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

Prepared by: Dr. Rosemarie Szostak
Dr. Godfried Abotsi
Dr. Mark Mitchell
Dr. Conrad Ingram
Dr. Eugene Dai
Miss Crystal McClure
Mr. Dolon Silimon

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

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Abstract

MeAPO-36 containing various types and concentrations of metals (Mn, Co, Mg and Zn) in the reaction mixture were synthesized. Various levels of crystallinity were observed depending on the type and concentration of these metals and crystallization parameter. Calcination of the samples at 550°C resulted in varying levels of reduction in crystallinity depending on the type of divalent metal incorporated. MAPO-36 had the highest thermal stability. Ammonia TPD and IR spectrum of pyridine absorption show that MAPO-36 have concentrations of both Bronsted and Lewis acid sites. Preliminary catalytic evaluation on a wide range of MeAPOs show that they were active for the hydroxylation of phenol.

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1.0 Introduction

For the past three months our research activities on the titled project have been concentrated mainly on the synthesis and preliminary characterization of a range of metal-containing aluminophosphate of type 36 structure (MeAPO-36) for the conversion of syngas to liquids. Thus ZAPO-36, MAPO-36, MnAPO-36 and CoAPO-36 were prepared. For comparison of catalytic activity, metal containing aluminophosphate of varying pore sizes (medium pore 11, large pore 5, 46 and 50) were prepared and evaluated for hydroxylation of phenol. This report documents a summary of our progress thus far.

2. Synthesis and characterization of MAPO-36

2.1 Experimental procedure

Preparation of MeAPO-36 with various metal/aluminum ratio

The preparation of samples with various metal/aluminum ratios were performed using synthesis procedure as in Report # 1 (September 28, 1994 - January 28, 1995). *Tables 1 and 2* show the molar composition of the reaction mixtures.

Table 1: Molar Composition of reaction mixtures for preparation of MAPO-36

Molar composition	Mg/P	Al/P	(Mg+Al)/P
1.8 Pr ₃ N:0.000 MgO:1.22 Al ₂ O ₃ :1.20 P ₂ O ₅ :52.6H ₂ O	0.00	1.01	1.01
1.8 Pr ₃ N:0.096 MgO:1.17Al ₂ O ₃ :1.20 P ₂ O ₅ :52.6H ₂ O:0.19 HoAC	0.067	0.975	1.04
1.8 Pr ₃ N:0.156 MgO:0.92Al ₂ O ₃ :0.936 P ₂ O ₅ :41.4H ₂ O:0.31 HoAC	0.083	0.969	1.06
1.8 Pr ₃ N:0.217 MgO:0.91Al ₂ O ₃ :0.933 P ₂ O ₅ :41.4H ₂ O:0.48 HoAC	0.12	0.98	1.09
1.8 Pr ₃ N:0.242 MgO:0.82Al ₂ O ₃ :0.933 P ₂ O ₅ :41.4H ₂ O:0.48 HoAC	0.13	0.88	1.01

Table 2: Molar Composition of reaction mixtures for preparation of MeAPO-36

ID	Molar composition	Me/P	Al/P	(Me+Al)/P
A	1.8 Pr ₃ N:0.163 MnO:0.92Al ₂ O ₃ :0.936 P ₂ O ₅ :41.4H ₂ O:0.31 HoAC	0.087	0.969	1.06
B	1.8 Pr ₃ N:0.163 ZnO:0.92Al ₂ O ₃ :0.936 P ₂ O ₅ :41.4H ₂ O:0.31 HoAC	0.087	0.969	1.06
C	1.8 Pr ₃ N:0.242 ZnO:0.82Al ₂ O ₃ :0.933 P ₂ O ₅ :41.4H ₂ O:0.48 HoAC	0.13	0.88	1.01
D	1.8 Pr ₃ N:0.163 CoO:0.92Al ₂ O ₃ :0.936 P ₂ O ₅ :41.4H ₂ O:0.31 HoAC	0.087	0.969	1.06
E	1.8 Pr ₃ N:0.242 CoO:0.92Al ₂ O ₃ :0.936 P ₂ O ₅ :41.4H ₂ O:0.48 HoAC	0.13	0.969	1.06

Characterization: Characterization using optical microscopy and X-Ray Diffraction was performed using techniques reported in our earlier communication. Thermogravimetric analysis was performed using a Seiko SSI TGA/DTA 220 Analyser. Samples were heated from 20 °C to 700 °C at a rate of 20°C/min. Infrared measurements of pyridine was performed using Diffuse Reflectance FTIR (on a Nicolet 400 IR spectrometer). The *in situ* acidity measurements were performed on samples which were diluted 10% in KBr. The sample was loaded in calcium fluoride cell which was subsequently sealed and evacuated to a pressure of 10⁻² Torr and a temperature of 400 °C for 1 hr. After cooling to 200°C, 10 Torr of fresh pyridine was adsorbed for 1 hr. The cell was then evacuated at 10⁻² Torr for 1 hr after which the IR spectrum was recorded.

3.0 Results and discussion

Synthesis of MAPO-36: Observations in *Table 3*, and **Figure 1** seem to suggest that the formation of the type 36 structure requires the presence of the divalent metal salt, since the absence of the latter result in the formation of AIPO-5 as the only crystalline phase. This is not unusual, since the synthesis AIPO-36 still poses a challenge to researchers. Another observation is that high levels of Mg tend to promote the formation of impurity phases in the product. However these syntheses will be repeated to evaluate the consistency of these observations.

Table 3. The effect of Mg/P ratio on product formation.

Mg/P (see <i>Table # 1</i>)	Crystallization conditions	Product
0.00	100 °C, 48 hr, 150°48 hr	AIPO-5
0.067	100 °C, 48 hr, 150°48 hr	un* (crystalline)
0.083	100 °C, 48 hr, 150°48 hr	MAPO-36
0.12	100 °C, 48 hr, 150°47 hr	MAPO36 (with minor impurity)
0.13	100 °C, 48 hr, 150°68 hr	MAPO-36 (with minor impurity)

un*-unidentified

Synthesis of other MeAPO-36s:

CoAPO-36: From reaction mixture in *Table 2* sample D, **Figure 2** shows that highly crystalline, deep blue, CoAPO-36 can be synthesized in 24 to 72 hr at 150 °C using conditions similar to that reported for MAPO-36.¹ With higher levels of Co added to the mixture (*Table 2*, sample E), the product was of poor crystallinity, containing either CoAPO-5 or 50/50 mixture of 5 and 36 structures.

