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

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II EXECUTIVE SUMMARY

The objective of this project was to prepare microporous aluminophosphates containing magnesium, manganese, cobalt and zinc (MeAPOs) and to evaluate their performance as oxidation catalysts for the removal of low levels of volatile organic compounds from gas streams. A range of molecular sieves were screened for their catalytic activities in the destruction of the chlorinated VOC, (methylene chloride). CoAPO-36 showed best catalytic activity for the process and compared well with CoY. Catalytic activity increased with cobalt content up to 4.8 wt.% and complete decomposition of the VOC occurred at 400°C. Decomposition products were tentatively identified by IR spectroscopy as CO₂, CO and possibly phosgene. These species were assigned to vibration bands occurring at 2363 cm⁻¹ and 2326 cm⁻¹ (CO₂), 2170 cm⁻¹ (CO) and 1788 cm⁻¹ and 1735 cm⁻¹ (corresponds to the C=O stretching and CCl₂ assymmetric stretching respectively, ascribed possible to phosgene). The Ti containing zeolite TS1, as well as the Mg, Co and Zn containing MeAPOs showed much lower activities compared with CoAPO-36 for VOC decomposition. The MeAPOs have demonstrated significant catalytic activities for the liquid phase hydroxylation of phenol with hydrogen peroxide to form hydroquinone and catechol. Substitution of transition metals cations, such as Fe, Co, and Mn significantly improve the levels of conversion. The external surface of these catalysts played a significant role in their catalytic activity. FeAPO-11 showed comparable performance to TS-1. The activity depends upon Al/Fe ratio and level of acidity of the molecular sieves.

TABLE OF CONTENTS

	Page No.
I DISCLAIMER	2
II EXECUTIVE SUMMARY	3
1. INTRODUCTION	5
2. BACKGROUND	5
3. EXPERIMENTAL PROCEDURES	7
3.1 Synthesis	7
3.1.1 Synthesis of MeAPOs	7
3.1.1.2 Synthesis of TS-1 catalyst	8
3.1.1.3 Preparation of cobalt exchanged zeolite Y	8
3.1.3 Characterization	8
3.1.3.1 Diffuse Reflectance Fourier Transform Infrared Spectroscopy	9
3.2 Catalysts evaluation	9
3.2.1 Hydroxylation reactions	9
3.2.2 Volatile organics decomposition	10
3.2.2.1 Fixed Bed Continuous Flow Reactor	10
3.2.2.2 Decomposition of VOCs	10
3.2.2.3 Studies on methylene chloride decomposition using DRIFTS	11
4.0 RESULTS AND DISCUSSION	12
4.1 Hydroxylation reactions	12
4.2 Decomposition of Volatile Organic Compounds	17
5.0 TECHNOLOGY TRANSFER	26
6.0 REFERENCES	27

1. INTRODUCTION

The objective of this project was to prepare microporous aluminophosphates containing magnesium, manganese, cobalt and zinc (MeAPOs) and to evaluate their performance as oxidation catalysts for the removal of low levels of volatile organic compounds (VOCs) from gas streams.

The tasks to be accomplished were as follows:

- To develop reliable synthesis methods for metal aluminophosphates containing manganese, cobalt and zinc in their framework.
- To characterize these materials for crystallinity, phase purity, the location and nature of the incorporated metal in the framework, and
- To evaluate the materials for their catalytic activities in the oxidation of volatile organic environmental pollutants.

2. BACKGROUND

Researchers in the detergent and bleach industry have been developing promoted catalysts oxidation systems for many years and have demonstrated several of them to be superior to earlier bleaching systems.¹ The most recent advance, the addition of a manganese catalyst to the bleaching formulation, has resulted in a change in the kinetics of the decomposition reaction such that the maximum decomposition of the oxidant takes place at 20°C instead of 60°C. Unlike the other bleaching additives, which are consumed upon generation of the bleaching agent, the manganese catalyst is continually regenerated thus requiring much lower concentrations. The manganese is environmentally safe and cost-effective than other organic based method of oxidation.

