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Subject: Semiannual Technical Progress Report for
DOE Contract No. DE-FG22-95PC95218

Dear Sir/Madam:

As requested, enclosed are three (3) copies of the Technical
Progress Report for the above referenced contract.

If any Additional Information is needed, please contact me at
(404) 880-6981.

Thank you.

Sincerely,

[Handwritten signature of Mavis Rossell]

Mavis Rossell
Project Assistant
Program Administration

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LOW TEMPERATURE VOC COMBUSTION OVER MANGANESE, COBALT AND ZINC
ALPO₄ MOLECULAR SIEVES

Semi-Annual Report -1

For

September 1, 1995 - February 29, 1996

Grant #: DOE-FG22-95PC95218

DOE Project Officer: Dr. Kamalendu Das

Contract Specialist: Dona G. Sheehan

Award Date: July 07, 1995

Anticipated Completion date: August 31, 1997

Principal Investigator: Dr. Rosemarie Szostak

Telephone Number: (404) 880-6861

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

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1.0 Introduction

The objective of this project is to prepare manganese, cobalt and zinc containing AlPO_4 large pore molecular sieves of structure type -36 and evaluate their ability to function as successful oxidation catalysts for the removal of low levels of VOC's from gas streams.

The tasks to be accomplished are as follows: 1) To develop reliable synthesis methods that produce the large pore metal aluminophosphates containing manganese, cobalt and zinc in their framework. 2) To characterize these materials to determine phase purity and the location of the incorporated metal in the framework. Characterization will also include the nature of the active sites within the structures and the effect manganese, cobalt and zinc has on the structures' acidity. 3) To screen the material for their catalytic activity in the oxidation of hydrocarbons and aromatics.

This report gives a summary of the status of the project as of 28th February 1996.

2.0 Work done

2.2 Synthesis and characterization of MeAPO-36

2.2.1 Materials and equipment

Pseudoboehmite alumina - Catapal B (Vista Chemical Co)
Aluminum hydroxide (Aldrich, or Pfaltz and Bauer)
Aluminum isopropoxide (Fluka)
Orthophosphoric acid (Fisher)
Tripropylamine (Aldrich)
Magnesium acetate (Fisher)
Manganese acetate (Fisher)
Zinc acetate (Fisher)
Cobalt acetate (Fisher)
Stainless steel Teflon lined autoclaves (15 and 25 mL capacities)
Fisher Isotemp ovens
Magnetic stirrers
Phillips X-Pert Diffractometer

2.2.2. Synthesis procedure

In a typical synthetic procedure, phosphoric acid was first mixed with deionized water in a plastic container. In a separate container, a known weight of manganese, cobalt or zinc acetate was first dissolved in deionized water and the resulting solution gradually added to the acid mixture. The aluminum source (alumina, aluminum hydroxide or aluminum isopropoxide) was then gradually added in small quantities and the mixture was stirred

continuously until a homogeneous gel was obtained. The structure directing agent, tripropylamine, was then slowly titrated in the stirred gel and the final mixture transferred into stainless steel Teflon lined autoclaves. The autoclaves were placed in ovens where the gel was allowed to crystallize hydrothermally under autogenous pressure initially at 100°C for 2 days, and then at 150°C for 2-4 days. The solid products were recovered by filtration and/or centrifugation and dried at temperatures varying from ambient to 100°C.

2.2.3 Catalysts characterization by XRD

As a preliminary characterization procedure, a sample of the "just crystallized", unfiltered solid product was smeared on a glass slide and the morphology of the crystallites was observed under an optical microscope. Structural characterization of samples were performed using a Phillips X-Pert Diffractometer equipped with Cu-K α radiation ($\lambda = 1.5406$ angstroms) and xenon detectors. Scans were recorded from 5.0 to 50.0 degrees 2θ . The system was controlled by a Gateway 2000 Computer with Phillips powder diffraction software.

2.2.4 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 NH $_3$, CO, NO and pyridine. These experiments are expected to give information on the oxidation states of metals as well as the strengths and distribution of acid sites in MeAPOs.

