NOVEL CATALYTIC METHODS FOR THE UPGRADING OF COAL LIQUIDS

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THESIS SUMMARY

Reproducible preparation of a number of modified clay and clay-like materials by both conventional and microwave-assisted chemistry, and their subsequent characterisation, has been achieved. These materials are designed as hydrocracking catalysts for the upgrading of liquids obtained by the processing of coal.

Contact with both coal derived liquids and heavy petroleum resids has demonstrated that these catalysts are superior to established proprietary catalysts in terms of both initial activity and deactivation resistance. Of particular activity were a chromium-pillared montmorillonite and a tin intercalated laponite. Layered Double Hydroxides (LDH's) have exhibited encouraging thermal stability.

Development of novel methods for hydrocracking coal derived liquids, using a commercial microwave oven, modified reaction vessels and coal model compounds has been attempted. Whilst safe and reliable operation of a high pressure microwave "bomb" apparatus employing hydrogen, has been achieved, no hydrotreatment reactions occurred.

KEYWORDS

Pillared Clays, Layered Double Hydroxides, Microwave Chemistry, Hydrocracking Catalysts, Coal.

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1 INTRODUCTION

1.1 COAL

1.1.1 COAL *vs* OIL AS NATURAL RESOURCES

The catalytic hydrocracking of petroleum derivatives is a long established and highly profitable industrial process. The demand for hydrocarbon fuels, lubricants and chemicals has risen dramatically throughout the twentieth century, which has in turn driven the science of exploitation of petroleum crudes to greater and greater extremes and underpins much of the world economy. The same cannot be said of coal, which has steadily diminished in its relative economic importance over the same time period.[1,2] Generation of electricity is now the primary economic use of coal,[2] and with the continuing implementation of actions laid down within the Non Fossil Fuel Obligation (NFFO), this is increasingly under threat from alternative sources including renewable energies, which are forecast to provide as much as 20 % of Britain's electricity by 2010, and up to 50% by 2025.[3] However with power generation set to increase, in absolute terms the utilisation of coal is likely to remain steady or slightly rise.[4]

The reason for this disparity is largely due to differences in the physical and chemical nature of the two resources,[1,2,5,6] although at a superficial level the two materials might appear to be similar.

Crude oil is a relatively simple liquid composed of a mixture of aliphatic and simple aromatic organic compounds. Generally these are of low molecular mass, contain only carbon and hydrogen and are simple to characterise and fractionate. Consequently, separation and catalytic upgrading of the various fractions is a commercially viable exercise. Coals, however, are complex heterogeneous solid systems containing inorganic crystalline minerals and organic carbonaceous macerals, whose composition and properties vary widely depending on their source.[7]

The value of converting coal into useful chemicals cannot however be overlooked. Interest in coal conversion technologies fluctuates with estimates of oil reserves. During periods of pessimism oil prices rise with a concomitant leaning toward coal as an attractive alternative. In the seventies, the OPEC oil embargo generated a world-wide energy crisis that demonstrated the dangers, both political and economic, of reliance on an imported energy source.[2] Coal use as a whole experienced a renaissance, and interest in converting coal, particularly as a source of synthetic fuels gathered momentum, which led to a number of new processes being developed for improved utilisation.[2,4,5]

Coal is potentially a source of fine chemicals to rival those derived from crude oil and the utilisation of coal as a raw material for chemical feedstocks has a long history.[2] For many years the by-products of the coking industry were a source of a wide variety of chemicals including solvents, drugs, dyes and artificial flavourings.[2] The modern organic chemical industry is today largely petrochemical based, as direct utilisation of coal in this way is not financially competitive due in part to the complex and widely varying composition of coal.[1,7]

It is for this reason that coal is generally burned for power generation, which is both wasteful and environmentally damaging, and thus much of the research into coal utilisation has focused on how to maximise energy output whilst minimising environmental impact. It is in this area that coal has found its greatest economic value, the coal based chemical industry being firmly anchored in by-product exploitation.[2]

From the mid-eighties onwards, oil prices have consistently dropped. In addition, increased environmental awareness and government action to further the use of non-fossil, renewable resources has increased interest in a variety of "clean" technologies, such as biomass, for power generation and chemical production. Such technologies, although currently in their infancy, act as yet further competition for coal and as such have served to highlight the need for cheap and efficient refining of the raw material.

1.1.2 WHAT IS COAL?[1-7]

Coal is described in various ways; vilified in some quarters as a dirty, environmentally damaging and essentially obsolete fuel; much vaunted by others as a source of clean gas or liquid fuels, or as a key step towards a non-polluting renewable energy based economy. Even within a scientific framework, the classification of coal varies; to Paleobotanists it is a biological fossil, extensive deposits of which are laid down only under very specific geological, climatic and hydrological conditions. To Geologists a carbon rich sedimentary rock exhibiting a wide range of physical properties that reveal information about geological processes experienced during maturation. To Chemists it is a complex array of macromolecules, supported within a mineral matrix, providing a seemingly endless arena for study.

In essence, all of the above statements have value and it is for this reason that the study and utilisation of coal has been, and continues to be both diverse and intellectually challenging.

Coal is a chemically heterogeneous array of polyaromatic organic macromolecules with a high proportion of heteroatoms, arranged within a mineral matrix. The complexity of the organic portion is a result of its source- the action of pressure and temperature on the organic polymers found in vegetable matter, such as lignins and celluloses, over millions of years. This geochemical process, *coalifaction*, results in a complex material whose chemical composition varies depending on the exact conditions experienced.[1,2,7] Coal composition is therefore as diverse as the many sources from which it is mined, differing geographical locations and geological periods produce coals with vastly different chemical composition.[1,2]

The vast majority of scientific and economic interest in coal is targeted at this organic material, as it is this that is of commercial value, whether viewed in terms of its calorific value when burned, as in power generation, or as a feed source for the chemical industry.

1.1.3 COAL CHARACTERISATION[1,2,7]

As a natural product, the composition of coal varies as much as the reserves from which it can be mined. *Coal* is used as a term to describe a wide variety of materials exhibiting differing appearance, physical attributes and chemical composition. The chemical arrangement of functional groups [illegible] [illegible] is in the [illegible], the [illegible] [illegible] [illegible] [illegible]

As indicated previously, coalifaction is extremely sensitive to environmental conditions. This vast array of variables is rationalised in *petrography*. From a geological point of view, the history of a coal can be traced by this simple visual inspection of the rock. Up to four principle *lithotypes* can be identified in a coal sample, which indicate the specific conditions the carbonaceous material was exposed to during maturation. Each lithotype is composed of varying proportions of three maceral groups that represent the plant matter from which it was derived, these are vitrinite, exinite and inertinite. These three maceral groupings exhibit differing reactivity, derived as they are from different molecular components of the parent plant matter.

At the most basic level, every coal is defined by its moisture content, volatile matter, ash and fixed carbon. This *proximate* analysis is carried out thermogravimetrically, and involves heating the coal to release each of the first three constituents to leave a black char. The fixed carbon content is calculated by difference.

The composition of coal in terms of the main elements present is analysed in the *ultimate* analysis. The percentage content of carbon, hydrogen, oxygen, sulfur and nitrogen present in the coal are traditionally determined by controlled burning or chemical reaction and isolation followed by analysis. Despite its name, the process is of very limited use in characterising a coal as it reveals nothing about the chemical environment or functional groups in which each element is to be found, the process does not even discriminate between organic and inorganic material.

Coal *rank* is the system used to group similar coals in terms of their chemical and physical properties. In essence, increasing rank follows an increase in carbon content and a decrease in hydrogen and oxygen content. This roughly follows the maturation of the coal from plant matter to the extreme top of the scale graphite, essentially 100% carbon.

Over the past twenty or thirty years, the wealth of knowledge relating to coal composition has steadily grown, and the chemical environments and molecular structure within coals are now open to more rigorous probing. An insight into the true nature of coal molecular structure draws ever closer.

1.1.4 COAL UTILISATION[1-6]

The diminishing use of coal in domestic fuel applications during the fifties was largely caused by a rapid growth in the use of oil and natural gas. This illustrates the advantage that these fuels have over coal; they are fluids. Over its long history, coal technology has developed and lumps of coal are not simply shovelled into furnaces, but ground to varying degrees to make introduction of coal more predictable and exact. No matter how advanced such processes become, however, this remains the inescapable disadvantage associated with coal utilisation.

The vast majority of fuelled machinery works on fluids. Furthermore, chemical manipulation of fluids is far more attractive than dealing with solid raw materials. Utilisation of coal as a fuel and source of chemicals has therefore been restricted by its very nature. The valuable, carbonaceous material exists as an almost intractable solid, with the further complication of the presence of unwanted mineral matter. In order that coal may be utilised to its full potential methods of extracting the organic material from the chemically and physically heterogeneous rock have been developed.

The first step in any genuinely viable coal utilisation process must be some form of extraction. This may be achieved in a number of ways, roughly divided into two categories:

1. Thermal

- Pyrolysis; Decomposition by heating in the absence of air, this is the basis of nearly all techniques of coal utilisation. Thermal treatment separates coal into a solid residue, coke, and volatile products, liquid and/or gas.

