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# QUARTERLY REPORT

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## Abstract

In this study, MAPO-36 was crystallized from a reaction mixture of molar composition :1.8 Pr<sub>3</sub>N:0.156 MgO:0.97Al<sub>2</sub>O<sub>3</sub>:0.936 P<sub>2</sub>O<sub>5</sub>:41.4H<sub>2</sub>O:0.31HOAC at 100°C for 48 h followed by 150 °C for 24 to 72 h. Its formation was dependent on the source of aluminum, template concentration and the reaction temperature and time. MAPO-5 was a competing impurity phase and its formation can be suppressed by changes in the reaction conditions. Preliminary catalytic testing of MAPO-36 is currently being conducted at Texaco. Minor students' participation in this project includes two African American (Mr. Dewayne Silimon and Miss Krystal McClure) who are presently gaining significant experience in synthesis and characterization techniques.

## 1.0 Introduction

Indirect liquefaction to produce hydrocarbon and oxygenate fuel products is a multi-step process. An intimate coupling of processes, for example, methanol production from CO/H<sub>2</sub> with methanol converted to desirable products, or CO/H<sub>2</sub> to higher alcohols with subsequent conversion to octane enhancing oxygenates would represent important process advances. Metal based catalysts are utilized for the synthesis of methanol, zeolites for the conversion of alcohols to hydrocarbon fuels or oxygenates. We have proposed to use novel metal containing aluminophosphate (MeAPOs) with type -36 and -46 topologies as integrated catalyst systems for coupling of the two processes. The metals proposed were Mg, Co, Zr and Ce. The MeAPOs were developed by Union Carbide in mid 1980s and have shows tremendous catalytic activity in a number of industrially important reactions.<sup>1-5</sup> Among the MeAPOs, type -36 have been found to be most highly active and thermally stable. Current methods for the synthesis of MeAPO-36 and -46 are not easily reproducible and often give rise to impure phases containing MAPO-5. Also, not much is known about the incorporation of Zr and Ce in the MeAPO framework. This project was undertaken to address these issues with the overall objectives as follows:

### Objectives:

- 1) produce new integrated catalytic processes for the conversion of synthesis gas to desirable hydrogen and oxygenate products.
- 2) establish research collaboration between Clark Atlanta University and Industry
- 3) to provide minority students at Clark Atlanta University the opportunity to gain experience in the chemistry and chemical engineering fields by working with members of the petroleum industry.

This report give a summary of the status of the project as of 28th January 1995.

## **2.0 Work done**

### **2.1 Purchasing of chemicals and supplies**

The Catalysis and Separation Science was only recently established. Since the initiation of this project, a significant amount of time was spent in ordering of materials and supplies, and the installation of equipment (autoclaves, centrifuges, ovens, microscope, etc.). This exercise gave students significant experience in dealing with suppliers, installing research equipment and the general commissioning of a research laboratory. Most of the chemicals needed for this phase of the project were acquired, and should paved the way for accelerated research activities in subsequent phases.

### **2.2 Synthesis and characterization of MAPO-36**

#### **2.2.1 Materials and Equipment**

psuedoboehemite alumina - Catapal B (Vista Chemical Co)

aluminum hydroxide (Pfaltz and Bauer)

orthophosphoric acid (Fisher)

magnesium acetate (Fisher)

tripropylamine (Aldrich)

zinc acetate (Fisher)

cobalt acetate (Fisher)

15 mL and 25mL stainless steel Teflon lined autoclaves

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 in a plastic container. A sample of metal acetate (metal = Mn, Zn or Co) was first dissolved in water and the solution gradually added to the acid mixture. Pseudoboehmite was gradually added (a small quantity per time) to the resulting solution and the mixture continuously stirred, until a homogeneous gel was obtained. The templating agent, tripropylamine, was then titrated in the stirred gel and the latter shared into autoclaves. The autoclaves were placed in ovens where the gel was allowed to crystallized hydrothermally under autogenous pressure. The solid products were recovered by filtration or centrifugation and dried at room at about 50°C.