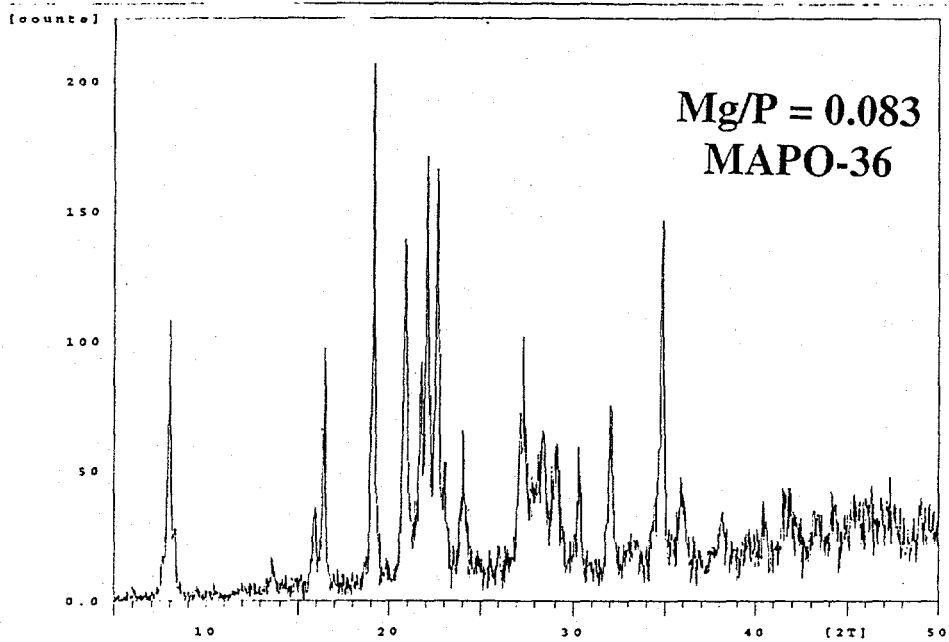
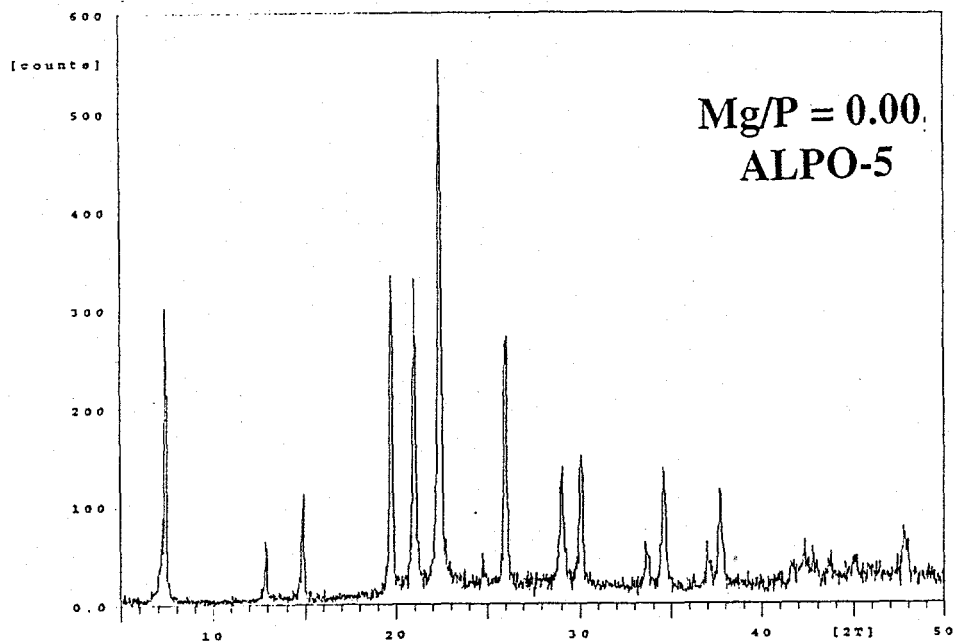
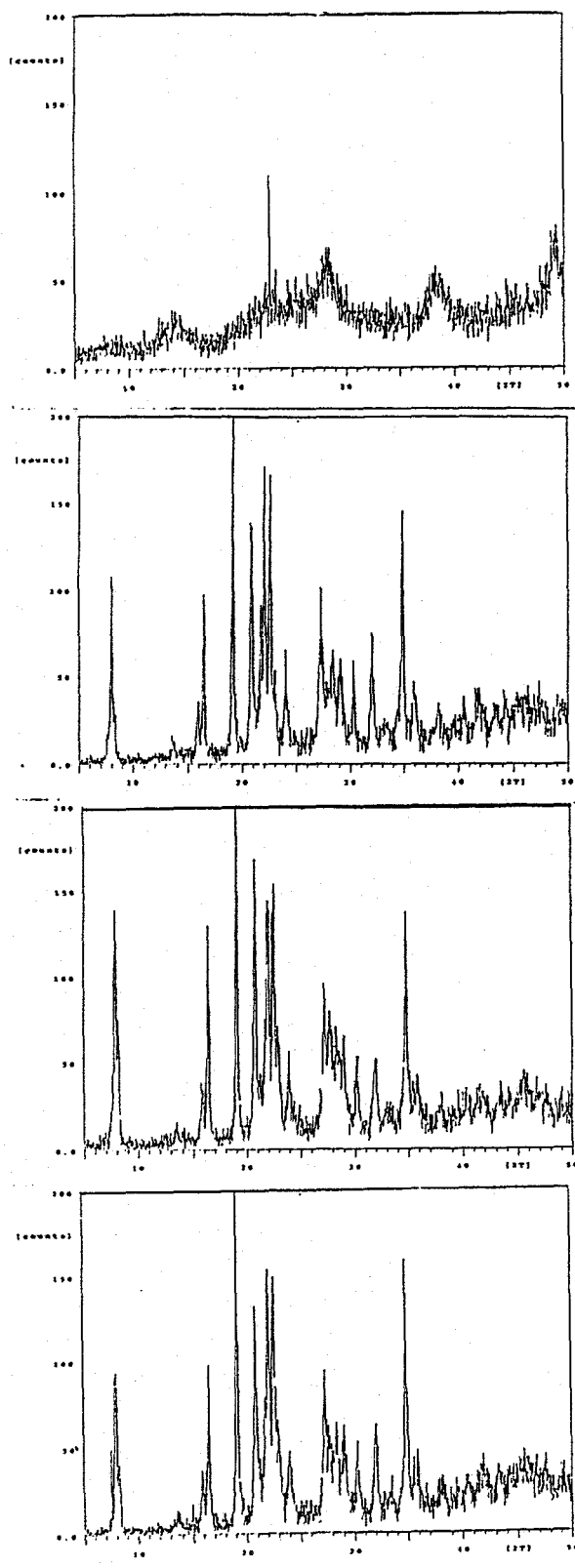