- Carbonisation; The industrial application of pyrolysis to generate coke or smokeless fuels, generally optimised to make best economic use of the liquid or gaseous by-products produced.

2. Thermochemical

- Gasification; Conversion of coal organic matter into a gaseous product using thermal decomposition in the presence of oxygen. As such it is very similar to combustion, the product being a CO/H_2 mixture of variable composition. This "syngas" is an extremely important raw material used in the generation of ammonia, methane and methanol. An alternative hydrogasification, utilising hydrogen rather than oxygen generates methane.

- Indirect liquefaction; Conversion of syngas to a liquid product using *Fischer-Tropsch* chemistry. The process is extremely versatile and by adjusting pressure, temperature, gas composition and catalyst generates alkenes, alcohols aldehydes and paraffin waxes.

- Direct liquefaction; Conversion of coal organic matter to a liquid product without gasification. This process is based on the hydrogenation of coal. Coal is suspended in a hydrogen donor solvent, such as tetralin or N-Methyl-2-Pyrrolidone (NMP), and heated in the presence of hydrogen. A catalyst may be used, depending on the nature of the solvent. Hydrogen donor ability and solvent ability being independent, a good solvent is not necessarily a good hydrogen donor, as in the case of NMP, and catalysts may therefore be used to enhance hydrogen transfer.

Of these processes, the area of primary interest in the context of this thesis is direct liquefaction and this is described in more detail below;

1.1.4.1 Direct Liquefaction of Coal[1,4,5,8]

The process of coal liquefaction is not trivial. More than one hundred years since it was first observed that coal could be converted to a heavy crude oil by chemical reduction, it remains "one of the most complicated consecutive reaction processes of one of the most complicated reactants.".[1] Consequently, systematic prediction of oil yields cannot be related to a single parameter defining the coal under study. Similarly the complexity and variation of product stream compositions mean activity toward upgrading processes, such as hydrocracking, are unpredictable. Unlocking the potential of coal as a source of chemicals is therefore considerably more complex than analogous utilisation of crude oils.

The chemical structure of the organic coal material can be described in very general terms as an irregular array of macromolecules incorporating a variety of aromatic compounds, organic residues, polar groups and heteroatom environments. The two-dimensional structure is represented by these non-uniform polymeric chains, in which polyaromatic units are joined by methylene bridges *vide infra*. The structure is extended into three dimensions by cross-linking of polymer chains via hydrogen bonding.[7]

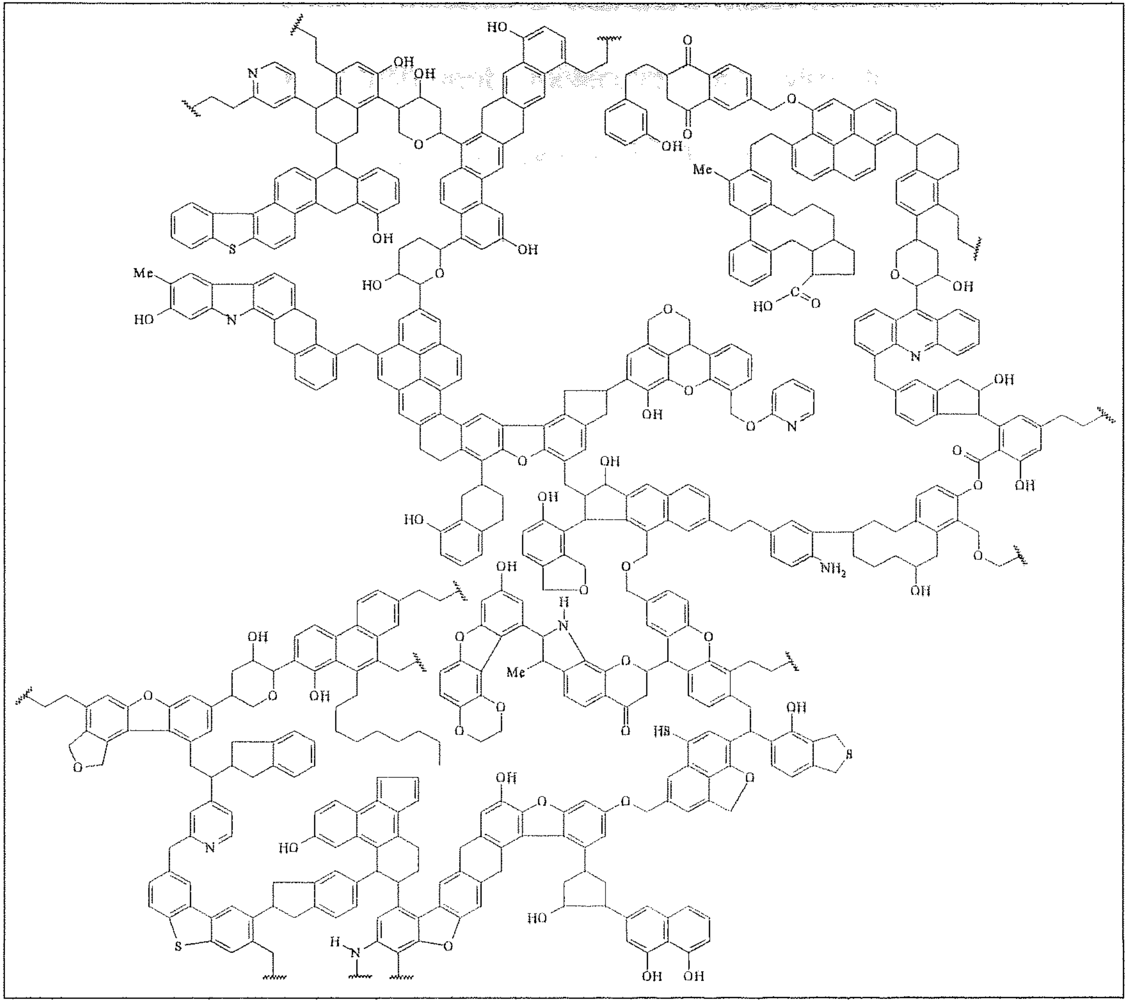


Figure 1 Representation of a coal macromolecule fragment, shown as a quasiplanar array for simplicity[7]

Behaviour of the organic material is therefore much the same as that of a thermoplastic; the constituent molecules are virtually insoluble and decomposition occurs rather than melting.[1,7] The fragments released by mild operations on the coal are considered to be the base structural units from which the coal macromolecule is built.

The macromolecules do, however, undergo thermal fragmentation and extraction as soluble products by hydrogenating liquefaction. This occurs *via* three nominally consecutive reactions; solubilisation, depolymerisation and hydrogen donation. Breaking of the hydrogen bonding by heating provides a degree of solubility, the "dissolved" coal may then be depolymerised and extracted in solvents. These act both as physical and heat transfer media, and as source of hydrogen, reducing the possibility of polymerisation and condensation of the solubilised fragments. By incorporating a flow of solvent and restricting the temperature, extraparticle secondary reactions are minimised, yielding the primary coal extracts.[9,10]

The following diagram represents the breakdown of coal macromolecules by liquefaction and the resulting products derived in the presence (1) and absence (2) of a solvent with suitable hydrogen donor properties.