Experimental Details: CoAPO-36 molecular sieve, (sample #DS030295A) and MgAPO-36 (sample ID# CI010695C) were synthesized from reaction mixtures of molar compositions given in Table 1. The samples were washed, dried and calcined in a tube furnace at 500°C in a flowing stream of dry nitrogen for 4 hr, and then at 550°C for 12 hr in flowing stream of dry air. XRD analysis shows that the samples remained highly crystalline before and after calcination. The IR spectra were recorded using a Nicolet 400 FTIR with diffuse reflectance attachments. A 20 mg sample was placed as a thin surface on top of a lower KBr layer in a DRIFT cell. The cell was evacuated at 1×10^{-4} torr for 0.5 hr at 25°, 100°, 200°, 300° and 400°C at which temperatures the IR spectra were also recorded. The cell was then water cooled to 100°C and a spectrum recorded as reference. 10 torr of dry ammonia was passed over the sample for 0.5 hr, followed by evacuation of excess and physisorbed ammonia for 0.5 hr at 1×10^{-4} torr. The IR spectrum was recorded. The sample was then heated to 400° for 2 hr under vacuum to desorb ammonia. On cooling to 100°C another spectrum was then recorded.

3.0 Results and Discussion

3.1 Synthesis of MeAPO-36

A range of MeAPO-36 with various types and amounts of metal in their frameworks was synthesized. The general mole ratio compositions of the reaction gels was $2.0(\text{CH}_3\text{CH}_2\text{CH}_2)_3\text{N}:x\text{MeO}:0.98\text{Al}_2\text{O}_3:1.0\text{P}_2\text{O}_5:40\text{H}_2\text{O}$, where Me represents Mg, Mn, Co and Zn. For each metal, four variations of x between 0.05 and 0.40 were prepared. Figure 1 shows a representative X-ray powder diffraction pattern of the samples.

3.2 Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS) studies on MeAPOs

On calcination in N_2 followed by air the sample #DS030295A showed a color change from blue to yellow-green with a small amount of blue remaining. The color change is ascribed to the oxidation of framework Co^{2+} to Co^{3+} while the remaining blue portion is proposed to be due to unoxidized Co^{2+} present in the pores of the molecular sieve as ion-exchanged cations. DRIFT spectra of calcined CoAPO-36 and MgAPO-36 after evacuation and successive heating to 400°C shows peaks at 3666 cm^{-1} for CoAPO-36 and 3674 cm^{-1} for MgAPO-36, assigned to the weak or non-acidic P-OH and Al-OH groups.¹ Figure 2 shows the stack spectra for CoAPO-36. A vibration band observed around 3599 cm^{-1} in both samples is not yet identified but is tentatively assigned to acidic hydroxyls of Al-OH-Me bond, based on similar vibration assigned to Bronsted acidic OH group in zeolite faujasite.²

On exposure of CoAPO-36 to ammonia, a partial reversal of color change from green-yellow back to grey-blue occurred. The difference spectrum of the sample after exposure to 10 torr of dry ammonia for 0.5 hr followed by evacuation, resulted in the disappearance of the vibration band around 3590 cm^{-1} and the presence of a negative peak at 3683 cm^{-1} possibly due to interaction of NH_3 with hydroxyls. On desorbing ammonia at 400°C , the vibration band at 3590 cm^{-1} returned, while the negative peak around 3683 cm^{-1} persisted.

These IR studies are preliminary and further experiments will be done that will hopefully clarify the oxidation states of the metals as well as the acid-base interaction phenomena observed in these samples.

3.3 Synthesis of TS-1 catalyst

TS1 is a silicon and titanium containing zeolite that has been demonstrated to be catalytically active in phenol hydroxylation as well as other oxidation reactions. A new method for its reproducible synthesis from a $\text{SiO}_2\text{-TiO}_2$ cogel was recently reported.³ Using this approach, we have successfully synthesized the zeolite which we intend to use as an oxidation catalyst in this VOC project. Powder XRD was used to confirm the structure while IR spectrum was used to confirm the presence of Si-O-Ti bond and therefore confirm that Ti is indeed part of the lattice structure of the zeolite.