The effect of the following parameters on the synthesis of MeAPO-36 are currently being investigated: temperature and time, source of aluminum, and metal to aluminum ratio.

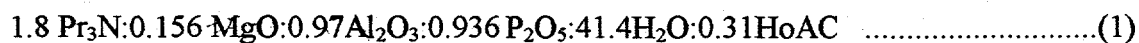
### 2.2.3 Characterization

As a preliminary characterization procedure, a sample of the "just crystallized", unfiltered solid product was smeared on a glass slide and the morphology of any crystallites present, was observed under an optical microscope. Structural characterization of samples were performed using a Phillips X-Pert Diffractometer equip with Cu-K $\alpha$  radiation ( $\lambda = 1.5406$  angstroms) and xenon detectors. Scans were recorder from  $2\theta$  of 5.00 to 50.00. The system was controlled by Gateway 2000 Computer with Phillips powder diffraction software.

## 3.0 Results

### 3.1 The effect of temperature and time:

Reactants for a typical synthesis recipe, giving MAPO-36 is presented in Table 1. The molar composition of the mixture was :



**Table 1: Reactants used for successful synthesis of MAPO-36**

Reactants	Wt. (g)
psuedoboehemite alumina - Catapal B (Vista Chemical Co.)	16.85
orthophosphoric acid (Fisher)	28.2
magnesium acetate (Fisher)	4.58
tripropylamine (Aldrich)	33.8
deionized water	88.9

**Table 2: Crystallization conditions used and the results obtained**

Initial temp. (C), time (h)	Final temp.(C), time (h)	Product
100, 48	—	amorphous
100, 49	150, 24	MAPO-36
100, 49	150, 48	MAPO-36
100, 49	150, 72	MAPO-36
—	150, 72	MAPO36, with minor impurity

Figure 1 shows the XRD diffraction patterns from the sequence of crystallization conditions in Table 2. It can be seen that heating at 100°C gave no crystalline phase. However MAPO-36 was crystallized after 24 h of heating at 150 °C with preliminary heating at 100 °C. The crystallinity of the MAPO-36 was improved on samples heated for a 48 h and 72 hr. This can be seen from the progressive increase in the heights of the peaks from the respective diffractograms.