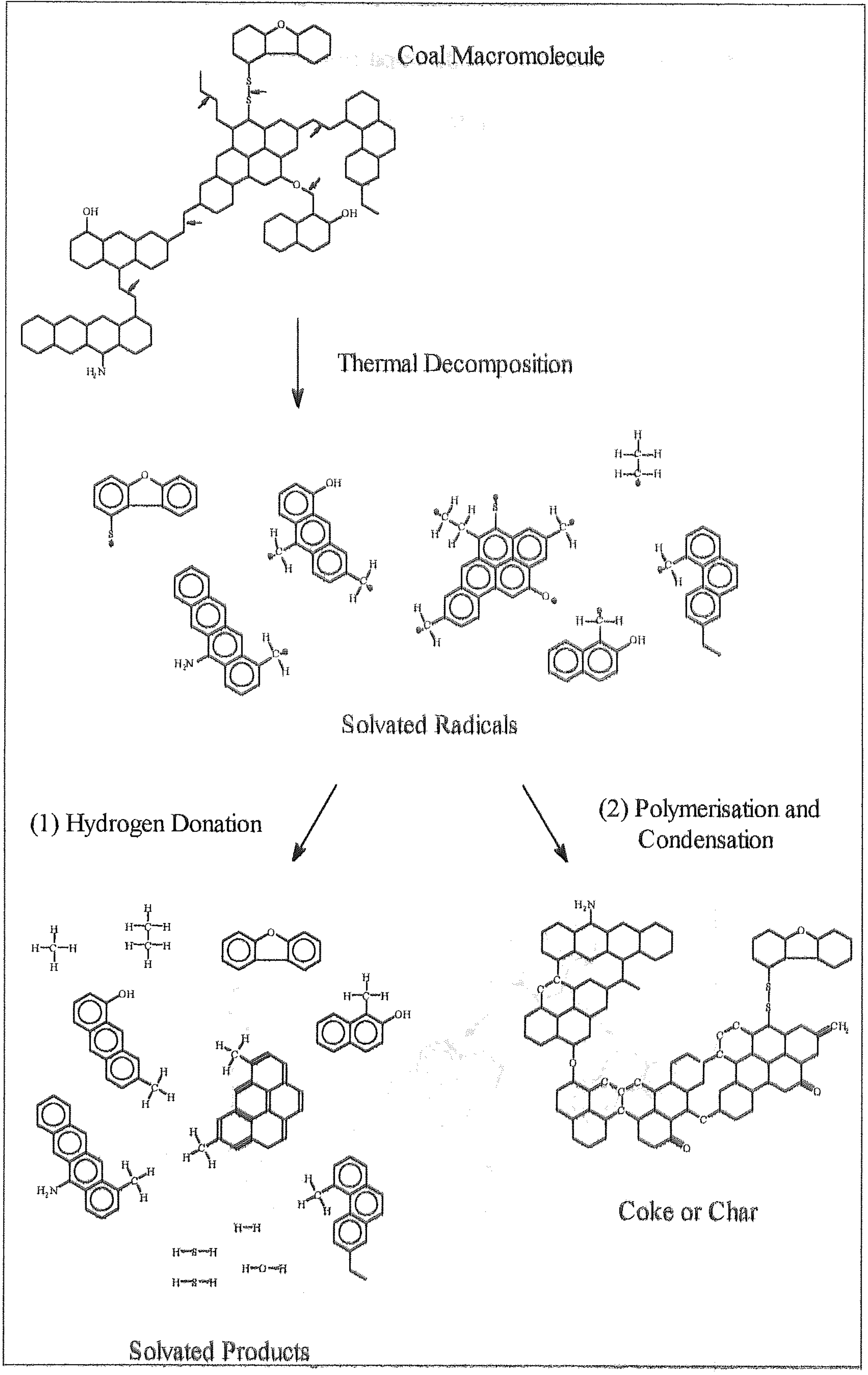


Figure 2 Representation of direct coal liquefaction processes.[1]
N.B. Hexagonal structures represent both aromatic and non-aromatic rings.

1.1.4.2 Hydrocracking of Liquefaction Extracts

The main purpose of upgrading liquefaction extracts is to convert the crude extract into oils with low heteroatom content, which can be used as feeds for further refining processes. These extracts may be upgraded by catalytic hydrocracking, to reduce molecular mass and heteroatom content by exposure of the liquefaction products to hydrogen at high pressure and temperature in the presence of a catalyst.[11,1] The hydrogenation of polyaromatics is exothermic, and results in a decrease in gas volume. Following thermolysis of the large fragments resulting from liquefaction, therefore, generation of napthenes and paraffins is driven by conditions of high pressure and temperature. This is illustrated by the reduction of pyrene below.[4]

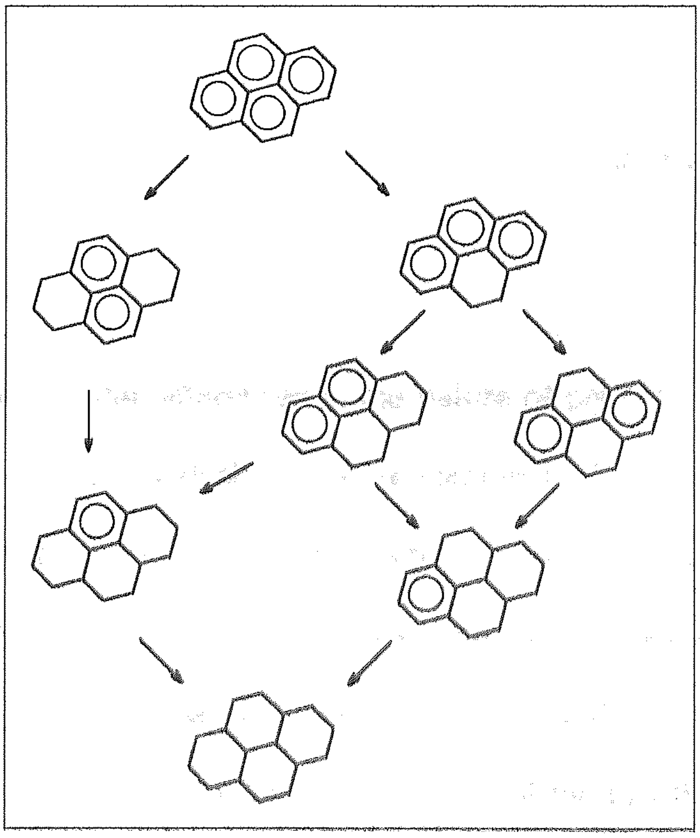


Figure 3 Alternative routes leading to the complete hydrogenation of pyrene

Recent work conducted at Imperial College reveals that fragments with very high relative molecular masses (RMM) and complex molecular structures[12] are present in the primary extracts released during coal liquefaction.

This work has highlighted the "remarkably refractory nature of primary coal extracts",[12] liquefaction extracts prepared under conditions minimising secondary reactions were observed to be extremely resistant to hydrocracking, even when rather severe conditions were employed.[13] This is at least in part due to the catalysts available, which are designed for dealing with petrochemical crudes.

Analysis of the extracts by size exclusion chromatography (SEC) laser desorption mass spectrometry (LD-MS) and, more recently matrix assisted laser desorption ionisation (MALDI) reveal the existence of molecular fragments with molecular masses in excess of 6,000 u with traces extending up to 20,000 u.[12]

Despite the fundamental differences in the nature of petrochemical and coal derived crudes, in both industries the requirements for catalysts offering efficiency, longevity and high product selectivity remain the same. Common zeolite hydrocracking catalysts designed for petroleum derivatives have poor activity when used for the upgrading of coal liquids, and are quickly deactivated by carbon build up, largely as a result of the fact that pore size is small compared to the distribution of molecular mass.[11,12,14] Catalysts specifically designed for upgrading coal liquids are also unsatisfactory; even under intense conditions, reaction rates and product selectivity are unimpressive and consumption of hydrogen is high, partially due to the refractive nature of primary coal extracts. Fuel and chemical feedstock production therefore continues to be uneconomic,[11] compared to the petroleum derived equivalents, in the absence of catalysts offering improved reaction rates and product selectivity during hydrocracking, whilst reducing hydrogen consumption.

1.2 MODIFIED CLAY CATALYSTS

The swelling property of smectite clays can be utilised to introduce crosslinking inorganic metal hydroxide oligomers which yield thermally stable pillared clays with properties similar to those characteristic of zeolites.[15] Although less thermally stable than zeolites and often exhibiting a distribution of pore sizes, these pillared clays are a potential solution to the problem of catalytic upgrading of coal derived liquids. Pore size can be extended beyond that attainable by zeolites and specific catalytic activity can be tailored by choice of the pillaring species and reaction conditions.[16-18]

1.2.1 CLAY MINERAL STRUCTURE AND COMPOSITION[19-22]

In order that a material's characteristics may be exploited or modified, it is necessary that there is some understanding of the underlying nature of the substance and of the source of its properties.

1.2.1.1 Layer Silicates

Clay minerals are layer silicates, in which the atoms (or ions) are arranged in parallel planes bound together to give a layer structure. This structure is based on the condensation of sheets of corner sharing SiO_4 tetrahedra, with those of edge sharing $M_{2-3}(OH)_6$ octahedra, where M is either a di- or trivalent cation. The basic structural units can be joined in several ways, and it is this arrangement which defines the characterisation of such minerals. The vast majority of clay minerals belong to the larger group of phyllosilicates; that is a planar network in which the basal oxygens in the tetrahedra are shared to give a repeating hexagonal mesh pattern, with the fourth directed normal to this sheet. This apical oxygen can then be shared with another cation, forming part of the adjacent octahedral sheet. An unshared hydroxyl group at the centre of each hexagon maintains coordinative saturation.

The linking of these layers is not limited to a single octahedral/tetrahedral junction, and this provides further subdivision within the phyllosilicate family into di-, tri- and tetramorphic clay minerals, based on the ratio of tetrahedral: octahedral layers.

In the scope of the present work, it is the trimorphic group, which includes the smectites, which is of interest. These minerals are the result of a 2:1 condensation in which a single octahedral layer is sandwiched between two sheets of inward pointing tetrahedra. This is generically referred to as the mica type structure.

If the general layer framework is visualised in terms of the oxygen atoms present, either as bridging oxygen atoms or hydroxide groups, then two types of vacancies exist. In an idealised model, Si^{4+} occupies those in the tetrahedral layer and vacancies in the octahedral layer are occupied to varying degrees by di- or trivalent cations. The degree of occupancy of these octahedral vacancies gives rise to a further subdivision within the mineral group; full occupation of these vacancies gives trioctahedral sheets, whereas those with two-thirds occupancy are dioctahedral.