Figure 1: XRD patterns showing crystalline phase obtained vs magnesium content



100°C, 4 days

100 °C, 2dys
150°C, 1dy

100 °C, 2dys
150°C, 3dy

150°C, 3dy

Figure 2: XRD patterns showing crystallization of CoAPO-36 vs temperature and time

MnAPO-36 and ZAPO-36: From reaction mixtures in *Table 2*, sample A and B, highly crystalline, ZAPO-36 and MnAPO-36 respectively, can be synthesized after 24 hr at 150°C after preliminary heating at 100°C for 48 hr. XRD pattern of the sample was essentially similar to that observed for the corresponding crystallization condition of CoAPO-36 shown in *Figure 2*. Samples prepared after longer crystallization times are not yet characterized.

TGA: *Figure 3* shows the thermograms (TG) of four highly crystalline samples of MeAPO-36 (Me = Mg, Zn, Mn and Co). The TG shows that in all samples various weight loss events were occurring as the samples were heated from 20°C to 700°C corresponding to the initial loss of water and the latter decomposition of the tripropylamine. In all cases, the decomposition of the amine was complete by 500°C, with the DTA curves showing significant exothermic peaks between 385°C and 500°C. A detailed quantitative assessment of the various weight loss events will be done at a later date.

Effect of calcination on the crystallinity: *Figure 4* shows a comparison of the precalcined and calcined MeAPO-36 samples. Varying degrees of loss of crystallinity can be observed depending on the metal content. MAPO-36 maintained high crystallinity. The order of thermal stability's was therefore: MAPO-36 > CoAPO-36 > ZAPO-36 > MnAPO-36. Color changes were also observed among the samples after calcination. CoAPO-36 turned green and MnAPO-36 turned violet, whereas MAPO-36 and ZAPO-36 remained white. These colour changes may result from of a changes in the oxidation states or coordination numbers of the transition metals and will therefore be the subject of further investigation.

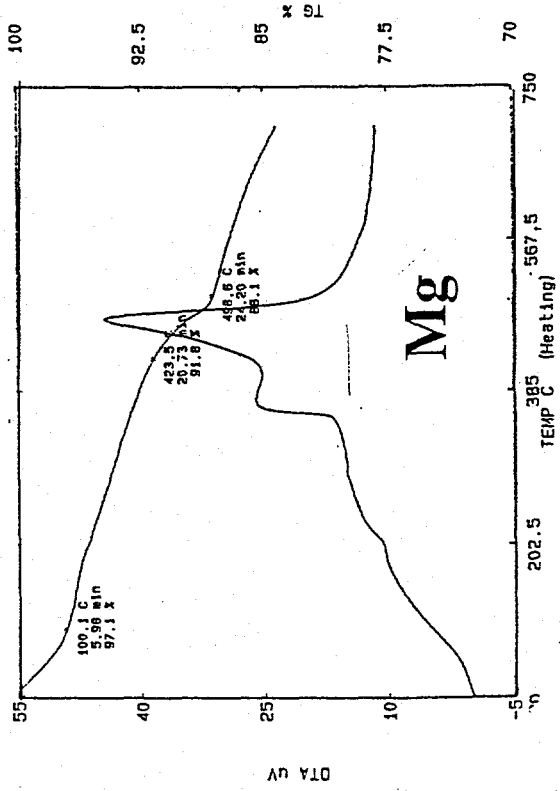
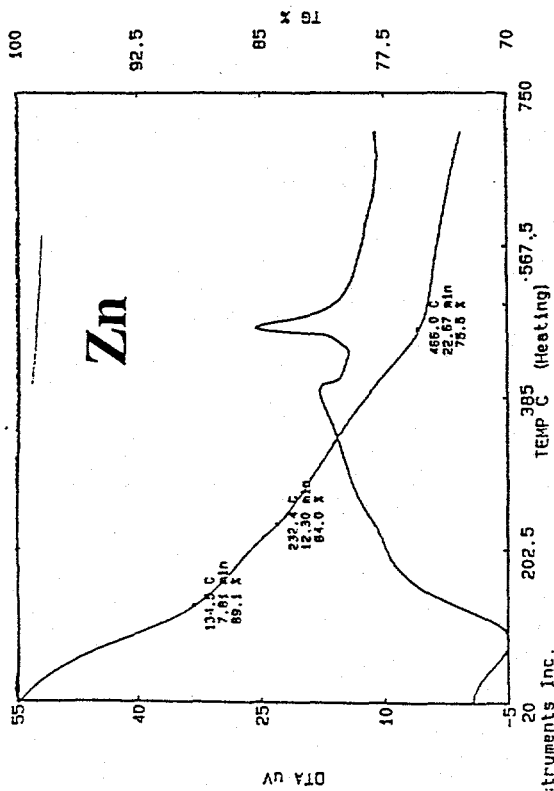
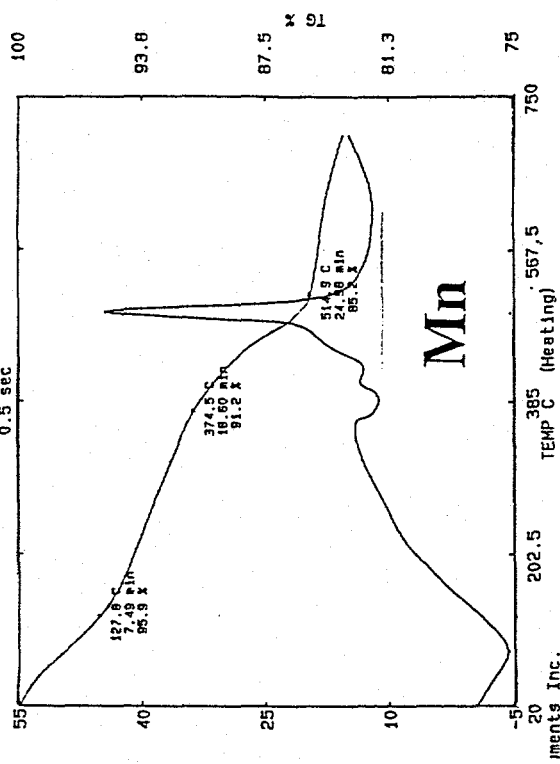
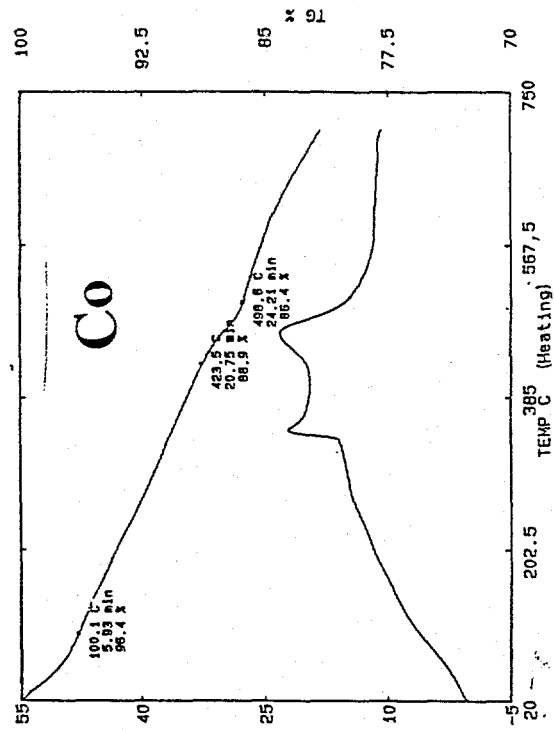