Vandersall, et.al.,² have reported a lower temperature complete oxidation of volatile organics over manganese, zinc cobalt oxide impregnated carbons. Using these formulations successful

conversions occurred at temperatures between 175°C and 275°C. Initial conversions at 99.7% and 99.9% were observed though rapid decline in conversion was noted within twenty hours on stream. When conversion dropped to less than 50% the catalyst was reactivated in air and the initial conversion rates returned. The advantages of these metal/oxide/support systems is their low cost as the active metals are inexpensive, the hydrophobic nature of the carbon, and the low energy input as seen by the low temperatures necessary for conversion. This disadvantage stem from the potential combustibility of the carbon based support and the inability to systematically control the dispersion of the metal oxide throughout the support to increase the efficiency of the carbon supported catalyst system.

The use of metal substituted aluminophosphates (MeAPOs) catalysts represents the next generation of environmental catalysts as they are both environmentally benign and have higher thermal stability than carbon support for this application. The MeAPOs were synthesized following their earlier counterparts, the pure aluminophosphates (AlPO_4).^{3,4} They are formed from the isomorphous substitution of aluminum for di- or trivalent metals in the framework of aluminophosphate molecular sieves. Substitution of metal cations with redox properties such as Fe, Co and Mn may be expected to afford novel heterogeneous catalysts for liquid and gas phase oxidation reactions. The framework phosphorus in AlPO_4 s can also be substituted with vanadium^{5,6}, another redox metal, to give vanadium-containing molecular sieves (VAPOs).

The potential of MeAPOs as oxidation catalysts has been investigated by several researchers. Sheldon and co-workers found that CoAPO-11 and CoAPO-5 are both effective, stable, and recyclable solid catalysts in the facile oxidation (with O_2) of p-cresol to p-hydroxybenzaldehyde at 50°C, with conversion and selectivity both reaching 90%.^{7,8} The superior performance of the catalysts over homogenous cobalt salt was attributed to the fact that unlike the cobalt salt, CoAPO cannot form μ -hydroxo bridged cobalt dimers. In other reports, Lin et al.⁹ showed CoAPO-5 to be an active and moderate catalyst for the auto-oxidation of cyclohexane in acetic acid. At 30-40% conversion, selectivities to adipic acid was up to 45 %. The oxidation of saturated hydrocarbons involving CoAPO molecular sieves has also been demonstrated by Kraushaar-Czarnetzki et al.¹⁰ The redox properties of the catalyst was related to the ability of the framework Co to change between the Co(II) and Co(III) oxidation states.

Sheldon and co-workers investigated also, the catalytic behavior of a variety of redox MeAPOs in liquid phase oxidations with O_2 and tetrabutylhydroperoxide (TBHP), examples of which include: the oxidation of alkanes, alkylaromatic, alcohols and the epoxidation or oxidative cleavage of olefins with TBHP. They reported for example, that CrAPO-5 is an excellent, recyclable, solid catalyst for the oxidation of secondary alcohols to the corresponding ketones using TBHP or O_2 as the oxidant.¹¹ Chen et al. reported that CrAPO-5 was an active, stable and selective catalyst in the decomposition of cyclohexyl hydroperoxide towards cyclohexanone, benzylic oxidations and the (auto)-oxidation of secondary alcohols with TBHP and O_2 .¹² VAPO-5 and VAPO-11 were both demonstrated by other researchers, to catalyze oxidations, such as epoxidation of allylic alcohols analogous to homogenous vanadium salts^{6,13} and benzylic oxidations with TBHP and oxygen.⁶

In project we investigated various metal substituted aluminophosphates for the low temperature oxidation of volatile organic compounds in a gas stream. Prior to VOC studies, the selective oxidative catalytic potential of the catalysts were first evaluated using the liquid phase the hydroxylation of phenol with hydrogen peroxide.

3. EXPERIMENTAL PROCEDURES

3.1 Synthesis

3.1.1 Synthesis of MeAPOs

Syntheses were conducted according reported procedures. Phosphoric acid (Fisher, 85 %) was the source of phosphorus; metal acetates (Fisher) were sources of Co, Mn and Mg, while ferric sulfate (Aldrich) was source of Fe. Aluminum source was either aluminum isopropoxide (Aldrich) or Catapal B (Vista Chemical Co.) and the source of silicon was Ludox HS 40 (Dupont). Organic amines (R) were obtained from Aldrich. These were as follows: di-n-propylamine for MgAPO-11 and MnAPO-11, diisopropylamine for CoAPO-11 and FeAPO-11, and tripropylamine for MeAPO-36. Phenol was obtained from Aldrich. The general molar composition of the reaction mixtures were: $R:xMeO:0.917Al_2O_3:P_2O_5: 0.33AcOH: 5.5$

$\text{C}_3\text{H}_7\text{OH}:\text{50H}_2\text{O}:\text{50 H}_2\text{O}$. Metal content was added in varied concentration as detailed in the synthesis composition tables below. The synthesis mixtures were crystallized in Teflon-lined autoclaves for 24 to 40 hours at temperatures between 100°C and 200°C.