The octahedral vacancies may either be two thirds filled with M^{3+}, such as Al^{3+} in pyrophyllite, or fully filled with M^{2+}, such as Mg^{2+} in talc. These two minerals have electronically neutral layers, and can be considered idealised structural types of the dioctahedral and trioctahedral mineral types respectively.

1.2.1.2 Deviation from Ideal Composition

Further variations arise due to deviation from these ideal structures, in which cations from the tetrahedral and/or octahedral sheet are replaced by alternative cations of similar size and lower valency. This results in a net negative charge to the layer, which is balanced by often exchangeable, interlayer hydrated cations. Such materials are termed cationic clays and can be described in terms of a structural unit defining the layer-interlayer composite. Classification is based on layer type, octahedral occupation, isomorphous substitution and interlayer material. All these factors have a profound effect on the morphology of the bulk material, and thus on its behaviour.

1.2.1.3 Cation Exchange Capacity

It is the exchangeable cations that are the source of the swelling and intercalation chemistry of smectite clays. The cation exchange capacity (CEC) is perhaps the most fundamental property of a clay mineral, varying from material to material according to the magnitude, source and location of the layer charge. Substitution of Al^{3+} for tetrahedral Si^{4+} results in negative charge localised at the site of substitution, as in the micas. In smectites the majority of substitution is in the octahedral layer, and it is therefore evenly distributed over the layer, associated with the framework oxygens.

The consequences of the two types of isomorphous substitution are manifested in the morphology of the clay platelets. This reflects the interlayer bonding which is a physical association rather than a true chemical bond. In micas, charge balancing cations (mainly potassium) are strongly associated with the layers due to a high degree of substitution (one in four Si^{4+} replaced by Al^{3+}), the localisation of the resulting negative charge and the strength of association for the interlayer potassium. The interlayer forces are therefore strong and regular layer stacking results giving a high degree of crystallinity and a CEC of zero.

In contrast, when substitution occurs primarily in the octahedral layer the net charge is delocalised over the framework, as in montmorillonite. There is a concomitant decrease in the crystallinity due to turbostratic (essentially random in the *ab* direction) stacking of layers within the clay platelets. This weakening of the interlayer association is exaggerated by the presence of alternative charge balancing cations, commonly sodium or calcium. It is this weakened layer affinity that allows swelling in the presence of polar reagents such as water, which solvate the interlayer cations. It is this swelling property, combined with the fact that the native charge balancing cations can be competitively replaced by practically any cationic species present in the external solution, which allows the modification of smectite clays by pillaring.

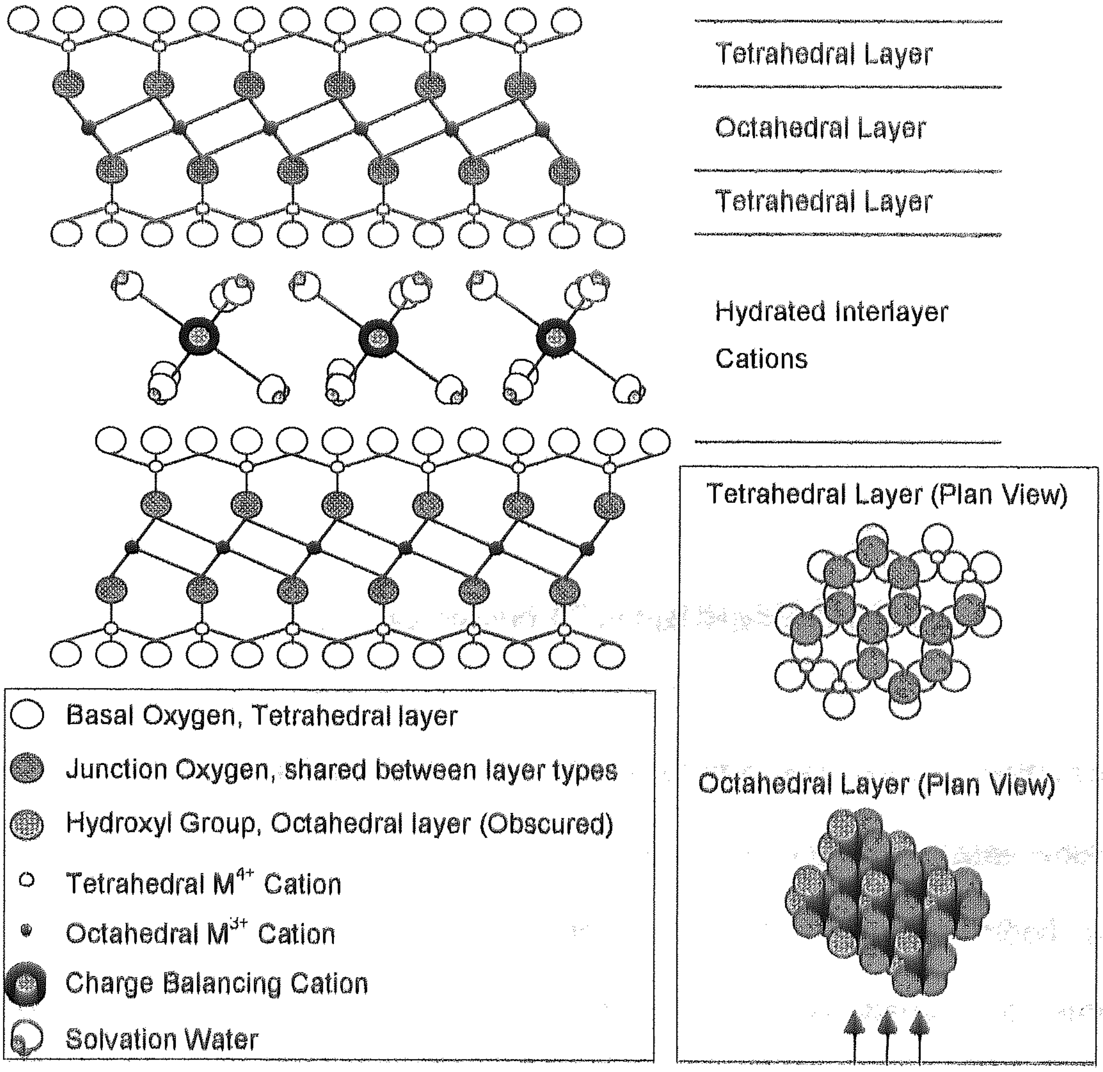


Figure 4 Idealised structure of 2:1 smectites[19]. Included are plan views of idealised hexagonal tetrahedral and octahedral layers. Shared oxygens indicated (heavy shading), along with otherwise obscured hydroxyl groups of octahedral layer (light shading).

1.2.1.4 Montmorillonite

Montmorillonite is described as a dioctahedral smectite, in which the isomorphous substitution occurs principally in the octahedral layer where Mg^{2+} replaces about a sixth of the Al^{3+}, the resulting negative charge being balanced by Na^{+}. Some water is also present, depending on conditions of temperature and humidity. It therefore has an idealised structural formula of $Na_{0.35}(Al_{1.65}Mg_{0.35})Si_4O_{10}(OH)_2.nH_2O$. However, due to the fact that this is a naturally occurring material, further deviations occur from one deposit to another. Isomorphous substitution of small amounts of aluminium and/or iron(III) in the tetrahedral layer, and of iron(II) in the octahedral layer are commonly encountered, along with carbonaceous deposits and particulate impurities such as quartz in the unrefined bulk material. Ignoring impurities then, the nature of dioctahedral smectite clays is that of an ensemble of solid solutions represented by the montmorillonite-beidellite-nontronite series, with the structural formula;[23]

$$(Al/Fe^{3+}{}_{2-y}Mg_y)(Si_{4-x}Al/Fe^{3+}{}_x)O_{10}(OH)_2E^{+}{}_{x+y}.nH_2O$$

Where E^{+} is the interlayer cation, x is the amount of octahedral substitution and y is the amount of tetrahedral substitution. Aluminous smectites where y>x, i.e. where the octahedral charge dominates, are described as montmorillonites, those with y<x, i.e. where tetrahedral charge is greater, are beidellites (or nontronites). Trivalent iron is commonly found isomorphously replacing aluminium in both these materials. Whilst this does

not affect the overall layer charge, other properties are significantly affected. Dioctahedral smectites containing large quantities of trivalent iron form the final major group of the series- nontronites.

Clay mineral	Montmorillonite	Beidellite	Nontronite
Octahedral	$Al_{1.65}Mg_{0.35}$	Al_2	$Fe^{3+}{}_2$
Tetrahedral	Si_4	$Si_{3.6}Al_{0.4}$	$Si_{3.6}(Al,Fe^{3+})_{0.4}$
Anion	$O_{10}(OH)_2$	$O_{10}(OH)_2$	$O_{10}(OH)_2$

Table 1 Summary of clay mineral composition of the major smectites.