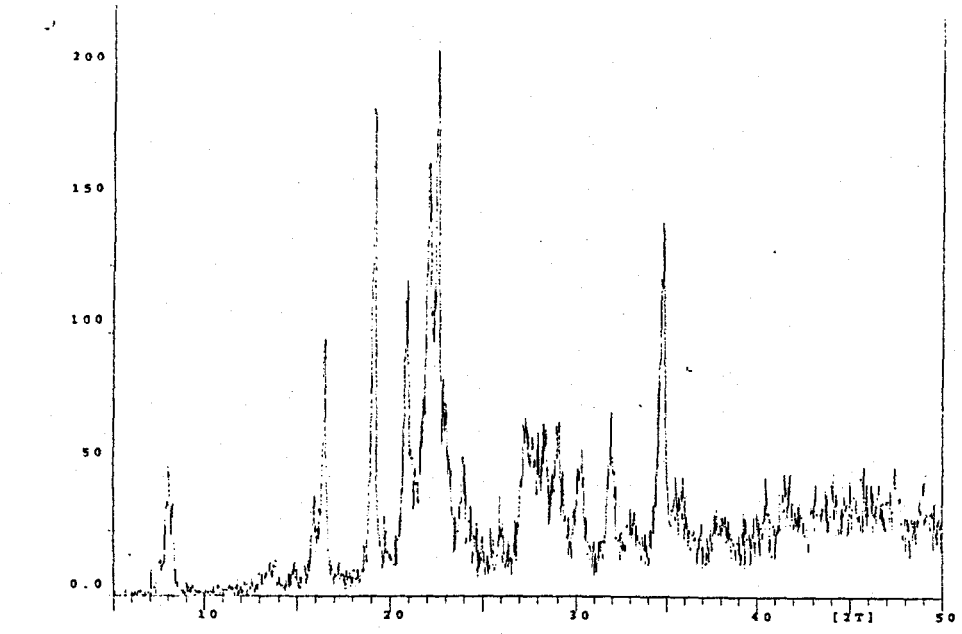


Figure 1. MAPO-36

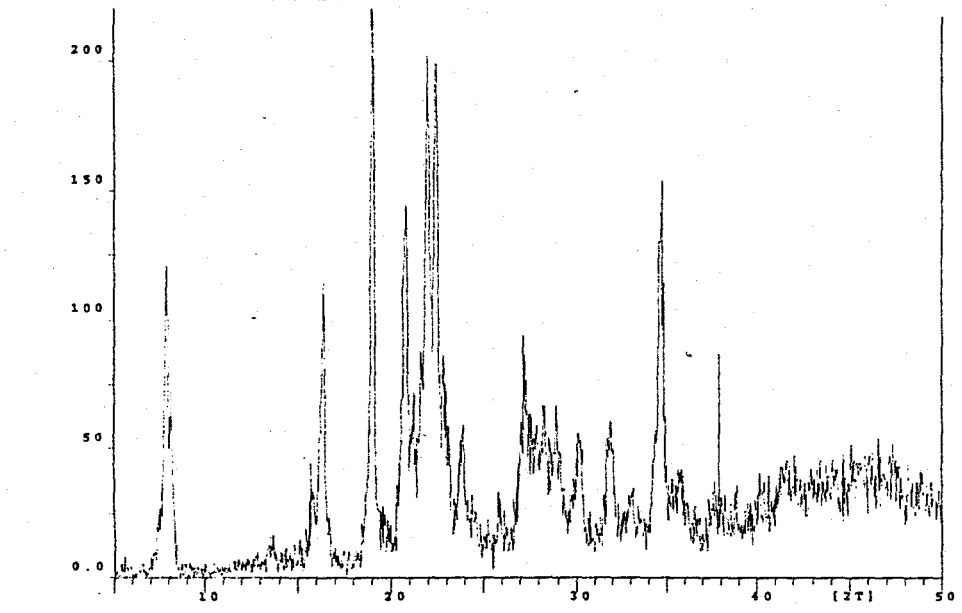
a). (100°C, 48 h,  
150°C, 24 h)

b). (100°C, 48 h,  
150°C, 48 h)

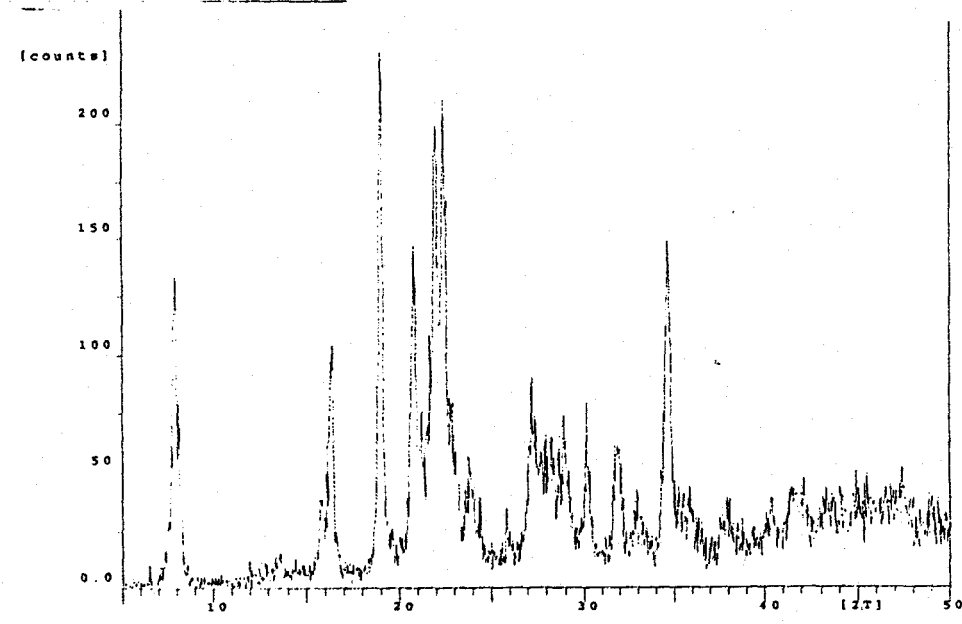
c). (100°C, 48 h,  
150°C, 72 h)