3.1.1.2 Synthesis of TS-1 catalyst

TS-1 is a medium-pore 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.¹⁴ Using this approach, we synthesized the zeolite and utilized it as an oxidation catalyst in Phenol hydroxylation reactions and VOCs decomposition experiments. X-Ray Diffraction analysis confirmed the structure to be characteristic of the MFI family of zeolites and Infrared spectral analysis showed a framework vibration band at 960 cm^{-1} which is characteristic of Si-O-Ti bond and thus confirmed that Ti is indeed part of the lattice. A reference sample of TS-1 was also obtained from Ueikon, (Switzerland).

3.1.1.3 Preparation of cobalt exchanged zeolite Y

Recently research have shown that cobalt exchanged zeolite Y is very active for the decomposition of chlorinated VOCs such as CH_2Cl_2 and carbon tetrachloride (CCl_4). For comparison purposes we prepared co-exchanged Zeolite Y as a reference material for the MeAPO catalysts from a commercial sample of Zeolite Y (LZY-62) obtained from Union Carbide. Co exchanged of this zeolite was conducted as follows: The zeolite (10 g) was mixed with 250 mL of 1M cobalt nitrate in a 500 mL round bottom flask. The stirred flask was heated at 60°C-70°C overnight after which the solid product was filtered and washed with deionized water. This procedure was repeated twice, after which the solid was dried and calcined at 500 °C for 12 hr.

3.1.3 Characterizatiuon

Catalysts chararacterization were perfromed using a Phillip X-Pert X-ray powder diffractometer (XRD) for crystal structure, scanning electron microscope (SEM) for crystal morphologies, and

Inductively Coupled Plasma/Mass Spectrometer or Atomic absorption spectrometer for elemental composition analysis. The surface acidic properties of selected MEAPOs were characterized using Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS) studies

3.1.3.1 Diffuse Reflectance Fourier Transform Infrared Spectroscopy

The acidic properties of MeAPO-36 (Me= Co and Mg) were investigated using DRIFTS. The materials were synthesized from reaction mixtures of molar compositions given in Table 1. Prior to DRIFTS experiments, 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 showed that the samples remained highly crystalline before and after calcination. The IR spectra were recorded using a Nicolet 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. Ten torrs 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.

3.2 Catalysts evaluation

Selected catalysts were evaluated for the phenol hydroxylation and VOCs decomposition.

3.2.1 Hydroxylation reactions

Hydroxylation reactions were performed in a stirred 250 mL round bottom flask fitted with a water cooled condenser. Reactions were done under atmospheric pressure , and temperatures were between ambient and 180°C. Unless otherwise stated, typically, 0.2 g of molecular sieve powder, 45 ml of water, 2 g of phenol (Aldrich) and 2 g of hydrogen peroxide (30%, Fisher) was added to the reaction flask. The reaction mixture was heated to desired temperature and the

progress of the reaction was monitored as a function of time. Reaction products were analyzed by gas chromatography.

3.2.2 Volatile organics decomposition

3.2.2.1 Fixed Bed Continuous Flow Reactor

A fixed bed upflow continuous flow reactor was constructed consisting of the following components. A Pyrex reactor tube of dimensions 30 cm long x 1 cm I. D. diameter, containing Kovar metal (1/4 inch) to glass seals at both ends and a porous frit at the center. A Thermolyne Tube Furnace equipped with temperature control features for use in heating the reactor tube. A stainless steel thermocouple inserted inside the catalyst bed for monitoring the temperature of the latter. A 200 mL Dreshnel type bottle with metal to glass seals attached to the inlet and outlet for containing liquid VOCs. A constant temperature bath used for equilibrating the content of the Dreshnel bottle. All components are connected through 1/4 inch or 1/8 inch stainless steel tubing. The reactor is interfaced to a Shamadzu 14A Gas Chromatograph via a heated transfer line (1/6" stainless steel tube) which is in turn attached to a heated Valco six port sampling valve: The GC column is currently a 6 ft x 1/8 inch Stainless Steel containing 3% OV1 on Chromosorb as stationary phase. The GC is equipped with both a Flame Ionization Detector (FID) and a Thermal Conductivity Detector (TCD). Chromatograms are recorded on a Shimadzu CR501 Integrator.