1.2.1.5 Laponite

In addition to the wealth of naturally occurring clay minerals, there is also a range of synthetic equivalents in the marketplace. These materials are in many ways superior to naturally occurring clays due to the control imposed over their structure during manufacture. These materials approach ideality more closely than their natural counterparts and differences between one sample to the next are reduced. Laponite is described as a synthetic hectorite, a trioctahedral smectite in which all octahedral sites are occupied by Mg^{2+} and Li^+ ions, with the tetrahedral layers composed in the same way as montmorillonite, with idealised composition $Na_{0.67}(Mg_{5.33}Li_{0.67})(Si_8O_{20}(OH)_4)$.[24]

1.2.2 LAYERED DOUBLE HYDROXIDES

Layered double hydroxides (LDH's) are a class of synthetic lamellar materials often described as the anti-type of 2:1 clay minerals.[25-28] Isomorphous substitution of high valence metals in octahedral positions in the hydroxide layer generates a residual positive charge. The interlayer region is thus occupied by charge balancing anions, such as carbonate, nitrate or chloride.[25,26] The properties of these materials and their pillared derivatives are akin to those of clay minerals and are of interest in much the same applications, particularly as sorbents and heterogeneous catalysts.[27]

LDH's can be synthesised by coprecipitation of metal salts. They have the general formula $[M(II)_{1-x}M(III)_x(OH)_2][A^{n-}]_{x/n}\cdot yH_2O$, where M(II) and M(III) are octahedrally co-ordinated metal ions, and A is the gallery anion.[26] They are described as having a brucite- (magnesium hydroxide-) like structure, shown below;[26]

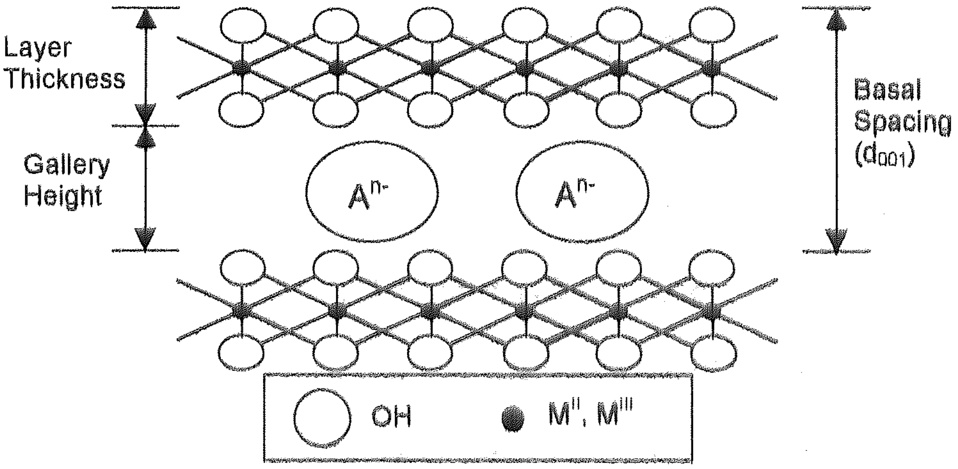


Figure 5 Schematic representation of Layered Double Hydroxide structure consisting of brucite-like layers intercalated by hydrated anions

1.2.3 CATALYTIC PROPERTIES OF CLAY MINERALS

Clay minerals are known to be catalytically active as a result of surface acidity in the form of either Brønsted or Lewis sites. The former arise from dissociation of water molecules in the hydration spheres of charge balancing cations which protonate surface bridging oxygens resulting in hydroxyl groups which are readily deprotonated. The latter are the result of coordinatively unsaturated surface species with electron pair acceptor properties. Furthermore, the layer structure, small particle size, intercalation properties and organophilicity of swelling phyllosilicates affords a high surface area for adsorption of organic molecules near these sites.[20]

The nature of layered double hydroxides is, as already stated, that of anti-type to the naturally occurring clay minerals.[28] In essence, the presence of catalytic hydroxide groups plays an analogous role to that of the acid sites present in clays. The catalytic properties are thus biased toward oxidation reactions, in contrast to the reduction based applications usual for clays.[25, 29-31]

These properties are principally responsible for the use of clays in the catalysis of a wide variety of proton assisted organic reactions typical of refining industries where their role is essentially that of a solid acid. It is for this reason that clay minerals were one of the first materials used for the catalytic upgrading of petrochemicals.[32-35] More recently, they have been replaced by zeolites, which offer greater thermal stability and product selectivity.[11,32,33,36]

In addition to the catalytic properties of smectites, greater understanding of their intercalation chemistry has lead to applications as catalyst supports.[17,18,31-35,37-47] Chemistry in the interlamellar region by, for example, immobilisation of metal complexes affords a solid-state system in which chemistry much like homogeneous solution catalysis can occur, without many of the associated technical problems.

The advent of pillared interlayer clays, in which metal oxide clusters are employed to generate larger pores whilst maintaining thermal stability, has revealed potential applications including the processing of fuels[11,35,42,47] for which zeolites and supported catalysts are unsuitable. By varying pillar dimensions, pillar spacing or both it is possible to tailor the pore size to a particular application. Furthermore, pore sizes that exceed those of zeolites are accessible,[32,34,42,43,48,49] offering opportunities for catalytic reactions with larger molecules e.g. upgrading of crude oil residues, or coal liquefaction extracts.

1.2.4 MODIFICATION OF CLAY PROPERTIES BY PILLARING

Penetration of water into the interlamellar region of swelling phyllosilicates causes the layer spacing to increase as a function of the partial pressure of water vapour. At the extreme, i.e. at 100 % humidity or in dilute aqueous suspension, total delamination occurs. This process is totally reversible and removal of this water by heating results in a return to the original spacing,[17-19] thus at temperatures necessary for catalytic coal treatment no pore size advantage is gained. Introduction of a large cationic species by ion exchange for the native charge balancing cation whilst the clay is dispersed provides a means to retain interlayer spacing of molecular dimensions after removal of the swelling agent. These "pillars" can take a number of forms but in the context of primary coal extracts only thermally robust species are suitable intercalates, otherwise collapse of pores, and loss of surface area and activity results.

Pillared interlayer clays (PILC) of this type are prepared by exchanging the native cations of the parent clay with large oligomeric hydroxy metal cations formed by hydrolysis of metal salts. Upon heating, these undergo dehydration/dehydroxylation,[18,19] resulting in thermally stable pillars composed of metal oxide clusters, as shown below. The resulting materials possess a two dimensional zeolite-like structure. The most commonly studied pillaring agent is the so-called Keggin ion,[17,18] $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$, formed as one of the products of the base hydrolysis of aluminium trichloride solution.[50] In solution, the Keggin ion structure can be described as a central, symmetric AlO_4 tetrahedron, surrounded by twelve AlO_6 pseudo-octahedra. Other polyhydroxy metal oligomers having this type of structure are also referred to as Keggin type structures.

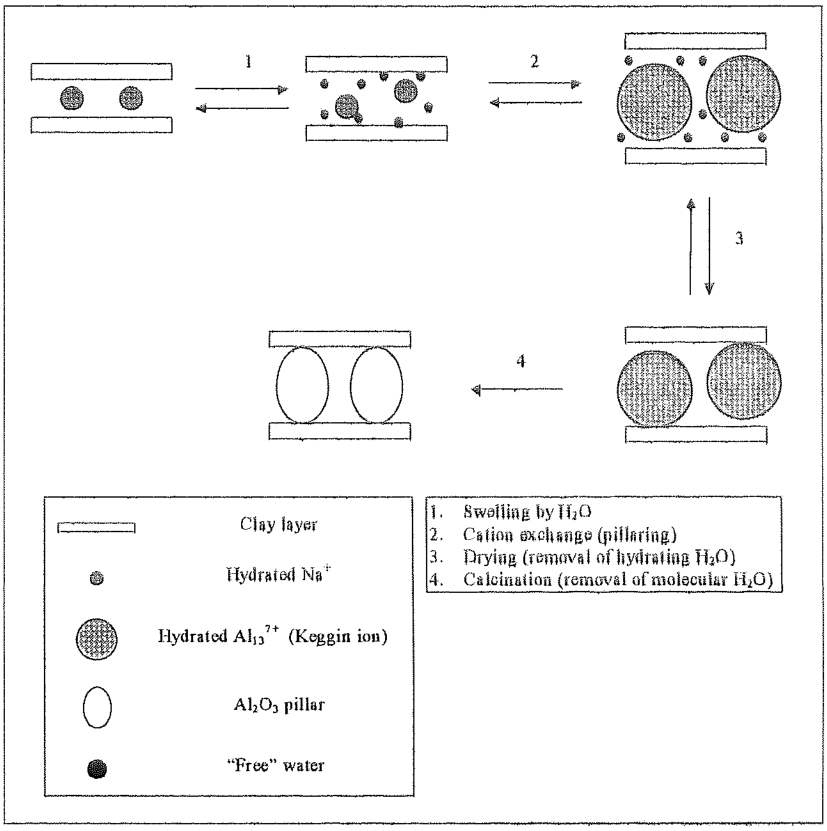


Figure 6 Schematic representation of the inclusion of a metal oxide pillar between the layers of a swelling laminate material

Moreover, although the original purpose of pillaring a swelling clay is to keep a large fraction of the internal surface area available for adsorption and catalytic processes,[32] there is the added potential of introducing non-innocent pillars containing active metal sites and exhibiting multifunctionality, perhaps for the reduction of organic molecules.[14,16-18,20,35,48,49]

Analogous theoretical considerations apply to LDH systems, repetition here would serve little purpose. However, the pillaring materials available differ in that overall charge must be negative for successful intercalation. This property allows the introduction of hetero- and iso- polyoxometallate species,[25,27-30,51-54] whose range of catalytic activity is potentially more versatile than the 'simple' Keggin type cationic species.