Figure 3: Thermal analysis curve of MeAPO-36

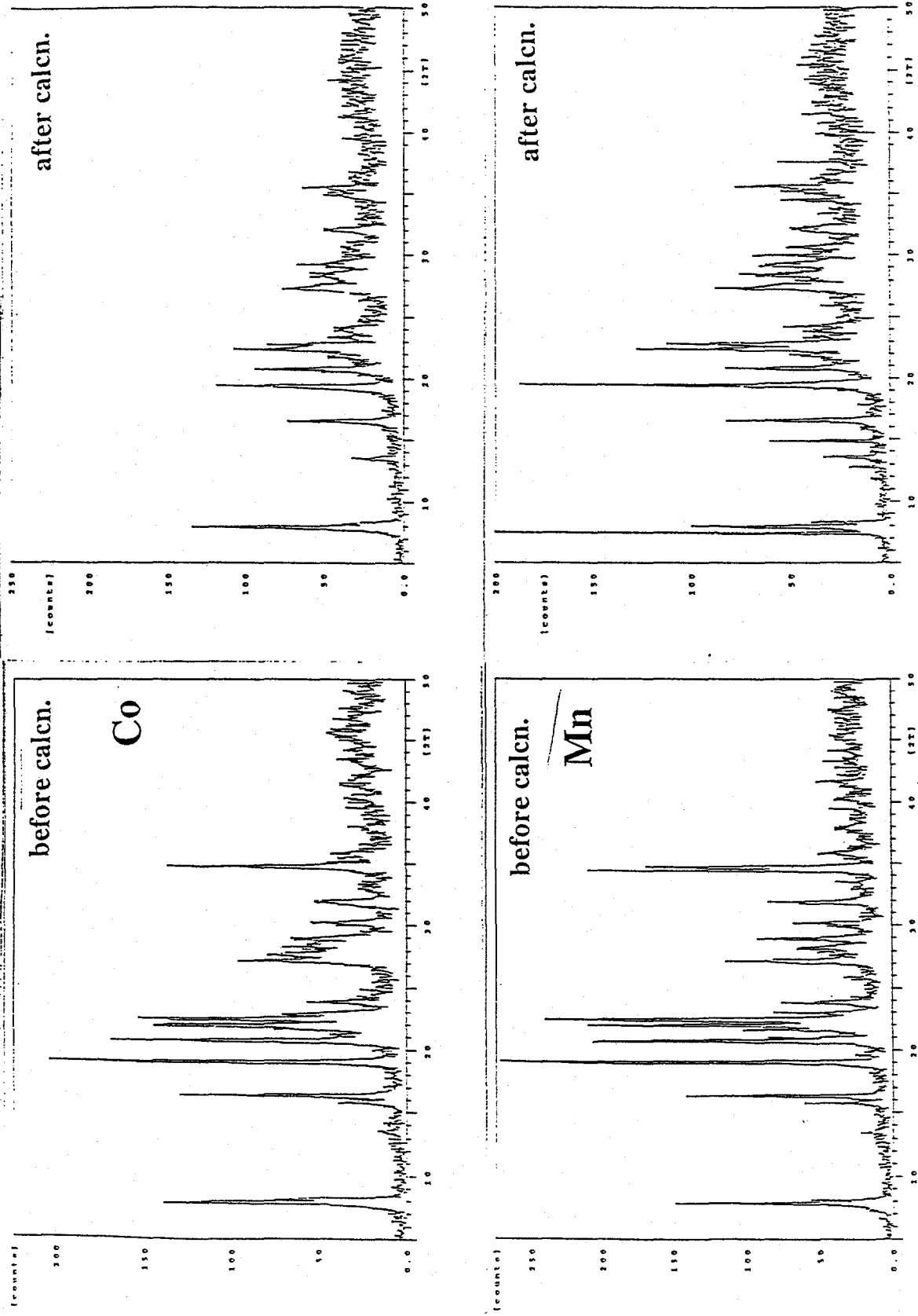


Figure 4: The effect of calcination on the crystallinity of MeAPOs

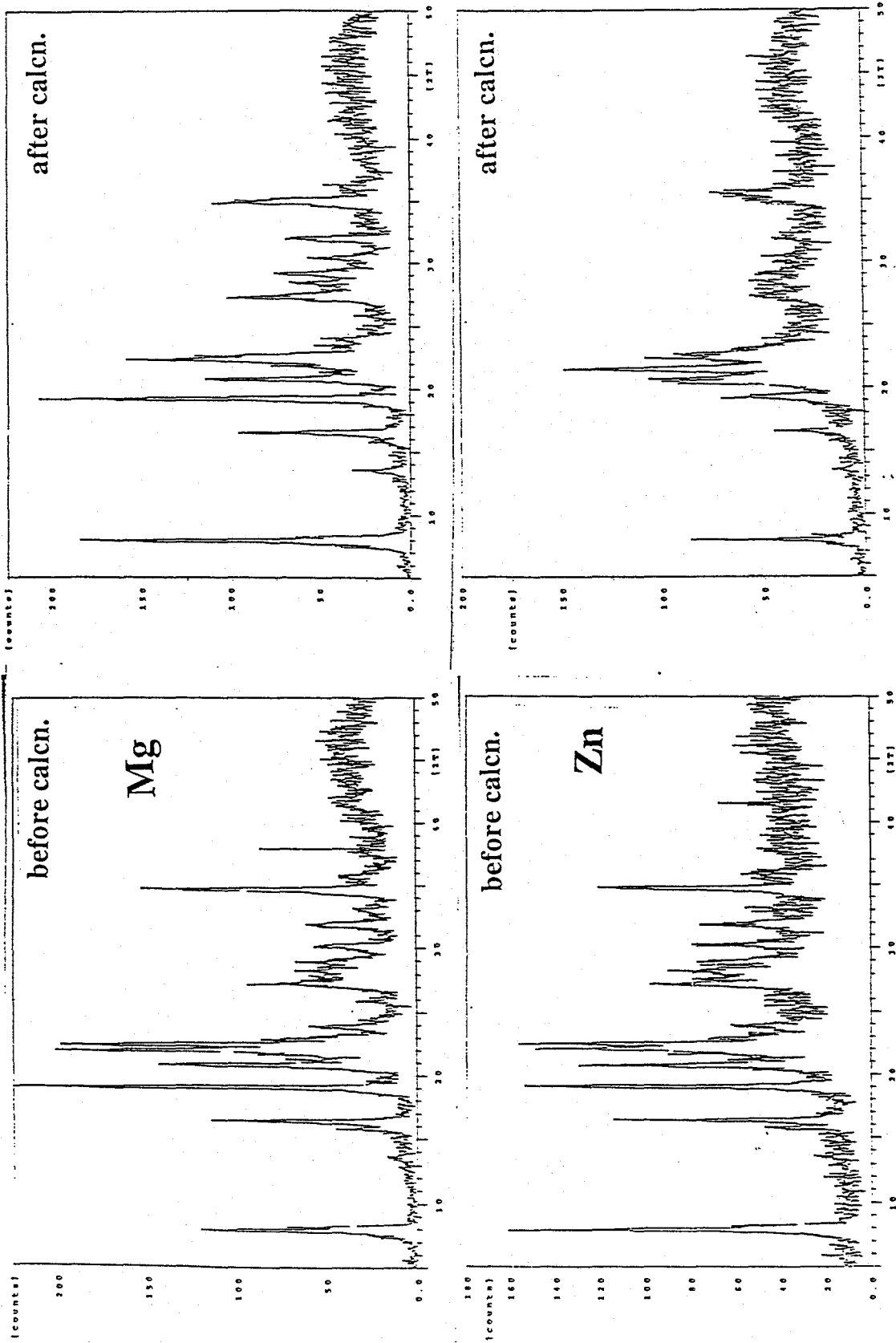
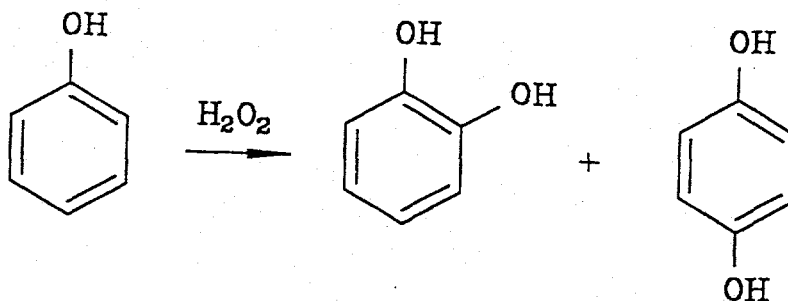


Figure 4 (contd.): The effect of calcination on the crystallinity of MeAPOs

Acidic properties from IR absorption of pyridine: The spectrum recorded after the absorption of pyridine gave rise the new absorption bands in the region $1400 - 1700 \text{ cm}^{-1}$. Figure 5 shows the spectrum resulting from the subtraction of the spectrum before and after the absorption of pyridine on calcined MAPO-36. The bands at 1449 , 1490 and 1545 cm^{-1} were ascribed to pyridine absorbed on Lewis, Lewis and/or Bronsted and Bronsted acid sites, respectively. This shows that MAPO-36 has Bronsted acidity, as expected from the hypothetical substitution of Mg^{2+} for Al^{3+} in the framework.