3.2.2.2 Decomposition of VOCs

The procedure for a typical catalytic run was as follows: A 0.50 g sample of catalyst was placed on the frit inside the reactor tube and was kept in place by a small plug of glass wool. The reactor tube was heated to the desired reaction temperature. Air was bubbled at flow rate of 1 cc/min through methylene chloride contained in a 200 mL Dreshel bottle which was ice cooled to 0°C. The methylene chloride saturated stream of air was made up with an additional 15 mL/min of air to give a combined flow rate of 16 mL/min of gas going through the catalyst bed at space velocity of approximately (1920 mL gas/mLcatalyst/hr). 250 μ L sample of the reactor effluent was injected into the gas chromatograph (GC) at regular intervals using the Valco six

port valve gas sample loop. The operating conditions for the GC were as follows: Injector port temperature 200°C, FID Detector temperature 200°C, and oven temperature isothermal at 100°C. Separation was done using an Altech stainless steel packed column of dimensions 6 ft x 1/8 inch, containing Porapak Q stationary phase. The retention time (RT) of methylene chloride under these conditions was 8.87 minutes.

3.2.2.3 Studies on methylene chloride decomposition using DRIFTS

DRIFTS was used to identify decomposition products for methylene chloride decomposition over both CoAPO-36 (Sample D) and CoY. The catalysts powder was placed on a KBr bed inside the reaction cell which was then evacuated to 10^{-5} torr while heating to 400°C for a minimum of 12 hrs. After cooling the cell to 300°C, the catalyst was allowed to interact with 15 torr of methylene chloride vapor for 1 hr. The cell was then evacuated at 10^{-5} torr for 1 h to remove physisorbed methylene chloride. Spectra were recorded (1000 scans) and ratioed against the pure activated molecular sieve to observe the interaction of chemisorbed methylene chloride with the catalyst surface. Oxidation of the chemisorbed methylene chloride was conducted as follows: 100 torrs of dry oxygen was allowed to interact with the chemisorbed methylene chloride at 300°C under static conditions. The transformation of the surface products was observed over time. The spectrum of chemisorbed methylene chloride was used as a background to obtain the spectra of the oxidized species.

4.0 RESULTS AND DISCUSSION

4.1 Hydroxylation reactions

The performance of AlPO-11s with a range of compositions are compared for the catalytic conversion of phenol (Table 1). The order of catalytic activity, expressed in terms of phenol conversion is as follows: FeAPO-11 >> AlPO₄-11 > MgAPO-11 = SAPO-11. The superior performance of FeAPO-11 can be attributed to the presence of the transition metal in the catalyst. It is known that strong Bronsted acidity catalyzes the decomposition of peroxides such as hydrogen peroxide and t-butyl peroxide (8). Both MgAPO-11 and SAPO-11 are characterized by

having greater total acidity than FeAPO-11 and AlPO₄-11. Competing hydrogen peroxide decomposition reactions catalyzed by the high concentration of Bronsted acidities in both SAPO-11 and MgAPO-11 resulted in a lower conversion compared to AlPO₄-11 and FeAPO-11. The samples showed approximately 1:1 selectivity for hydroquinone: catechol, with the exception of MgAPO-11 which show a low selectivity for hydroquinone formation.

Table 1: Performance of various AlPO₄-11 in the hydroxylation of phenol.