4.0 Future work

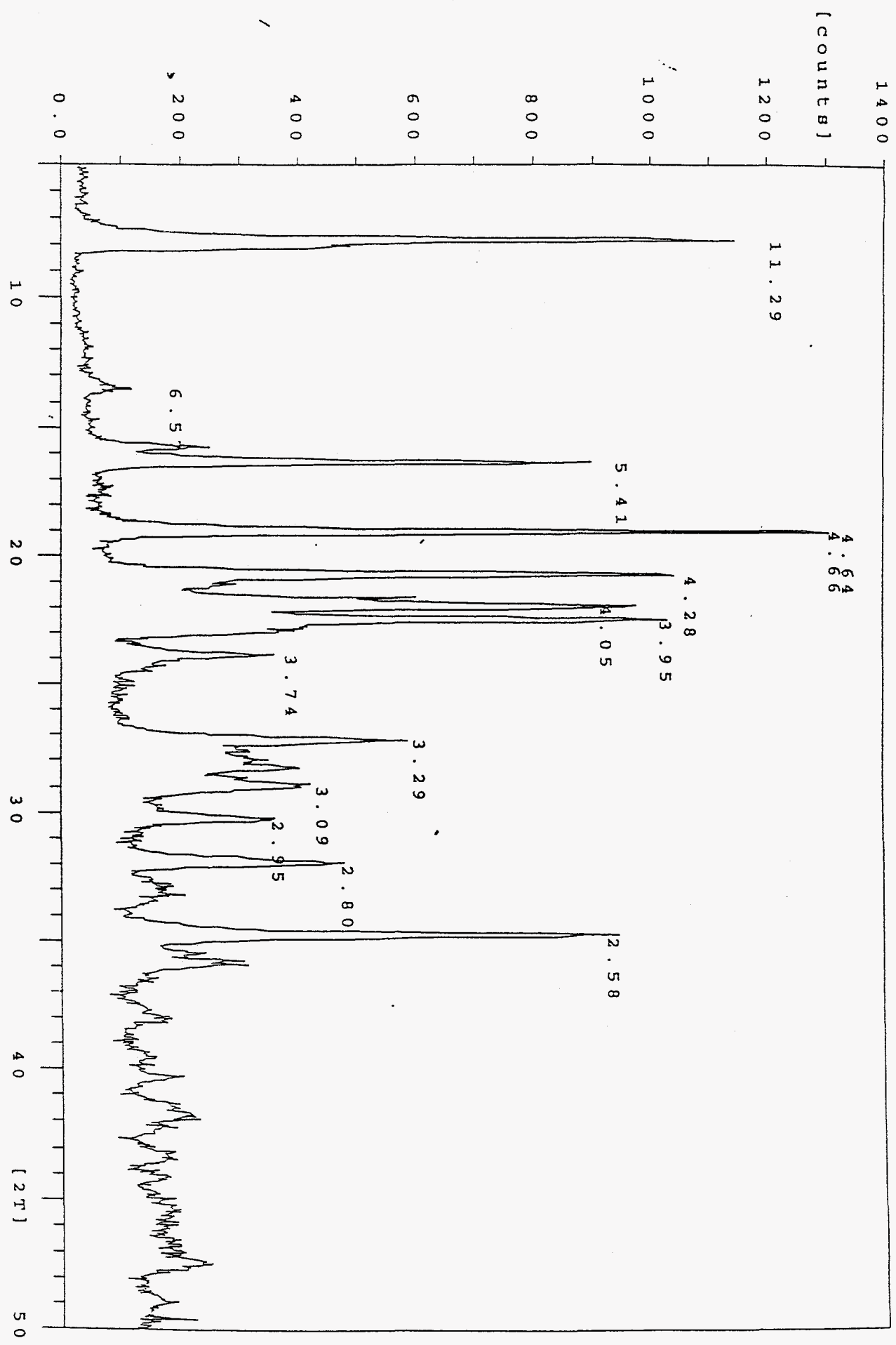
In keeping with overall objectives of this project, our effort will focus on the following activities: (1) Characterize MeAPO-36 samples for phase purity, location and amount of incorporated metal in their framework using XRD, acidity by ammonia TPD and surface area by nitrogen BET. (2) Modification of small bench scale catalytic reactor for screening of catalytic activity of materials. (3) Catalytic screening of samples for low temperature oxidation of VOCs.