Acidic properties from ammonia TPD: These experiments were performed at Texaco R& D on MgAPO-36 and CoAPO-50 in order to quantify the concentration of acid sites in the materials. Figure 6a, b and c shows that in TPD profiles of some APO-36 samples. The summary of these figures is that a large concentration of weak acid sites were observed below 320°C , a smaller concentration of medium strength at 320°C to 450°C , and still a smaller concentration of very strong acid sites between 450°C and 520°C for all samples. Figure 7 shows the variation of acidity as a function of crystallization time for MgAPSO-46. It can be observed that maximum acidity of all types was observed after crystallization at 200° for 94 hr. Figure 8 shows that, with the APO-50 large pore structure, a large various levels of strengths and concentration of acid sites were observed depending on the metal content. The order was $\text{Mn} > \text{Co/Mn} > \text{Co}$.

Catalytic evaluation for the hydroxylation of phenol: The hydroxylation of phenol to hydroquinone and cathecol a metal catalyzed reaction and is represented by the following equation:



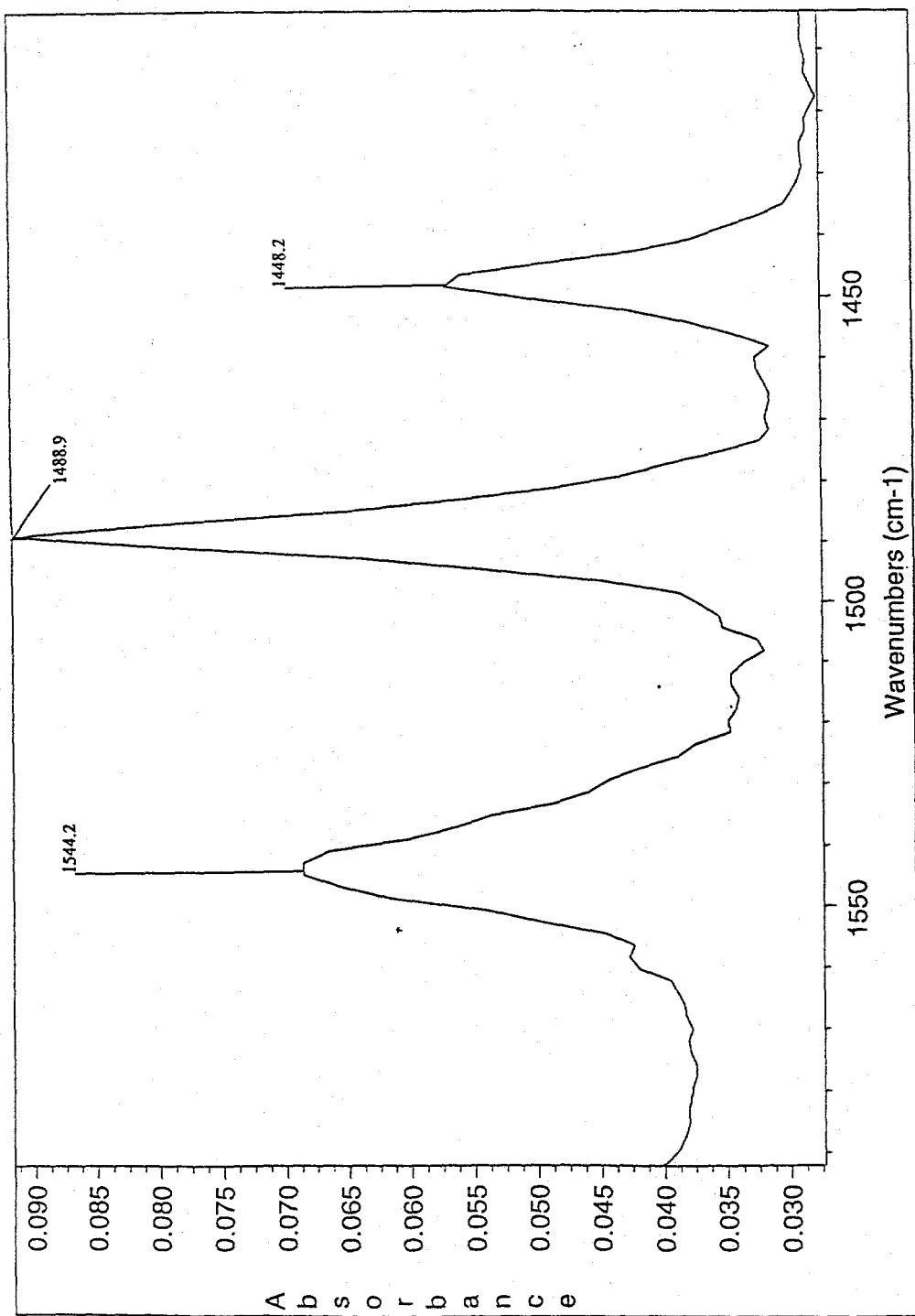
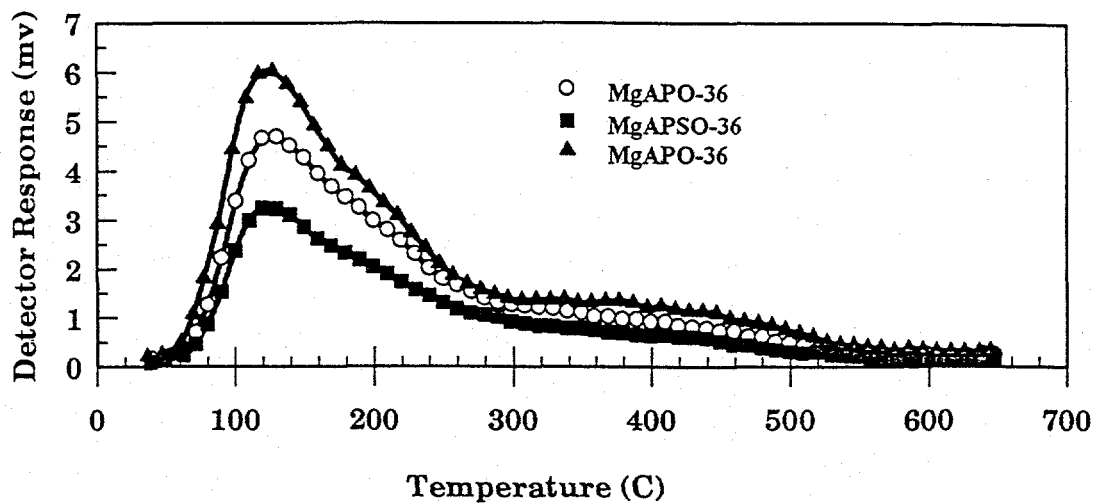
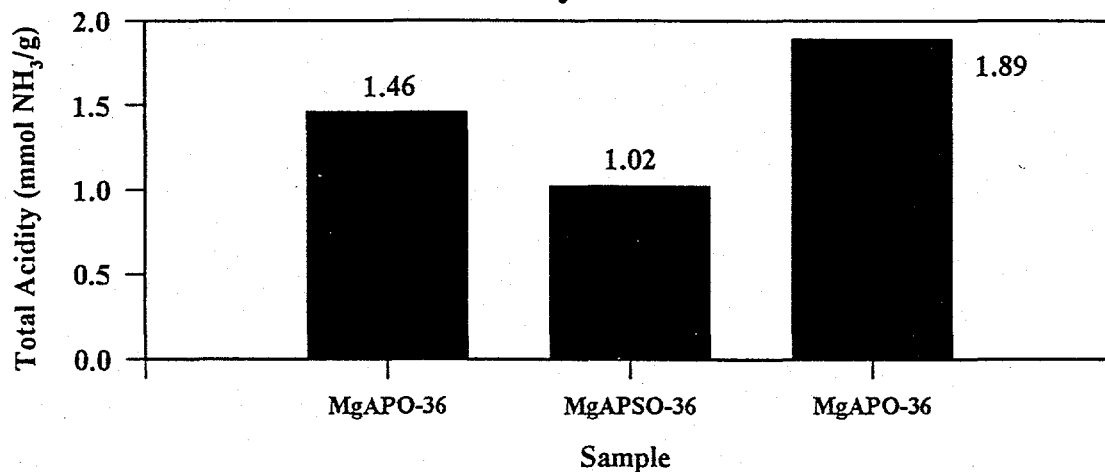