I0106958 I0106958.A2



I010695C I010695C.A2



I010695D I010695D.A2

Table 3. X-ray diffraction data for MAPO-36 (see Figure 1C.)

Sample identification: I010695D

Anode material: Cu

a1 Wavelength [Å]: 1.54060

a2 Wavelength [Å]: 1.54439

Intensity measured with FIXED slit

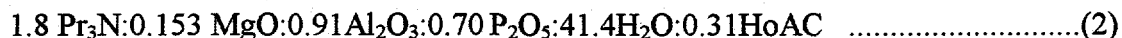
## P E A K S E A R C H:

d-value [Å]	Angle [°2 $\theta$ ]	Tip width [°2 $\theta$ ]	Height [counts]	Background [counts]	Rel. int. [%]	Significance
11.04270	8.000	0.180	149	1	80.5	1.55
5.91522	14.965	0.180	16	4	8.7	0.84
5.55726	15.935	0.180	35	4	18.8	1.18
5.35051	16.555	0.150	102	4	55.2	1.90
4.63571	19.130	0.210	169	6	91.4	5.71
4.48819	19.765	0.240	29	6	15.8	1.36
4.24795	20.895	0.120	112	7	60.7	0.91
4.02798	22.050	0.120	139	7	75.3	1.37
3.94756	22.505	0.180	185	8	100.0	2.75
3.87702	22.920	0.180	62	8	33.7	1.05
3.71485	23.935	0.180	31	9	17.0	1.20
3.41720	26.055	0.240	24	10	13.0	1.21
3.27294	27.225	0.240	42	12	22.8	0.81
3.06876	29.075	0.180	36	12	19.5	0.88
2.94742	30.300	0.180	35	14	18.8	1.27
2.80572	31.870	0.180	24	16	13.0	0.79
2.57698	34.785	0.300	55	23	29.6	3.27
2.17145	41.555	0.360	9	23	4.9	1.74
2.07016	43.690	0.720	2	25	1.2	0.85
1.91281	47.495	0.720	3	25	1.8	0.98

Sample crystallized at 150°C for 72 h, without preliminary heating at 100°C, also formed MAPO-36, but with reduced crystallinity and traces of impurities. However, measuring crystallinity by monitoring peak heights, should be complimented by other techniques such as surface area measurements, as it is known that factor such as particle size can affect peak heights. Surface area measurements will therefore be performed using nitrogen BET. For each divalent metal substituent in MePO-36, ( Me= Co, Mn and Zn), the effect of temperature on their crystallization is currently under investigation. Sample of have been prepared and were submitted for XRD analysis.