1.3 MICROWAVE DRIVEN CHEMISTRY

The past fifteen years have seen the gradual introduction of the microwave oven in the chemistry laboratory. Initial use of the microwave oven was limited to rapid sample preparation in certain sectors of analytical chemistry.[55,56] More recently interest has grown in the effect of microwave irradiation on reaction chemistry.[57-73] The field of microwave induced chemistry has now matured into a well established laboratory scale technique with a number of advantages over conventional heating including massively accelerated rates of reaction,[55,62,68,71-73] improved product selectivity,[60] facile one-pot reactions[66] and, in a growing number of cases, complete exclusion of solvents.[58,62] Exploitation of microwave methodology has found favour in fields as diverse as synthetic pharmacy,[58,71] organic chemistry,[55,58-60,62,68,72,73] organometallic chemistry,[57,66] coordination chemistry,[57] solid state inorganic syntheses,[57,67] polymer syntheses, decontamination of land,[58] and coal science.[65,66]

Taking the field of coal science as an example, microwave driven reactions have added to the wealth of techniques used in desulfurisation, gasification and pyrolysis, moisture determination, SO_x and NO_x reduction and coal characterisation.[65,66]

1.3.1 MICROWAVE DIELECTRIC HEATING[57,58]

Chemistry based on microwave dielectric heating utilises the ability of suitable receptors, both solid and liquid, to convert electromagnetic radiation into thermal energy that can be used to drive reactions at accelerated rates. Although there still remains some debate as to the existence of an intrinsic, athermal "microwave effect" responsible for activation of the molecules within reaction mixtures,[58,70,] the majority of the scientific community now recognise the sources of rate enhancement by microwave irradiation are thermal in nature.[64,70]

The mechanism by which microwave irradiation induces heating is two-fold; dipolar polarisation and conduction.

1.3.1.1 Dipolar Polarisation

In the case of dielectric materials, i.e. non-conducting solids or liquids, the heating effect is generated at a molecular level by virtue of the response to an external polarising field. Microwaves are electromagnetic waves with frequencies toward the upper end of the radio-frequency range.

Under the influence of an electric field polar molecules, such as water, are forced to change their position and begin to align with the direction of the field. As the direction of the field switches to the opposite sense rapidly, the motion of the molecules lag behind the alternating field. This directional switching occurs around $2.5x10^9$ times a second resulting in a rapid wobbling motion of the molecules, which imparts kinetic energy to the system and disrupts thermal equilibrium.

1.3.1.2 Conduction

The motion of electrons or ions within the material heats conducting solids and non-stoichiometric materials including semiconductors and minerals such as pyrite. When exposed to microwaves, charged species experience an extremely high voltage, which generates a rapidly alternating current within the material. Heating in such materials is therefore ohmic in nature, caused by the resistance of the material to current flow.

1.3.2 REACTION ACCELERATION IN THE MICROWAVE OVEN

1.3.2.1 Microwave Irradiation of Homogeneous Systems; Superheating of Solvents[64,68,70,73]

As explained above, when exposed to microwave irradiation solvents can be heated above their normal boiling point. It is this superheating which is responsible for increased reaction rates. When reaction vessels are heated by conventional (direct) methods such as a hot plate, thermal transfer is required to allow the whole of the solution to heat. Consequently a temperature gradient exists within the solvent and complete heating is slow - the highest temperature being at the walls of the vessel. It is at these surfaces that bubbles initially nucleate when the solution begins to boil. In some respects, microwave irradiation could be seen as providing the "true" boiling point of a solvent as, at least for low volumes, the whole is heated equally and a higher temperature is reached before bubbles can form.

The following table contains some data relating to solvents encountered during the experimental work of this thesis. The efficiency with which solvents respond to microwave irradiation, i.e. the magnitude of the dielectric loss varies with the frequency of the incident radiation. For water, this is optimum at 20 GHz, but commercial microwave ovens generally operate at 2.45 GHz as a result of their domestic application for heating of the water in food and the necessity for heating throughout the whole of the food medium.[57]

SOLVENT	NORMAL BOILING POINT atmospheric pressure conventional heating (°C)	ELEVATED BOILING POINT atmospheric pressure microwave heating (°C)	DIELECTRIC CONSTANT (ε) (293.2K) relative to vacuum
WATER	100	104	80.1
ACETONITRILE	82	107	36.6
NITROMETHANE	101		37.3
NMP	202		32.6
TETRALIN	208		2.8
ETHANOL	78	103	25.3

Table 2 Data for common solvents relevant to microwave applications[63,74]

1.3.2.2 The Search for a Microwave Effect

Much of the microwave induced chemistry conducted to date has been targeted at organic syntheses in relation to pharmaceutical chemicals. Unmodified microwave ovens have been extensively utilised in catalytic transfer hydrogenation (CTH) reactions.[60-62,69,71] In these experiments the reduction of unsaturation of compounds such as beta-lactams, sterols/ bile alcohols to produce their saturated congeners has been achieved by hydrogen abstraction from a donor molecule assisted by catalysis at elevated temperatures without the need for high pressure hydrogen. To date this has been limited to relatively small molecules with few double bonds.

From the beginning of microwave enhanced chemistry there has been discussion as to the source of the rate enhancements observed. Particularly in the early nineteen-eighties, various papers addressed this problem attributing certain decreases in reaction time to an intrinsic, athermal "microwave effect". However, subsequent re-examination of these reactions, often by the original practitioners,[64,70,75] left most in no doubt that a lack of experimental rigor was responsible for misleading conclusions. Work by Laurent *et al* led to the conclusion that "It seems likely that the main problem [in proving the case for or against specific activation by microwaves] arises from differences in experimental conditions resulting from imprecise monitoring and improper controls."[70]

Laurent *et al* initially claimed to have discovered the first example of a specific activation in a homogenous system,[70] and a year later concluded that heating mode had no effect on the rate of reaction.[75] More recently Gedye *et al* re-examined some of the better known reactions and concluded that, under comparable conditions of pressure and temperature, there is little or no rate enhancement generated by exposure to microwaves.[64] In both these cases however, a distinction was drawn between homogenous solvent based systems, and heterogeneously catalysed reactions. In the former, it was recognised that, if superheating is avoided such that the reaction in question is conducted at conventional reflux temperatures, then the rate is independent of heating method. However, in the case of heterogeneous catalysis[67,70] and, as examined in separate articles, in solvent free environments, hot spots generated at solid surfaces (and equally at other phase boundaries) are responsible for impressive rate enhancements.[55,61,]

Some controversy still remains, in a recent article Wroe is quoted[58] as claiming to have "proved" the existence of a microwave effect in the sintering of ceramics. It would appear that the argument is now one of semantics fundamentally based on disagreement as to what constitutes a thermal effect. What is clear is that the very nature of the heating achieved by microwave irradiation precludes thermal equilibrium; as a result bulk temperature measurements are not representative of the actual reaction conditions.[57,58,63,64,70] This is also at the source of the true value of microwave irradiation- heating is localised, targeting receptive molecules or functional groups. This mechanism, which does not require convective heat transfer, distributes kinetic energy within the system more efficiently, hence greatly accelerating many reactions.

The rate enhancements observed in reactions undertaken within a microwave field are therefore attributed to processes which are fundamentally thermal, that is the kinetic energy of the system is increased, or redistributed. A number of processes are responsible for this, alone or in combination depending on the nature of the system;

- Increase of reaction temperature and pressure above that of conventional reflux as a result of superheating of solvents by suppression of boiling
- Generation of hot-spots, either at solid surfaces by dielectric relaxation on a molecular scale, or in a process analogous in some ways to the phenomenon of ultrasonically induced cavitation within fluids, albeit caused by an electromagnetic waveform.
- Transport phenomena; improved reactant/product movement about catalytic sites or movement to or from surfaces in heterogeneous solid-fluid or liquid-liquid systems
- Improved particle suspension by fragmentation.

It is clear that serious attempts to identify a non-thermal microwave effect in organic reactions have all concluded that rate enhancement can be attributed to thermal effects, and that when these effects are avoided by careful experimental design, none is observed.