Catalyst	*Conversion (%)	Selectivity (%)	
		CT	HQ
FeAPO-11**	26.2	51.1	48.9
AlPO ₄ -11	11.5	44.1	55.8
SAPO-11	7.2	52.2	47.8
MgAPO-11	7.3	75.8	24.2

** calcined @ 550°C for 8 hr in N₂, 4 hr in air: * 80°C, 15 hr

The performance of FeAPO-11 with reaction time during the conversion of phenol is compared for both the as-synthesized (Figure 1A) and calcined (Figure 1B) forms of the catalyst. The catalytic activity was similar in both cases and reached a constant as early as half an hour reaction time. The products electivity also remained constant at approximately 1:1 hydroquinone:catechol. The halt in phenol conversion may result from deactivation of the catalyst or a depletion of hydrogen peroxide from the reaction mixture (*vide infra*). The as-synthesized form has little pore access due to inclusion the organic amine used in the synthesis mixture. This comparable activity demonstrated by the as-synthesized catalyst strongly suggests that active sites on the external surfaces of the catalysts play a significant role in the phenol conversion reaction.

Figure 1. Hydroxylation of phenol over (A-Above) "as synthesized" and (B-Below) calcined FeAPO-11.

As with the case of Fe, substitution of framework aluminum by other transition metal cations, such as Mn and Co appears to significantly improve the conversion of phenol. Figure 2 shows

the conversion of phenol as a function of time for MnAPO-11. The activity was similar for both the as-synthesized (Figure 2A) and calcined (Figure 2B) catalyst, but lower than that of FeAPO-11. Here again the significance of active external surface species in the catalysis process is inferred. A high hydroquinone selectivity was observed using the calcined MnAPO-11 catalyst. This high selectivity may be associated with a more rapid diffusion of hydroquinone over catechol through the main channel of the catalyst. MeAPO-11 catalyst system containing both Fe and Mn was also evaluated for phenol conversion. The activity was found to be similar for both the as-synthesized samples. Furthermore the activity falls between those catalysts containing the respective single transition-metal cations. The overall activity of calcined materials followed the order of FeAPO-11 > FeMnAPO-11 > MnAPO-11. The transition metal containing catalysts (including CoAPO-11) in their as synthesized forms showed comparable activities. In this case it was observed that CoAPO-11 gave higher activity than FeMnAPO-11. Overall activities of the MeAPO-11s were comparable to TS-1, but TS-1 giving a higher hydroquinone selectivity. With regards to product selectivity, in general FeAPO-11, FeMnAPO-11 and CoAPO-11 give similar product selectivities of about 1:1 of hydroquinone:catechol, whereas MnAPO-11 favor the production of catechol. The effect of hydrogen peroxide concentration on the hydroxylation of phenol was also investigated. The activity, yield (conversion x selectivity) and selectivity all show strong dependence on the hydrogen peroxide concentration (Figure 3).

Phenol conversion and yield of hydroquinone increased significantly as the H_2O_2 /phenol mole ratio was increased from 0.5 to 5.5. The results suggest that the phenol conversion reaction progressed directly to the main products, hydroquinone and catechol with little or no side products. Like in most cases in this study, an increase in conversion is accompanied by an increased selectivity towards catechol, and corresponding decreased selectivity for hydroquinone. This may be due to secondary isomerization of hydroquinone to catechol at higher conversion levels. The effect of Al/Fe ratio of FeAPO-11 is shown in Table 2. For samples A to C, an increase in phenol conversion and a decrease in hydroquinone selectivity were observed for catalyst of different Al/Fe ratios as the reaction time was increased from 1 hour to 5 hours. For large changes in the Al/Fe ratio of the catalyst however, no significant effect on the catalytic activity was observed. With a greater than 10 fold increase in the amount

of iron in the FeAPO-11 synthesis mixture between sample C and A, only a small enhancement in phenol conversion was obtained, while the selectivity to hydroquinone remained unchanged. On the contrary, sample D with twice as much Fe as sample C, showed a dramatic increase in phenol conversion and a lower hydroquinone selectivity.