Figure 5: IR Spectrum of pyridine adsorbed on MAPO-36

Ammonia TPD Curves for APO-36 Zeolites



Total Acidity of APO-36 Zeolites



Percent Acidity of APO-36 Zeolites

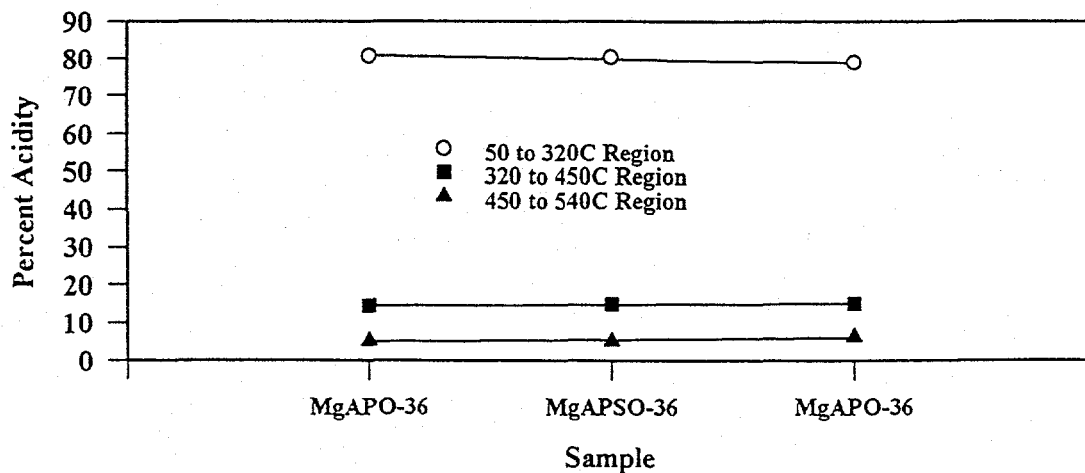


Figure 6: Ammonia TPD and Acidities of APO-36 zeolites

Ammonia TPD Curves for MgAPSO-46 Zeolites

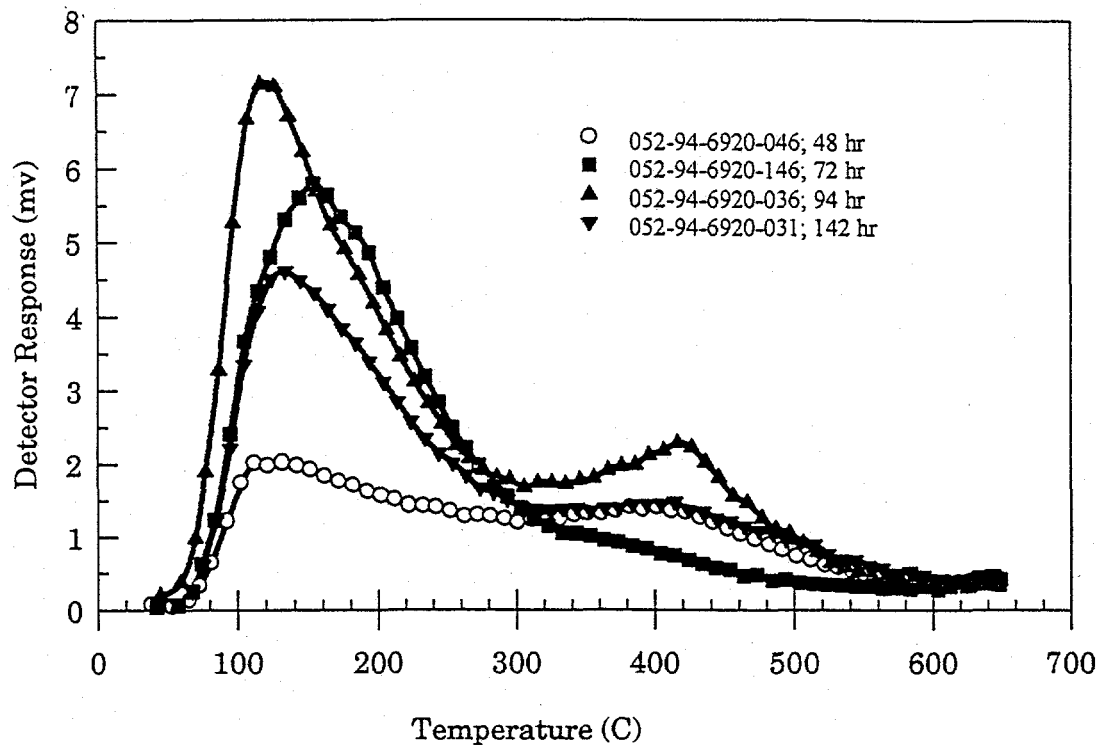


Figure 7: Acidity as a function of crystallization time for MgAPSO-46

Ammonia TPD Curves for MeAPO-50 Zeolites

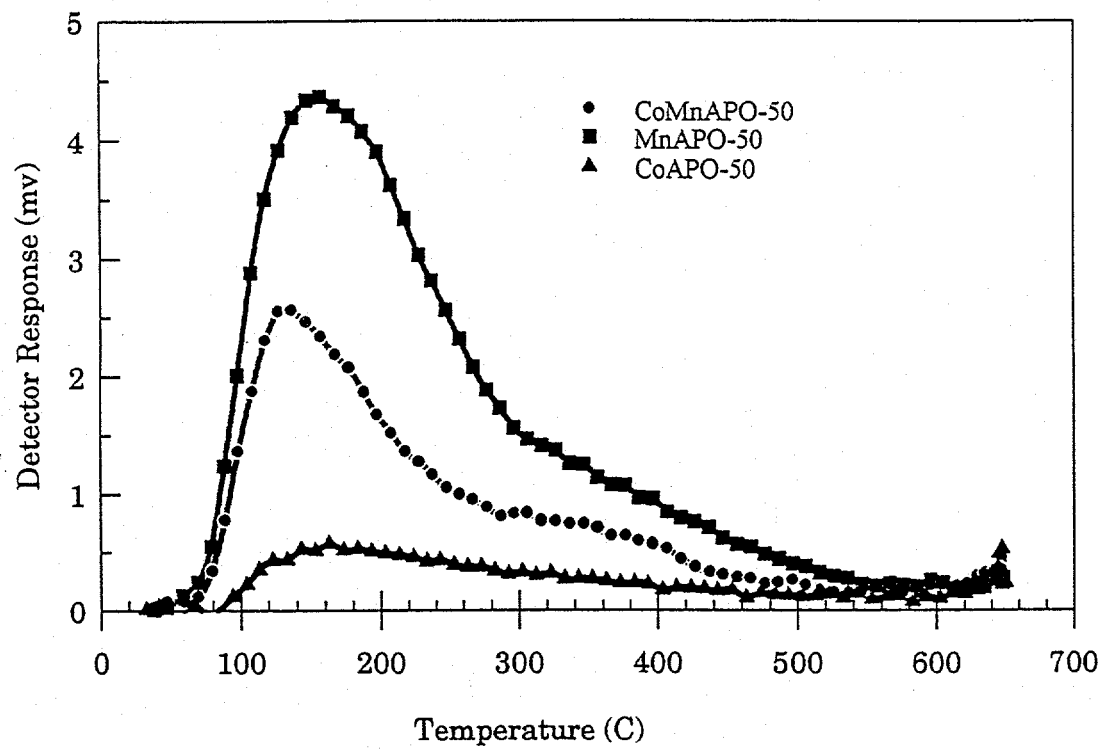


Figure 8: Acidity as a function of metal content for APO-50 zeolite

Table 3 shows that CoAPO of various large pore sizes were active for the conversion of phenol, while *Table 4* shows that metals incorporated in medium pore MeAPO-11 structure were also active for phenol hydroxylation. Varying levels of conversion and selectivities were observed but this will be discussed at a later date. Suffice it to say at this time, that the metal incorporated in these MeAPOs are active in metal catalyzed reactions and therefore set the precedence for their usage in our syngas work.

TABLE 3

**SUMMARY OF HYDROXYLATION OF
PHENOL OVER CoAPO**

CATALYST	*PH CONV. %	CT SEL. %	HQ SEL. %
CoAPO-5	6	62.7	37.3
CoAPO-11	25.5	56	44
CoAPO-36	6.4	36.2	63.8
CoAPO-50	9.2	39.6	60.4

*Run At 80C For 15-Hrs.

TABLE 4

SUMMARY OF HYDROXYLATION OF PHENOL OVER MeAPO-11

CATALYST	*PH CONV. %	CT SEL. %	HQ SEL. %
FeAPO-11	26.2	51.1	48.9
ALPO-11	11.5	44.1	55.8
SAPO-11	7.2	52.2	47.8
MgAPO-11	7.3	75.8	24.2