### 3.2 The effect of aluminum source

Preliminary studies shows, that while psuedobohemite alumina gave MAPO-36, aluminum isopropoxide gave MAPO-5 under otherwise, similar crystallization conditions (Figure 2). MAPO-5 have been reported by earlier researchers, as a strong competing phase during the crystallization of MAPO-36, and can easily formed from slight changes in the reaction conditions. Though the most significant alteration in this procedure was the change of aluminium source, there were also changes in the molar composition of the reaction mixture compared with (1) above. The molar composition of this mixture was:



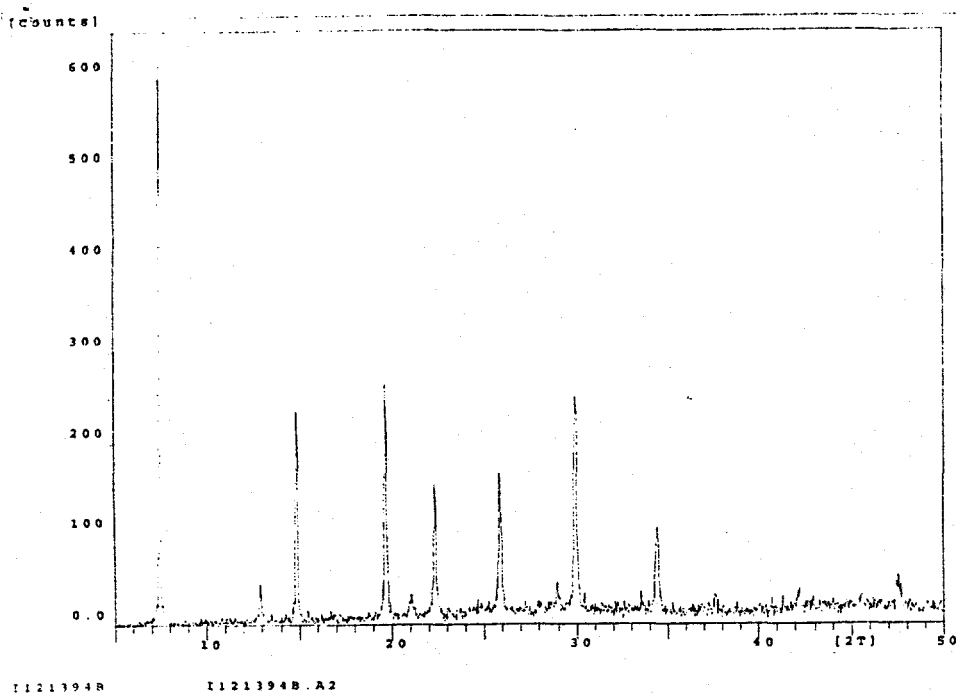
This experiment will therefore be repeated, keeping the mole ratios of the reactants and temperature conditions as in Section 3.1, while varying the aluminum source.

### 3.3 The effect of template (tripropylamine) concentration

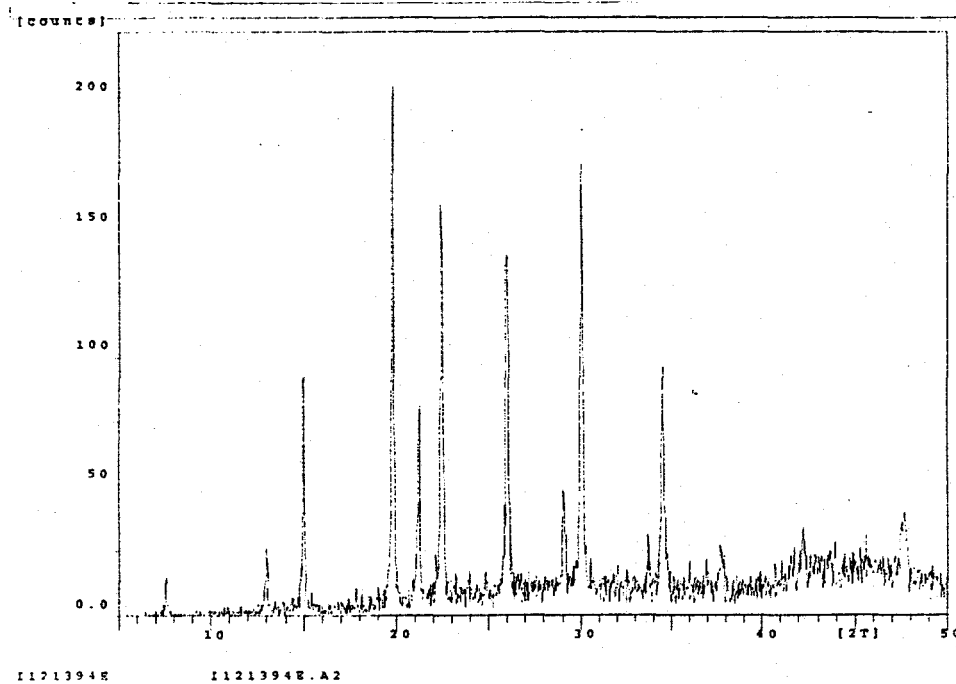
Samples were crystallized from reaction mixtures similar to that in Table 1, but with varying amounts of amine added. The weight of amine added were 0.33x, 0.5x and 0.75x wt in Table 1. Crystallization of these reaction mixtures gave no MAPO-36 phase. Instead highly crystalline