References

- ¹ J. Janchen, M. J. Haanepen, M. P.J. Peeters, J. H. M.C. van Wolput, J. P. Wolthuizen, J. H. C. van Hooff, *Studies in Surface Science and Catalysis* **84**, (1994) 365.
- ² M. A. Markarova, A. Garforth, V. I. Zholobenko, J. Dwyer, G. J. Earl, D. Rawlence, *Studies in Surface Science and Catalysis* **84**, (1994) 365.
- ³ M. Uguina, G. Ovejero, R. van Grieken, D. Serrano, M. Camacho, *J. Chem Soc. Chem. Commun.*, (1994) 27.

Sample Identification: e031196a

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E03116A1.SD

Figure 1. XRD of COAPO-36

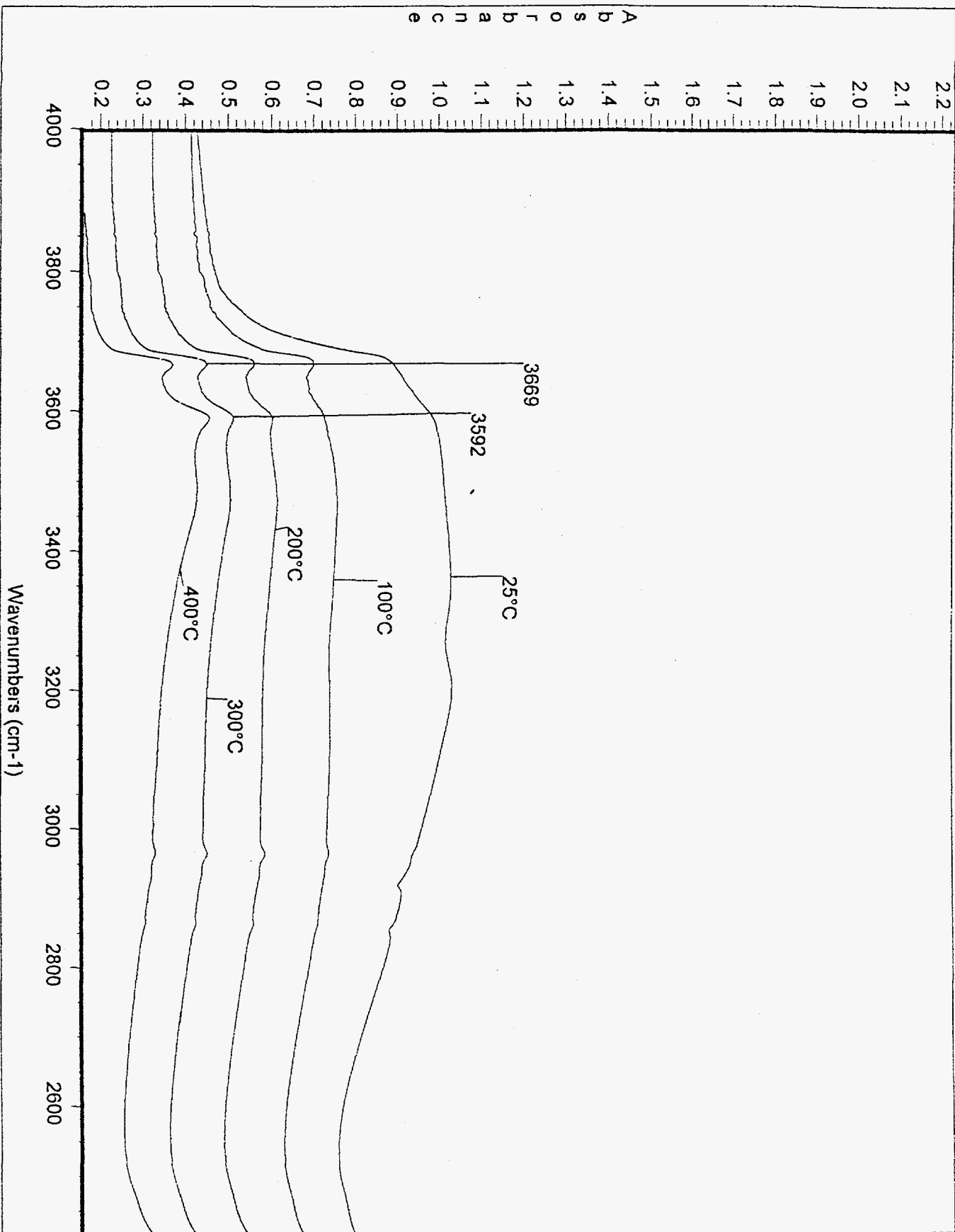


Figure . DRIFT spectra of CoAPO-36 at various temperatures

Table 1. MeAPO-36 prepared with varying metal content in synthesis gel

<u>Sample ID</u>	<u>*Mole ratio compositions of synthesis gel</u>
CoAPO-36	
CE032096B	2.0R:0.05MgO: 0.98Al ₂ O ₃ :1.0P ₂ O ₅ :40H ₂ O
CE031196A,B	2.0R:0.10MgO: 0.95Al ₂ O ₃ :1.0P ₂ O ₅ :37H ₂ O
DS030295A,B,C	2.0R:0.18MgO: 0.98Al ₂ O ₃ :1.0P ₂ O ₅ :37H ₂ O
CI052395A	1.9R:0.26MgO: 0.91Al ₂ O ₃ :1.0P ₂ O ₅ :38H ₂ O
MgAPO-36	