*Run At 80C For 15-Hrs.

4.0 Status of project

MeAPO-36 containing various types and concentrations of metals (Mn, Co, Mg and Zn) in the reaction mixture were synthesized. Various levels of crystallinity were observed depending on the types and concentrations of these metals and crystallization parameters

Calcination at 550°C resulted in some loss of crystallinity in all samples except MAPO-36. Ammonia TPD and IR spectrum of pyridine absorption show that MeAPOs have concentrations of both bronsted and lewis acid sites.

Preliminary catalytic evaluation show that MeAPOs are active for the hydroxylation of phenol.

5.0 Future work

In keeping with overall objectives of this project, our effort will focus on the following future activities:

Continue research on optimizing reaction parameters for the crystallization of MeAPOs

Characterize samples for phase purity, location and amount of incorporated metal in the framework using XRD, acidity by ammonia TPD and surface area by nitrogen BET.

Explore secondary synthesis methods using for example ammonium metal fluoride containing salts for incorporation of magnesium, cobalt and zirconium.

Prepare and characterize metal impregnated MeAPOs to develop co-catalysts with dual functionality for methanol, hydrocarbon or ether formation.

Building of a small bench scale catalytic reactor for screening of catalytic activity of materials.

Submit small and larger quantities of materials for catalytic testing at Texaco.