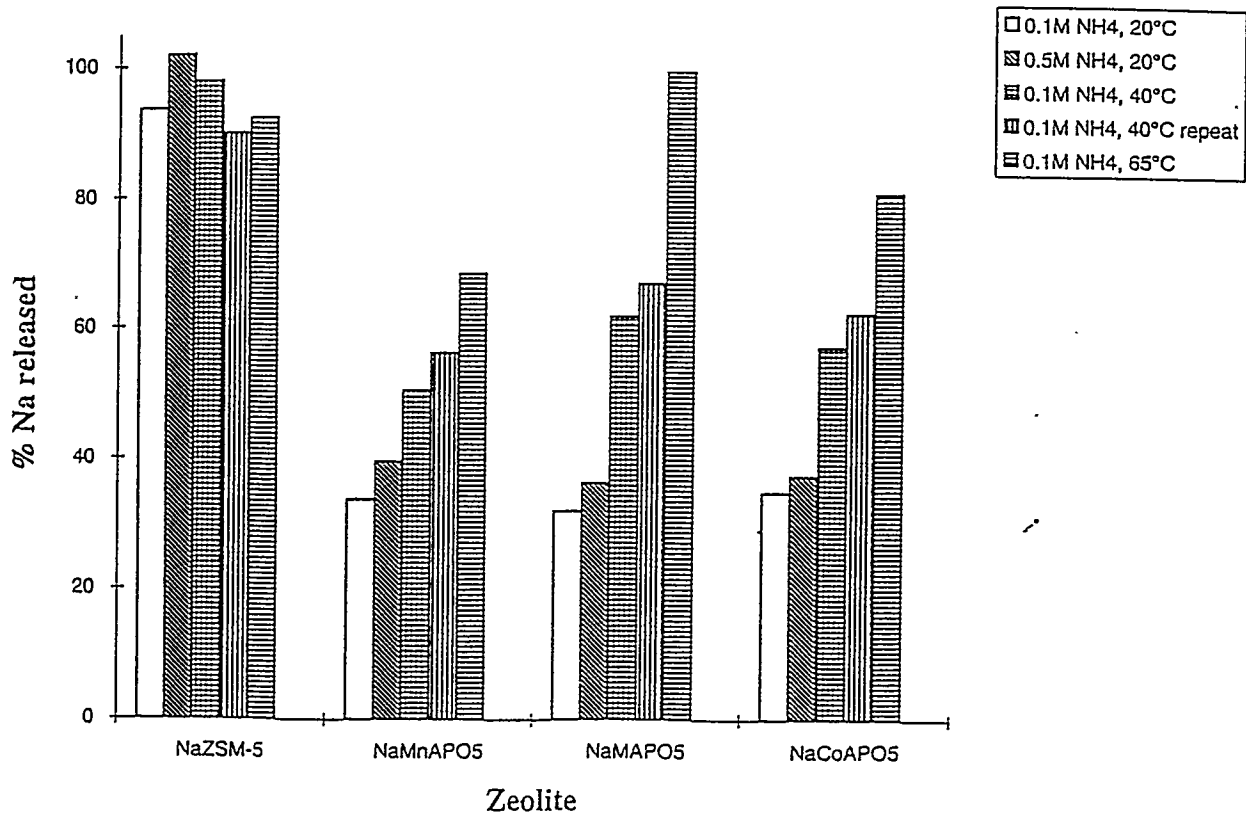


Figure 2

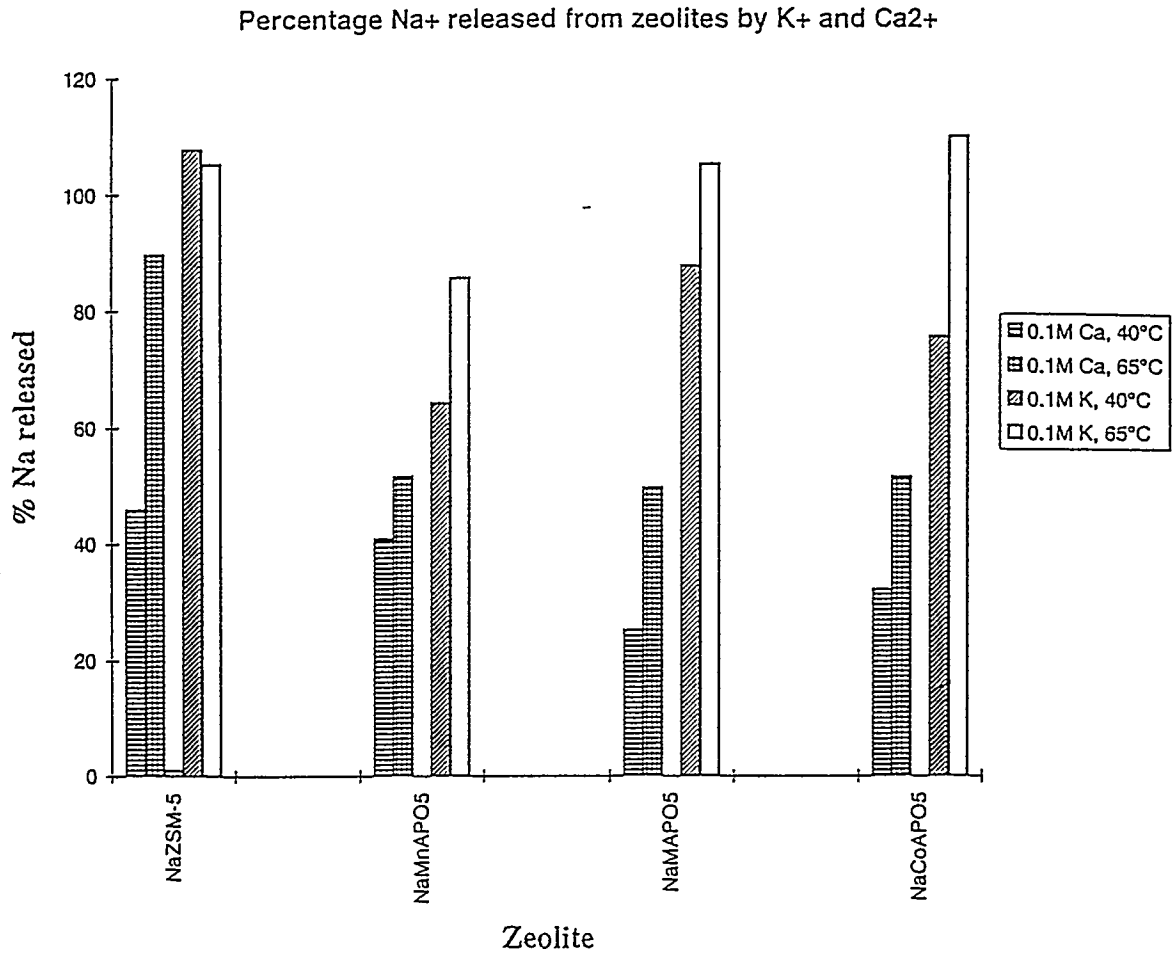