Figure 2. Hydroxylation of phenol over (A-Above) "as synthesized" and (B-Below) calcined MnAPO-11

Figure 3. Hydroxylation of phenol over (A) "as synthesized" and (B) calcined FeMnAPO-11

Table 2: The effect of iron content of FeAPO-11 on phenol hydroxylation

**Catalyst ID	Al/Fe in synthesis mixture	Reaction time (hr)	* Conversion (%)	Selectivity (%)	
				CT	HQ
A	216.5	1	8.2	39.2	60.8
		3	12.4	39.9	60.1
		5	15.1	42.2	57.8
B	38.4	1	10.2	38.1	61.9
		3	11.9	39.8	60.2
		5	16.3	44.2	55.9
C	19.3	1	10.8	39.3	60.7
		3	11.9	38.6	61.4
		5	17.5	47.2	52.8
D	9.0	1	24.6	48.8	51.1
		3	25.1	50.7	49.3
		5	24.4	48.9	51.1

MeAPOs have demonstrated significant catalytic activities for the liquid phase hydroxylation of phenol with hydrogen peroxide to form hydroquinone and catechol. Substitution of transition metals cations, such as Fe, Co, and Mn significantly improved the levels of conversion. The external surface of these catalysts played a significant role in their catalytic activity. FeAPO-11 showed comparable performance to TS-1. The activity depends upon Al/Fe ratio and level of acidity of the molecular sieves.

4.2 Decomposition of VOCs

A range of molecular sieves were screened for their catalytic activities in the destruction of the chlorinated VOC, (methylene chloride). CoAPO-36 showed best catalytic activity for the process and compared well with CoY. Catalytic activity increased with cobalt content up to 4.8

wt.%. The Ti containing zeolite TS1, as well as the Mg, Co and Zn containing MeAPOs showed much lower activities compared with CoAPO-36.

Table 3: Catalytic activities of various molecular sieves for methylene chloride oxidation

Catalysts	<u>Conversion (%)</u>		
	300°C	350°C	400°C
CoY	45.4	93.6	97.5
CoAPO-36 (4.8wt%, Co)	37.1	77.6	100
MnAPO-36	7.5	16.4	37.2
MAPO-36	7.8	12.3	19.8
ZnAPO-36	3.9	4.1	12.7
TS1	2.1	11.6	14.6
Homogeneous run (no cat.)	0	---	14.1

The results from the reactor runs for the oxidation of methylene chloride using various molecular sieves are tabulated in Table 3. Though all catalysts, with the exception of TS1 and CoY were synthesized from reaction mixtures of similar molar composition ratios, wide variation in their catalytic activities were observed. CoAPO-36 showed catalytic activity closest to the reference catalyst, CoY, which showed highest methylene chloride conversion. The Ti, Mn, Mg and Zn containing molecular sieves all showed low catalytic activities at 400°C. Further experiments were therefore focused on Co containing samples.

Figure 4 shows the catalytic activity of CoAPO-36 as a function of temperature and cobalt content of the catalysts. Table 4 shows the chemical compositions of the CoAPO-36 synthesis mixtures and the final solid products. Methylene chloride conversion showed distinct temperature dependency. Exponential increases in conversion levels were observed in the temperature range from 250°C to 400°C, reaching 100% conversion at the higher temperature. Chatterjee and Greene reported similar results using zeolite Y exchanged with H, Ce and Cr.¹⁵ Catalytic activity increased with Co content up to approximately 4.8 wt % Co. No further

increase in activity was observed for samples with higher Co content. CoY consistently showed higher conversion than CoAPO-36, though the former contained a lower Co content (2.5 wt. %). This may be a result of the higher concentration of Bronsted acid sites that is available in its structure in comparison with CoAPO-36, as was revealed by DRIFTS.

With regards to stability of the catalysts under reaction conditions, CoAPO-36 samples maintained high crystallinity as was indicated by XRD. Peak positions (2θ values) and peaks heights in the X-ray diffractograms remained unchanged from a comparison of the calcined catalysts before and after catalytic runs.

Table 4. Synthesis gel compositions and wt. % Co and Al in products of CoAPO-36

Sample ID	** Molar composition of reaction mixtures	* Wt % composition by chemical analysis	
		% Co	% Al
A	2.0R:0.05CoO:0.98Al ₂ O ₃ :1P ₂ O ₅ :40H ₂ O	2.5	25.0
B	2.0R:0.10CoO:0.96Al ₂ O ₃ :1P ₂ O ₅ :40H ₂ O	4.8	23.5
C	2.0R:0.18CoO:0.98Al ₂ O ₃ :1P ₂ O ₅ :37H ₂ O	6.5	24.4
D	1.9R:0.26CoO:0.91Al ₂ O ₃ :1P ₂ O ₅ :40H ₂ O	5.0	22.1
E	1.9R:0.40CoO:0.84Al ₂ O ₃ :1P ₂ O ₅ :40H ₂ O	10.8	20.1
CoY	nd	2.5	nd