1.3.2.3 The Application of Microwave Irradiation to Coal Science

As mentioned previously, low rank coals have sufficient receptivity to microwaves to be of interest to practitioners of microwave enhanced chemistry. There are various receptive functionalities within as-mined coal-both organic and mineral in nature. For example, on heating the pyrite present within coal it decomposes to a non-stoichiometric FeS_x. When exposed to microwaves at a frequency of 2.45 GHz, this material experiences dielectric loss, and as a result the surrounding matrix is heated by thermal conduction.[76,77]

The target of the work described within this thesis is the development of improved methods for the upgrading, by hydrocracking, of liquid extracts of coal. The aim is to reduce the high molecular mass, polyaromatic and heteroatom rich coal macromolecules to fragments that may be used for the generation of value added products. The reactions mentioned above, whilst illustrating the use of microwave ovens in assisting hydrogenation reactions, fail to reproduce the conditions encountered in the processing of coal molecules, in terms of the size of molecules, degree of unsaturation and amount of heteroatom content.

The process of hydrocracking requires far more intense conditions, and is a far more complex system, both physically and chemically. However the work conducted in the field of CTH has served to highlight that solid phase or heterogeneous reactions utilising alumina, silica and clay, as reactant supports are both possible and extremely efficient. In particular, it has demonstrated that under microwave irradiation, reactions can be completed in minutes that give barely measurable yields under thermal heating.[66]

The study of hydrocracking coal derived liquids pre-supposes the as-mined coal has been exposed to an extraction process involving partial decomposition and separation of the organic material into a solvent and removal from the mineral material of the rock. Colleagues at Imperial College have addressed the extraction process in detail.[78]

Recent literature has addressed the application of microwave heating to processing of coal and related resources for the generation of value added products.

Work conducted by Bradhurst and Worner[79] explored the microwave retorting of Australian shales - a family of hydrocarbon bearing minerals closely related to coals but containing a higher ash and hydrogen content. In this latter respect they are more comparable to petroleum than to coal.

It was shown that a higher quality product than that achieved by conventional heating could be obtained, shifted towards light hydrocarbons and containing a reduced heteroatom content, whilst maintaining high yields.

A number of conclusions were reached;

1. The product quality was higher than that obtained from conventional heating alone containing a higher proportion of lighter hydrocarbons and lower sulfur and nitrogen content.
2. The price of the "syncrude" derived from hydrotreatment of this product was comparable with that of crudes from more conventional sources.
3. Use of microwave irradiation was of greatest efficacy when combined with conventional pre-heating. An economic industrial process was conceivable, provided microwave irradiation was confined to use once the substrate had reached temperatures exceeding 260 °C, achieved by a conventional pre-heating process.
4. The use of microwave retorting produces value-added products for use as refinery feedstocks.

In general, microwave processing of coal has involved the generation of discharge plasmas to produce active species. Djebabra *et al* explored the gasification of coal by generation of a microwave plasma in an atmosphere of water vapour over a coal sample.[80] In the reaction, decomposition of the water acted as a source of dihydrogen. Similarly, a one step conversion process for the generation of fuels and synthesis gases, whilst upgrading carbon content without the use of high pressure hydrogen has been discussed for an Australian brown coal. In this case, a single step liquefaction/upgrading was achieved under reduced pressure, a methane microwave plasma being the source of the reactive species, with high yields of C_{13}-C_{34} aliphatic compounds. In a related study Amano *et al* generated C_5 to C_{22} cyclic paraffins by conversion of coal using a hydrogen plasma.[81] In these and similar reports[82,83] the generation of high-energy plasma is required to achieve successful conversion, by virtue of the fact that the activation energy of the coal-gas reaction is reduced.

Direct coal pyrolysis has also been conducted utilising microwave induced plasma discharge.[83,84] However, in this application it has also been possible to induce pyrolysis of the coal in very short reaction times by the addition of receptive solids such as chars, coke or transition metal oxides[84] to form an intimate mixture and exposure to microwaves at 2.45 GHz.

Microwave irradiation has also been applied to problems relevant to hydrocracking, particularly in the field of catalyst generation. Work involving the synthesis of crystalline alumino-silicate hydrotreatment catalysts uncovered a link between catalytic activity and variations in crystallite size and morphology caused by the heating method.[67] Such materials prepared under microwave conditions were shown to offer improved catalytic activity over the conventionally prepared counterparts, despite a reduction in surface area. Here it was concluded that microwave irradiation modifies crystal morphology in such a way that activity of each site is enhanced to such a degree that the loss of surface area was negated.

2 OBJECTIVES

As explained in the introduction, work at Imperial College has revealed that primary liquefaction extracts from coal contain species of very high molecular mass.[12] The refractory nature of these fragments prevents upgrading to species with reduced RMM, aromaticity and heteroatom content, except under severe conditions employing high temperatures and high hydrogen pressures. Catalysts designed for hydrocracking and heteroatom removal for the petrochemical industry have been employed, but activity when applied to hydrocracking of coal derived crudes is poor and deactivation rapid. Consequently the catalytic hydrocracking of these materials remains prohibitively expensive.

The need for improvements in this area is the basis of a joint project, funded by the British Coal Utilisation Research Association (BCURA) and the Department of Trade and Industry (DTI), conducted at Imperial College[78] and Aston University. The project as a whole has two broad aims.

- To improve the efficiency of the hydrocracking of coal liquefaction extracts through the use of novel catalysts.
- To further the understanding of large molecular masses found in coal extracts during the early stages of catalytic hydrocracking processes.[78]

It is the first of these two objectives which is addressed in this thesis, whilst the second has been dealt with concurrently in a thesis by Mlle Vanessa Begon at Imperial College.[78] Some results obtained at Imperial College will be presented relating to this work, and will be referenced as necessary.

The work contained herein is separated into two distinct areas.

- Preparation, modification and characterisation of novel materials based on clay and clay-like systems, which have potential as catalysts, involving both conventional reaction chemistry and microwave assisted methodology.
- Design of a reactor system to facilitate microwave assisted hydrocracking and preliminary investigations using model compounds.

3 EXPERIMENTAL

3.1 CHEMICALS AND EQUIPMENT SPECIFICATIONS

3.1.1 STARTING MATERIALS AND CHEMICALS

Wyoming Bentonite was obtained from AKZO Nobel and pre-treated (*vide infra*) to obtain monoionic sodium montmorillonite.

Laponite RD was obtained from Laporte Ltd and used as received.

Other chemicals were obtained from Aldrich Chemical Company and used as received, unless otherwise stated.

10% Hydrogen in Argon was obtained from Air Products Ltd.

Other pressurised gases were obtained from BOC.

COSHH data sheets are held within the laboratory in which experiments were conducted.

3.1.2 NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

All spectra were recorded using a Brucker AC-300 (Reference materials are quoted where necessary).

Solution spectra were obtained at room temperature.

Solid State spectra were obtained using magic angle spinning (MAS). Spinning speeds were varied as necessary to identify spinning side bands and to avoid their obscuring low intensity resonances.

3.1.3 ELECTRONIC SPECTROSCOPY (UV/VIS)

Measurements were carried out on a Perkin-Elmer Lambda 12 spectrophotometer. Aqueous samples (transmission mode) were held in 1 cm quartz cells. Solid samples (diffuse reflectance mode) were analysed undiluted.

3.1.4 X-RAY DIFFRACTION (XRD)

Analysis was conducted using a PW1710 diffractometer, monochromator and Cu tube anode. Diffractograms were obtained by scanning in steps of 0.020 $°2\theta$ between 3 and 60 $°2\theta$. Data collection and analysis was conducted at the Department of Earth Sciences, University of Keele.

3.1.5 X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

XPS analysis was conducted using a Fison VG ESCALab 200D spectrometer using a MgK-alpha source and 20 eV analyser, at the Department of Electronic Engineering and Applied Physics, Aston University,

Photoelectron collection angle (Take-Off Angle, TOA) can be varied between 0 and 70 ° from normal to the substrate support plane, giving sampling depths between 50 and 10 Å.

3.1.6 THERMAL GRAVIMETRIC ANALYSIS AND DIFFERENTIAL THERMAL ANALYSIS (D/TGA)

D/TGA analysis was conducted on a PL Thermal Sciences STA 1500 analyser. Samples weighing 40 - 70 mg were heated to 1000 °C under air at a rate of 20 °Cmin^{-1}, with data sampling at 0.5 s intervals.

3.1.7 USE OF MICROWAVE IRRADIATION

Microwave irradiation was carried out using the CEM MES1000 digestion oven, and modified CEM Teflon reaction vessels. Irradiation time, internal pressure and internal temperature are user programmable and computer controlled to allow microwave power up to 1000 W, at a frequency of 2.45 GHz, to irradiate the sample. The software includes fail-safes to ensure neither maximum internal pressure of 200 PSI, nor maximum temperature of 200 °C are exceeded during operation.

3.1.8 GAS-LIQUID CHROMATOGRAPHY (GLC)

Analysis was conducted on an ATI UNICAM 610 Series gas chromatograph, with PC link, fitted with a 25 % silicone grease/ diatomite column, and Hydrogen Flame Ionisation Detector (FID).

3.2 CATALYST PREPARATION

3.2.1 MODIFICATION OF COMMERCIAL CLAYS

Modifications of both natural and synthetic clays have been carried out using aluminium, chromium and tin compounds, in either aqueous or ethanolic solution. Subsequent calcination was carried out in air or under argon as appropriate.