KC041296D,A	2.0R:0.05MgO: 0.98Al ₂ O ₃ :1.0P ₂ O ₅ :38H ₂ O
CM112995A,C	2.0R:0.10MgO: 0.87Al ₂ O ₃ :1.0P ₂ O ₅ :38H ₂ O
CI010695C,D,E	1.9R:0.18MgO: 0.98Al ₂ O ₃ :1.0P ₂ O ₅ :37H ₂ O
CI031595A,B	1.9R:0.26MgO: 0.91Al ₂ O ₃ :1.0P ₂ O ₅ :39H ₂ O
CM092595B,E,C	2.0R:0.40MgO: 0.79Al ₂ O ₃ :1.0P ₂ O ₅ :30H ₂ O
ZnAPO-36	
CE030796C,D	2.0R:0.05MgO: 0.98Al ₂ O ₃ :1.0P ₂ O ₅ :26H ₂ O
CM082895A	1.9R:0.09MgO: 0.96Al ₂ O ₃ :1.0P ₂ O ₅ :42H ₂ O
CM082495B	1.9R:0.17MgO: 0.91Al ₂ O ₃ :1.0P ₂ O ₅ :42H ₂ O
CI052495A,B,D,E	1.9R:0.18MgO: 0.93Al ₂ O ₃ :1.0P ₂ O ₅ :31H ₂ O
DS022195B	1.9R:0.26MgO: 0.99Al ₂ O ₃ :1.0P ₂ O ₅ :31H ₂ O
CE030896A,BCD	1.9R:0.20MgO: 0.91Al ₂ O ₃ :1.0P ₂ O ₅ :28.5H ₂ O
DS03149A,B	1.9R:0.40MgO: 0.88Al ₂ O ₃ :1.0P ₂ O ₅ :45H ₂ O
MnAPO-36	
CM112095A	2.0R:0.15MgO: 0.85Al ₂ O ₃ :1.0P ₂ O ₅ :56H ₂ O
DS030995A,B,C	1.9R:0.09MgO: 0.98Al ₂ O ₃ :1.0P ₂ O ₅ :32H ₂ O
CM110995,B,C,D	2.0R:0.20MgO: 0.79Al ₂ O ₃ :1.0P ₂ O ₅ :47H ₂ O
CI060695A,B,C,D	2.1R:0.25MgO: 0.87Al ₂ O ₃ :1.0P ₂ O ₅ :28.5H ₂ O

*R = tripropylamine

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