Figure 3

Kinetics of Na release on MgAPO-5

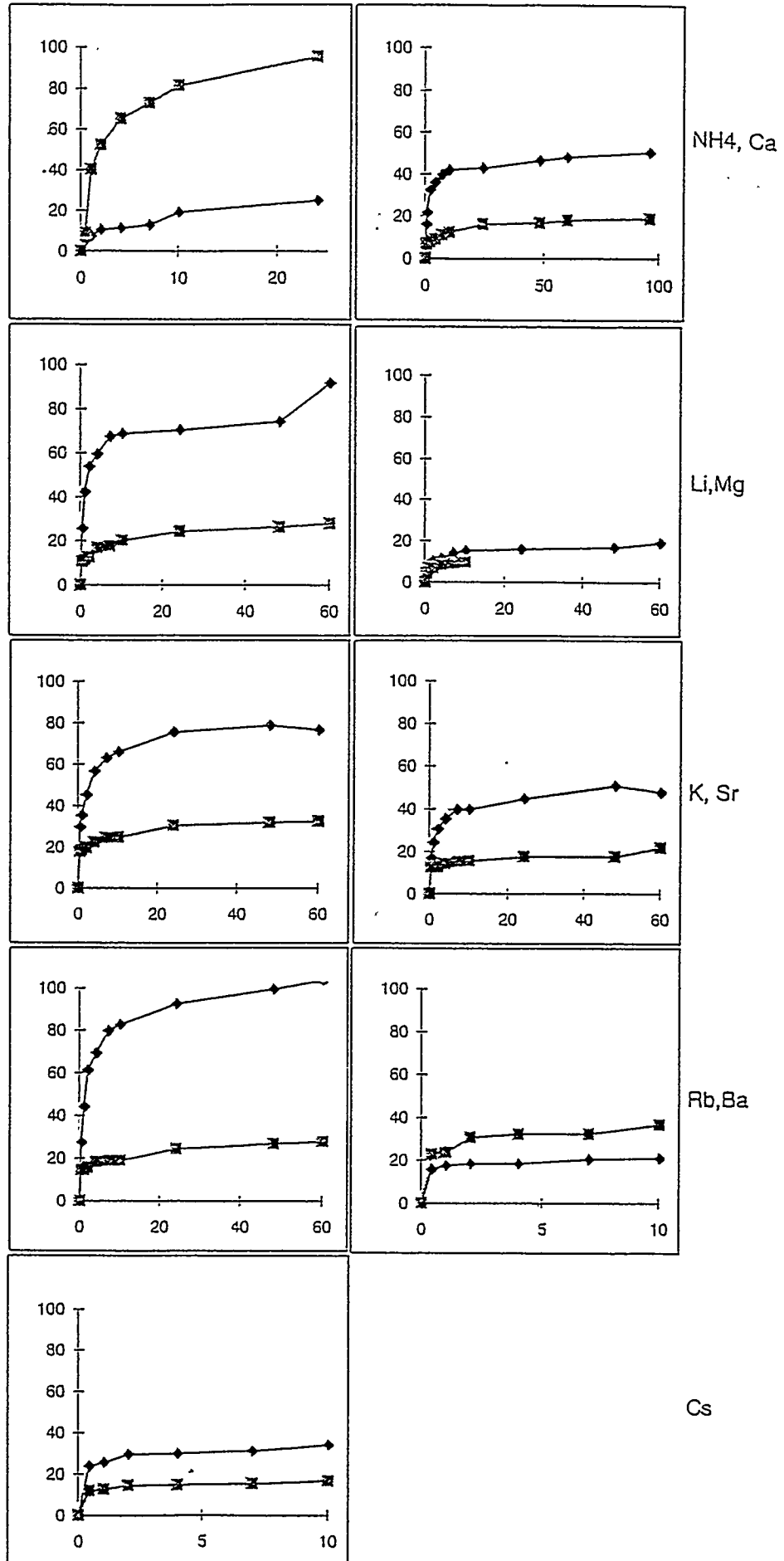
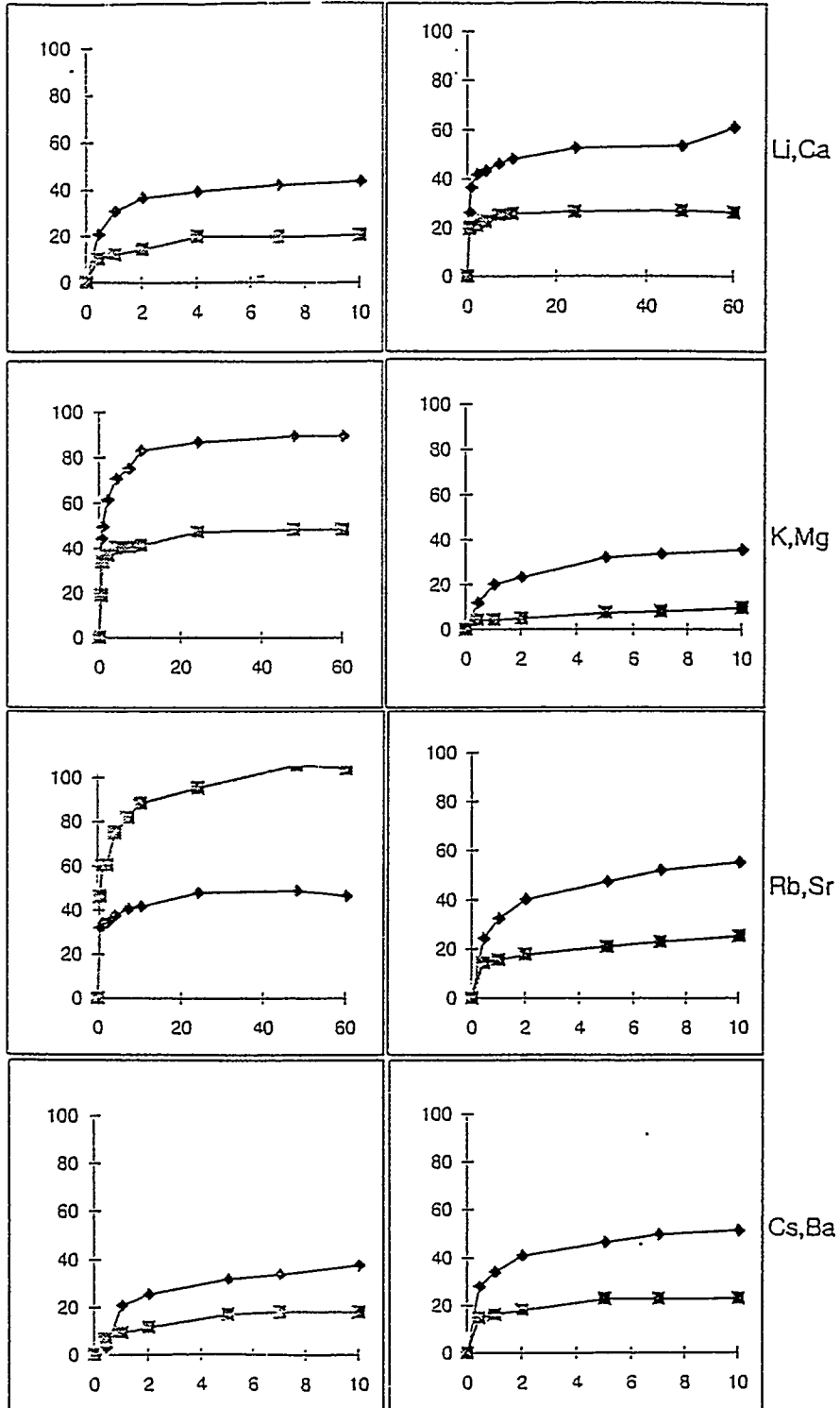