** R = tripropylamine

* Wt. % of metal in product determined by ICP/MS

nd = not determined

The promising activity shown by the Co containing molecular sieves prompted us to investigate the activity of other Co containing topologies from the aluminophosphate family (Figure 5). Thus large pore CoAPO-5 (pore dimension of 0.73 nm) and medium pore CoAPO-11 (pore dimensions 0.63 nm x 0.39 nm) were investigated and compared with large pore CoAPO-36 (pore dimension of 0.65 nm x 0.75 nm).¹⁶ Here again CoAPO-36 shows highest catalytic activity among the three. Though CoAPO-36 and CoAPO-5 are both large pore materials, it is known that the former contains stronger Bronsted acid sites as demonstrated in its n-butane cracking activity.¹⁷ Since acid sites seem to play an important role in methylene chloride oxidation, this may explain why CoAPO-36 shows greater catalytic activity. In the case of CoAPO-11 which is also known to possess strong Bronsted acid sites, its lower catalytic activity may be related to its smaller pore dimensions causing slow diffusion of methylene chloride into its pores.

Qualitative analysis for the presence of HCl as a product was assessed as a function of temperature, by passing the reactor effluent through 20 mL of deionized water for 10 minutes using CoAPO-36 (D). The change in pH was monitored using a pH meter and the increase in H_3O^+ concentration was determined as a function of temperature. A direct correlation was observed between methylene chloride conversion levels and HCl concentration (Figure 6).

Figure 4: Methylene chloride conversion vs. reaction temperature and Co content of CoAPO-36.

Figure 5: Conversion of methylene chloride on Co containing MeAPOs of various topologies.

Figure 6: HCl production vs. methylene chloride conversion on CoAPO-36 (B)

Figures 7 and 8 show the Infrared spectra of CoAPO-36 (D) at 300°C before and after methylene chloride was chemisorbed respectively. The negative peaks observed at 3672 cm^{-1} and 3589 cm^{-1} after the adsorption of methylene chloride are due to the interaction of the VOC with the hydroxyls on the catalyst surface. Figure 9 shows results from oxidation of chemisorbed methylene in air at 300°C. The hydroxyl band at 3666 cm^{-1} gradually reappears as the time of oxidation was increased, suggesting the gradual oxidation of the VOC and an important role played by these acidic centers. The spent catalyst was observed to undergo a color change from yellow green to blue and this is attributed to a change in the oxidation state of the cobalt from 3^{+} to 2^{+} . The above suggests that the VOC is simultaneously interacting with both the acid site and the Co center.

Among the main reaction products expected from this reaction are CO_2 and CO. The double bands appearing at 2363 cm^{-1} and 2326 cm^{-1} in Figure 10 is assigned to CO_2 .¹⁸ The intensities of these bands and therefore the amount of CO_2 produced increased with oxidation time up 60 minutes. The band at 2170 is assigned to CO and its intensity did not appear to increase with oxidation time (Spectra 1-4). In Figure 11 bands at 1788 cm^{-1} and 1735 cm^{-1} corresponds to the C=O stretching and CCl_2 assymetric stretching respectively in accordance with published work. The intensities of both peaks increased with increase in the time of oxidation, and could possibly be due to the formation of phosgene on the surface of the catalysts.

In these studies both CO and CO₂ were identified in the reaction products along with some intermediates which were tentatively identified.

IR Spectrum showing OH region of CoAPO-36 (D) after heating and evacuation.

Figure 7

IR Spectrum showing OH region of CoAPO-36 (D) after methylene chloride was chemisorbed at 300°C.

Figure 8

IR spectra of CoAPO-36 (D) showing the return of OH groups with time during the oxidation of chemisorbed methylene chloride.

Figure 9

IR spectra of CoAPO-36 (D) showing the formation of CO and CO₂ with time during the oxidation of chemisorbed methylene chloride.

Figure 10

IR spectra of CoAPO-36 (D) showing the formation of carbonyl species (possibly COHCl intermediate) with time during the oxidation of chemisorbed methylene chloride.