Figure 2. MAPO-5

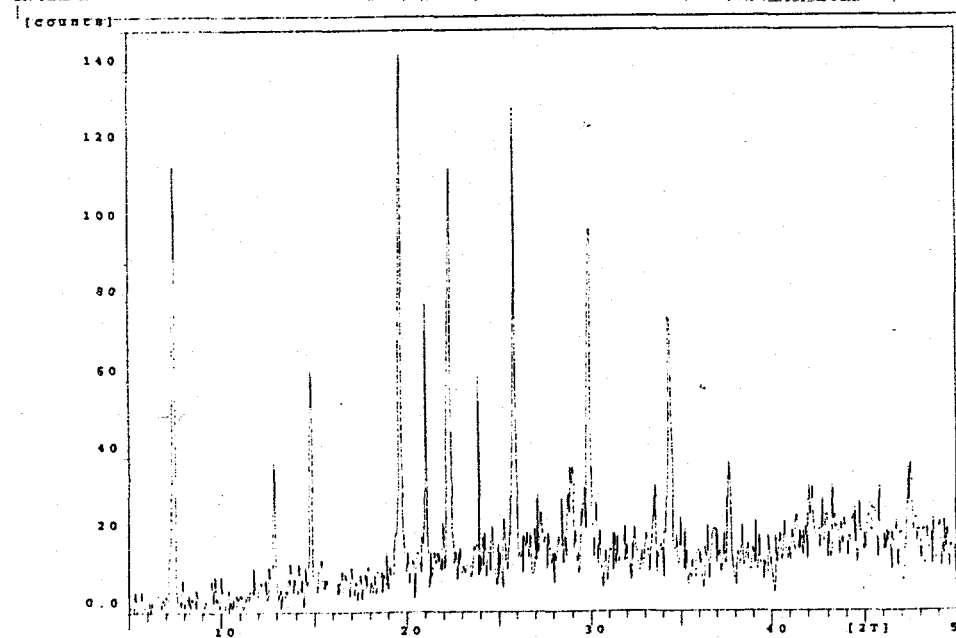
a). (100°C, 48 h,  
150°C, 24 h)



b). (100°C, 48 h,  
150°C, 48 h)



c). (100°C, 48 h,  
150°C, 72 h)



MAPO-5 was formed. More detail investigation on the effect of amine concentration on the crystallization of MeAPOs will be conducted.

#### **4.0 Status of project**

- 1) Reaction conditions were established for the formation of highly crystalline MAPO-36
- 2) Parameters (such as source of reactants and temperature/time affecting the crystallization of MAPO-36) are currently being investigated.
- 3) A sample of MAPO-36 was sent to Texaco R & D, (Port Arthur, Texas) for catalytic testing in the conversion of syn gas.