Figure 4

Kinetics of Na release on MnAPO-5



APPENDIX 1

Dr. Rosemarie Szostak
Department of Chemistry
223 James P. Brawley Drive
Clark Atlanta University
Atlanta Georgia 30314
USA
Phone: 404-880-6861
Fax: 404-880-6890
E-mail: rszostak@cau.edu

21st November, 1995

Professor Imre Kiricsi
Applied Chemistry Department
Josef Attila University
H-6720 Szeged
Rerrich Bela ter 1
Hungary

Re: Metal substituted aluminophosphate molecular sieves as phenol hydroxylation catalysts.

Dear Professor Kiricsi,

Enclosed please find three copies of the revised manuscript with the captioned title. We hope that our revised version will satisfy the referees' comments.

Sincerely,



Conrad Ingram, Ph.D.

for Rosemarie Szostak

Appendix 2

Prof. Imre Kiricsi
Applied Chemistry Department, József Attila University,
H-6720 Szeged, Rerrich Béla tér 1, Hungary
Phone: 36-62-321-523, Fax: 36-62-321-523,
E-mail: I.KIRICSI@CHEM.U-SZEGED.HU



Professor R. Szostak
Chemistry Department
Clark Atlanta University
Atlanta, Georgia
USA

Dear Professor Szostak,

Your paper has been accepted for publication in the Special Issue of Applied Catalysis. Enclosed, please find the comments of the referees. Please, revise the manuscript in accordance with the recommendations and send it to me in due course.

Szeged, October 24, 1995.