Figure 11

5.0 TECHNOLOGY TRANSFER

- Catalytic Hydroxylation of Phenol Over MeAPO-11 Molecular Sieves; Presented at the Symposium on Selective Hydrocarbon Oxidation, 211 ACS National Meeting, New Orleans, March, 1996.
- Catalytic Hydroxylation of Phenol Over MeAPO-11 Molecular Sieves; presented at the 5th ACS Mid Atlantic Regional Meeting, Villanova University, Pennsylvania, May 1996.
- Metal Substituted Aluminophosphate Molecular Sieves as Phenol Hydroxylation Catalysts, Applied Catalysis A: General 143 (1996)101-110.
- Oxidative Catalysis of Chlorinated Hydrocarbons by Metal Substituted Aluminophosphate Molecular Sieves: MeAPO-36; C. W. Ingram, K. Cleare, F. Porbeni, R. Szostak; *Fifth*

Historical Black Colleges and Universities/Private Sector/Energy Research and Development Technology Transfer Symposium, Baton Rouge, LA, March, 1997.

6.0 REFERENCES

- ¹ D. Parker, Chemical Trends 24, (1991).
- ² S. G. Vandersall, W. H. Maroldo, K. Brendley, R. S. Drago, Environmental Catalysis, J. Armor, ed., 331 (1994)
- ³ E. M. Flanigen, B. Lok, R. Patton, S. Wilson, Pure & Appl. Chem., **58** (1986) 1351-1358.
- ⁴ S. T. Wilson, B. M. Lok, C.A. Messina, T.R. Cannan and E. M. Flannigen, J. Am. Chem. Chem. Soc., **104** (1982) 1146.
- ⁵ C. Montes, M. E. Davis, B. Murray, M. Narayana, J. Phys. Chem., 94, (1990), 6431: S. H. Jung, Y. S. Uh, H. Chon. Appl. Catal., **62** (1990), 61.
- ⁶ S. Rigutto, H. van Bekkum, J. Mol. Catal., 81, (1993) 77, M. S. Regutto, H. van Bekkum, Extended Abstracts of the 9th International Zeolite Conference, Montreal, 1992, abstract no. RP54.
- ⁷ J. Dakka, R. A. Sheldon, Netherlands Patent. 9,200,968, (1992).
- ⁸ R. A. Sheldon and N. de Heij in W. Ando and Y. Morita (eds.): The role of Oxygen in Chemistry and Biochemistry, Elsevier, Amsterdam (1988) 243.
- ⁹ S. S. Lin, H. S. Weng, Appl. Catal. A, **105** (1993), 289.
- ¹⁰ B. Kraushaar-Czarnetzki, W.G.M. Hoogervorst and W.H.J Stork, in Zeolites and Related Microporous Materials: State of the Art, J. Weitkamp, H. G. Karge, H. Pfeifer and W. Holderich (Eds.), **Studies in Surface Science and Catalysis**, 84, Elsevier, Amsterdam, (1994) 1869.
- ¹¹ R. A. Sheldon, J. D. Chen, J. Dakka, E. Neeleman, Preprints of the 1st World Congress on Selective Oxidation, Belmaneda, Spain, paper G1.
- ¹² J. D. Chen, J. Dakka, E. Neelman, R. A. Sheldon, J. Chem. Soc. Chem. Commun., (1993) 1379: J. Dakka, R. A. Sheldon, Appl. Catal. A, **108** (1994) L1.
- ¹³ M. J. Haanepan and J. H. C. van Hoff in Tagungsbericht 9204, Proceedings of the GMK Conference on Selective Oxidations in Petrochemistry, Sept. 16-18, (1992), GOSLAR, Germany, 227.

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- ¹⁴ M. Uguina, G. Ovejero, R. van Grieken, D. Serrano, M. Camacho, J. Chem Soc. Chem. Commun., (1994) 27.
- ¹⁵ Chatterjee, S., Greene, H., *Appl. Catal. A: General* 98 (1993)139-158.
- Meier, W. M., Olson, D. H., Atlas of zeolite structure types 3rd ed., Butterworth-Heinemann, MA (1992).
- ¹⁷ Nakashiro, K., Y. Ono, *J. Chem. Soc. Faraday Trans. 1*, 87 19 (1991).
- ¹⁸ Ramachandran, B., Greene, H., Chatterjee, S., *Appl. Catal. B., Environmental* 8 (1996)157-182.