#### **5.0 Future work**

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

- 1) Continue research on the effect of reaction parameters on the crystallization of MAPO-36. In addition to those mentioned above, other parameters include pH and Mg to Al ratio.
- 2) Prepare other MeAPO-36 (Me=Co, Zr and Ce).
- 3) Prepare MeAPO-46 (Me = Co, Zr and Ce).
- 4) 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.
- 5) Explore secondary synthesis methods using for example ammonium metal fluoride containing salts for incorporation of magnesium, cobalt and zirconium.
- 6) Prepare and characterize metal impregnated MeAPOs to develop Co-catalysts with dual functionality for methanol, hydrocarbon or ether formation.

- 7) Building of a small bench scale catalytic reactor for screening of catalytic activity of materials.
- 8) Submit small and larger quantities of materials for catalytic testing at Texaco.

#### **5. Educational benefits and minority participation**

The two African American students are presently working on this project. Mr. Dewayne Silimon is a dual degree student who complete the engineering component of his degree at Georgia Institute of Technology. Miss Krystal McClure is a junior science student at Clark Atlanta University. Through daily interaction with the senior researchers during their course of work, the students are developing the essentials of the synthesis, characterization and catalytic testing of these industrial important materials.

Dr. Conrad Ingram joined the Catalysis and Separation Science Center in September of 1994. Dr. Ingram brought with him, tremendous experience in the field of synthesis characterization and applications of zeolites and molecular sieves and has been actively involved in this project as a Co-Principal Investigator. A short biosketch is attached.

**Dr. Conrad Ingram**  
*Department of Chemistry*  
*Clark Atlanta University*

Education

Doctor of Philosophy, Chemistry	1994
University of the West Indies, Jamaica	
Bachelor of Science (Hons), Applied Chemistry	1987

Employment History

Clark Atlanta University	
Research Scientist	1994-present
University of the Salford, U.K	
Research Scientist	2/93- 8/93
University of the West Indies, JA.	
Scientific Officer (GC and GC/MS)	1990-1994
Teaching Assistant (Chemistry)	1987-1990
College of Arts Science and Technology, JA.	
Lecturer (Physical/ Organic Chemistry)	1989-1990

Dr. Ingram has been actively involved in the molecular sieve field since 1987. He received his training in molecular sieves during his Ph. D career and through collaborative research at the University of Salford with Prof. Alan dyer, a pioneer in the field of zeolite technology. His doctorate dissertation work on "the catalytic conversion of ethanol to gasoline use H-ZSM-5 zeolite and metal aluminophosphate catalysts" pioneered the establishment of zeolite synthesis and catalysis research in the caribbean. Dr. Ingram also has great tremendous expertise in the characterization of hydrocarbons using GC and GC/MS and have received British Council Award for training in this area.

## Publications

1. R. Szostak and C. Ingram, "Pillared layer structures (PLS): from microporous to Nanophases", *Studies in Surface Science and Catalysis*, (1995) in press.
2. K. Vinje, C. Ingram, R. Szostak and K. Lillrud, "Ferrierite: As Synthesized and Dealuminated from 10 to Infinity", ACS National Meeting, Anaheim, April 2-6, 1995.
3. A. Baker, A. Greenaway and C. Ingram, "Microwave digestion based determination of low molecular of weight organics from Bayer Process liquor", *Talanta*, 1995, in press.
4. C. Ingram and R. Lancashire, "On the formation of C<sub>3</sub> species during the conversion of ethanol using H-ZSM-5 catalyst", *Catalysis Letters*, (1995), in press.
5. C. Ingram and R. Lancashire "Conversion of ethanol to gasoline using H-ZSM-5 zeolite", International Symposium on Zeolites and Microporous Crystals, August, Japan Association of Zeolites, Nagoya, Japan. Prepr. (1993), 332-333.
6. C. Ingram and A. Dyer "Ion exchange on selected metal aluminophosphates", (in preparation).
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