Yours sincerely



January 24, 1996

Dear Colleague

Your paper has been scheduled for an oral presentation and the draft schedule of the symposium is enclosed. You should book your transportation to and from New Orleans right away if you have not already done this. Housing and registration information should be available from the American Chemical Society in the January 22 issue of Chemical and Engineering News. A copy of this information is enclosed and you should arrange for your registration and hotel as soon as possible to allow the registration badge and materials to arrive to you before leaving for the meeting. Both registration and hotel arrangements may be made via FAX to the American Chemical Society at 2028724081 by providing a credit card for your registration and to guarantee your hotel. Arrangements should be made right away for best location and prices. The advance registration fee will be \$200 and the on-site registration fee will be \$235. Please register before the deadline of Feb. 23. The symposium will be held in the Hilton Hotel near the Convention Center. Those interested in staying in the Hilton should write Hilton and not Hilton Towers on your form if you want the cheaper rates at the Hilton. The final schedule will be published in the February 19 issue of Chemical and Engineering News. I look forward to seeing you in New Orleans.

Sincerely,

S. Ted Oyama
Associate Professor

See pg 3.

Panel 1
Jan 6:6

Catalysis: Heterogeneous Hydrocarbon Oxidation
Spring ACS Meeting, New Orleans, LA
March 24-29, 1996

B. K. Warren and S. T. Oyama, organizers

Sunday AM, C. M. Friend, presiding

Characterization of Catalytic Surfaces and Reactive Intermediates

8:50 B. K. Warren
Welcome and Introduction

9:00 A. Guerrero-Ruiz and I. Rodriguez-Ramos
Interaction of CO₂ with ZnO Powders of Different Microcrystalline Surfaces
Facultad de Ciencias, UNED
SPAIN

9:25 C. W. J. Bol and C. M. Friend
Partial Oxidation of Alkyl Fragments on Rhodium
Harvard University
USA

9:50 X.-C. Guo and R. J. Madix
Not Partial?
Stanford University
USA

10:15 BREAK

10:30 E. M. Gaigneaux, D. Herla, P. Tsiakaras, U. Roland, P. Ruiz and B. Delmon
Catalytic Cooperation via Spillover of Oxygen: Dehydration-Dehydrogenation of Sec-Butanol Over SnO₂-MoO₃ Catalysts
Université Catholique de Louvain
BELGIUM

10:55 D. Wei, A. Hagen and G. L. Haller
Catalytic Behavior of Vanadium and Titanium Substituted Mesoporous Molecular Sieves in Gas and Liquid Phase Oxidations of Hydrocarbons
Dept. of Chemical Engineering, Yale University
USA

11:20 S. Ted Oyama and W. Zhang
Observation of True and Spectator Intermediates During Catalytic Ethanol Oxidation by In Situ Laser Raman Spectroscopy
Virginia Polytechnic Institute and State University
USA

8:55 Ag. Kh. Mamedov
Heterogeneous-Oxidative Catalysis by CO₂ Properties and Reactivity of the
Oxygen, Generated from CO₂
Institute of Petrochemical Processes
AZERBAIJAN

9:20 P.-S. E. Dai, R. H. Petty, C. W. Ingram and R. Szostak
Catalytic Hydroxylation of Phenol over MeAPO-11 Molecular Sieves
Texaco Research, Port Arthur, and Clark Atlanta University
USA

9:55 BREAK

Advanced Materials for Catalytic Oxidation

10:10 I. E. Wachs, G. Deo, J. M. Jehng, D. S. Kim and H. Hu
The Properties of Supported Metal Oxide Catalysts During Oxidation Reactions
Lehigh University
USA

10:35 Kiyotomi Kaneda and Shinji Ueno
Development of Hydrotalcite Catalysts in Heterogeneous Baeyer-Villiger Oxidation
Osaka University
JAPAN

11:00 T. Hayashi, K. Tanaka and M. Haruta
Selective Partial Oxidation of Hydrocarbons over Au/TiO₂ Catalysts
Nippon Shokubai Co., Ltd.
JAPAN

11:25 I. Peeters, J. van Grondelle, R. A. van Santen
The Oxidative Ammonolysis of Ethylene to Acetonitrile over γ -Al₂O₃
Supported Molybdenum Catalysts
Eindhoven University of Technology
THE NETHERLANDS

Monday PM, I E. Wachs presiding

1:30 L.-C. Kao, H. C. Foley and A. M. Gaffney
Direct Oxidation of Propylene over Carbogenic Catalytic Materials
ARCO Chemical Company
USA

1:55 E. van Steen, M. Schnobel and C. T. O'Connor
Selective Partial Oxidation of α -Olefins over Iron Antimony Oxide
University of Cape Town
SOUTH AFRICA