Wyoming Bentonite is a naturally occurring dioctahedral smectite clay mineral composed of approximately 85% montmorillonite (SiO_2, 55.6; TiO_2, 0.1; Al_2O_3, 16.5; Fe_2O_3, 5.1; CaO, 1.9; MgO, 2.0; Na_2O, 1.2; K_2O, 0.6; Mn_3O_4, 0.1%).

The material has been extensively studied at Aston where it has been rigorously characterised[22] and has been the subject of various pillaring reactions *via* ion exchange (cation exchange capacity, 70 meq 100 g^{-1}).

Pre-treatment of the raw material is a three-fold process involving removal of silica, carbonaceous material and calcium and magnesium counter ions to yield the monoionic sodium montmorillonite starting material, to be used in the pillaring reactions. A typical pre-treatment process is outlined below;

Laponite is a synthetic, virtually iron-free trioctahedral smectite clay of the hectorite-type, with an ideal composition $Na_{0.67}(Li_{0.67}Mg_{5.33}(Si_8O_{20}(OH)_4)$.

There is therefore analogy to montmorillonite, although being synthetic the structure can be more exactly determined and is more consistent.

3.2.1.1 Preparation of Monoionic Sodium Montmorillonite[22]

Wyoming bentonite (20 g) was first suspended in 1 M NaCl solution (2 L), and stirred overnight. Silica was removed by subsequent sedimentation and decantation. The resulting suspension was acidified to *p*H 3 with 1M HCl. Following a short period of stirring, the suspension was allowed to settle, and the supernatant NaCl solution discarded. The residue was made up to 2L with 1M NaCl solution and again acidifed. This process was repeated twice more, the suspension being stirred for 24 hours after the final addition, followed by centrifuging to obtain a slurry of sodium montmorillonite. This slurry was transferred to a semi-permeable membrane and dialysed against de-ionised water until the wash water was free of chloride, as indicated by addition of silver nitrate. The resulting material was dried overnight at 80 °C and ground for subsequent use in pillaring experiments.

3.2.1.2 Pillaring of Sodium Montmorillonite with Hydrolysed-Aluminium Solutions (The Keggin Ion).[18,85,86]

Alumina pillared montmorillonite was obtained by treating an aqueous clay suspension with freshly prepared aluminium hydroxy polymer solution. The polymer solution was prepared by rapid addition of 1.23 M $Na_2(CO_3)$ solution (41 mL) to a vigorously stirred, boiling 1.67 M $AlCl_3$ solution (25 mL). The preparation was abandoned on the formation of any permanent precipitate, but completed as quickly as possible. On completion, the resulting solution was cooled in ice to avoid further ageing. Once cool, the solution was added dropwise to a stirred suspension of sodium montmorillonite (2 g) in de-ionised water (134 mL). This addition was completed in 1 h. The now flocculated clay was repeatedly centrifuged and washed with de-ionised water until the wash water was free of chloride, as indicated by addition of silver nitrate. The resulting material was dried overnight at 80 °C, followed by calcination under air for 1 h at 400- 500 °C.

The behaviour of aqueous aluminium solutions under conditions of microwave irradiation were studied to assess the feasibility of a microwave induced "rapid ageing" procedure.

50 mL of sodium hydroxide (0.5 M) solution was added drop-wise to 50 mL of stirred aluminium trichloride solution (0.2 M) as fast as possible avoiding the formation of permanent precipitate. 10 mL samples of the resulting solution were exposed to microwave radiation for between 0 and 10 minutes. The procedure was repeated using freshly prepared aluminium trichloride solution. The resulting solutions were analysed using solution ^{27}Al NMR.

3.2.1.3 Pillaring of Sodium Montmorillonite and Laponite with Hydrolysed-Chromium Nitrate Solutions.[48,49]

Chromia (Cr_2O_3) pillared montmorillonites have been reported within the literature as producing some of the largest gallery heights yet achieved.[49] Montmorillonites intercalated with polyoxychromium oligomers have been prepared following a literature method.[49] However, whilst the solution chemistry used to produce the pillar precursor is less demanding than that required for the equivalent aluminium species, calcination to generate chromium oxide pillars with a suitable thermal stability introduces a further problem; that is that calcination in an oxidising atmosphere results in formation of Cr(VI)[87] (a carcinogen). To obviate this problem, apparatus has been designed and assembled which allows calcination under an inert atmosphere.

Chromia pillared montmorillonite was prepared in much the same way as alumina pillared montmorillonite. The chromium oligomer solution was prepared by addition of solid Na_2CO_3 (1.6 g) to a solution containing $Cr(NO_3)_3$ (12 g) in de-ionised water (300 mL). The resulting green solution was refluxed for 16 h. Once cool, the solution was added dropwise to a stirred suspension of sodium montmorillonite (2 g) in de-ionised water (200 mL). The addition was completed in 3 h. The now flocculated clay was repeatedly centrifuged and washed with de-ionised water until the wash water was colourless. The resulting material was filtered, partially air dried and left overnight in a vacuum desiccator., followed by calcination under N_2 for 1 h at 600 °C.

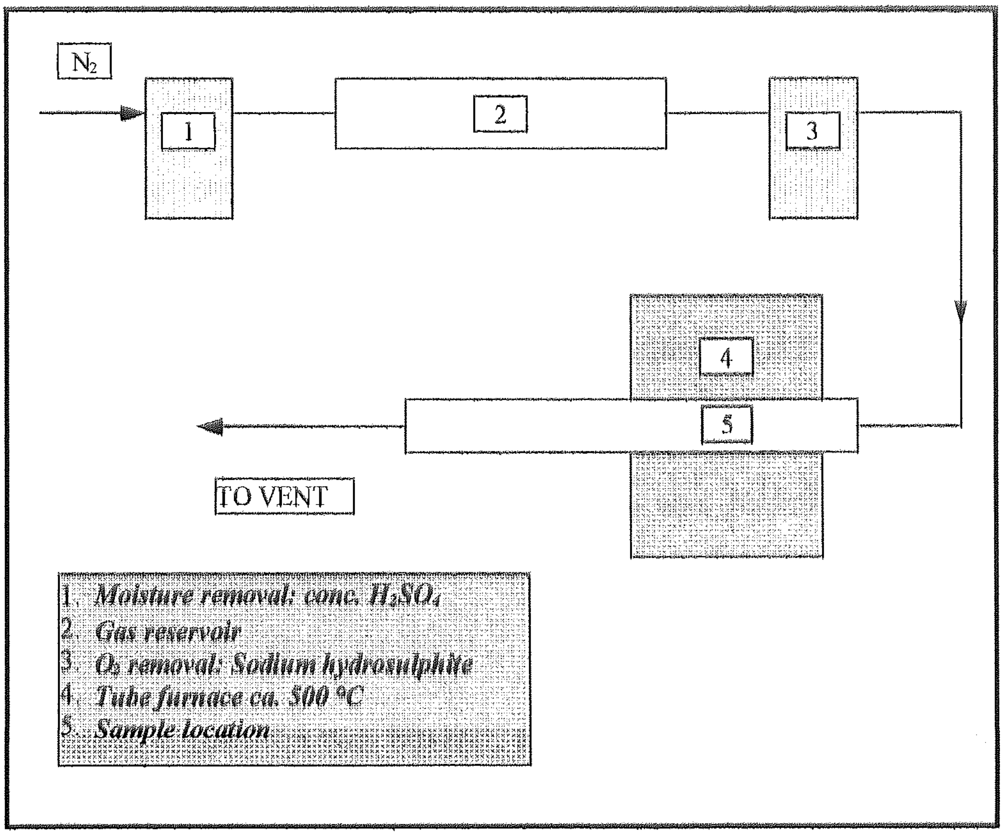


Figure 7 Schematic representation of calcination apparatus

The same method was used to pillar samples of laponite, to produce chromia pillared laponite.

3.2.1.4 Tin Pillared Laponite

An *in situ* preparation of the tin pillared laponite involving mechanical agitation, and a second utilising microwave heating, have been undertaken, following a literature method.[24] The procedure for intercalation of organotin compounds and their conversion to form tin(IV) oxide pillars under mild conditions is outlined below.

Sodium-exchanged laponite RD (5.0 g) and triphenyltin chloride (1.5 g) were mixed with dry ethanol (100 cm^3) in a stoppered conical flask and mechanically shaken for one week. The clay was filtered and washed with ethanol (4 x 25 mL).

Microwave treatment involves use of similar proportions of reactants in a sealed Teflon vessel being irradiated for a total of eight minutes, delivered as 1 minute bursts at a power of 1000 W and a frequency of 2.45 GHz. Periods of irradiation were followed by rapid cooling to room temperature by immersion in liquid nitrogen. The suspension was maintained by manual agitation during these periods.

The ethanolic suspension was filtered, washed with portions of ethanol, and dried to constant weight in a conventional oven at 80 °C.

3.2.2 SYNTHESIS OF "2:1" LAYERED DOUBLE HYDROXIDES

Preparations of LDH based catalysts have been conducted both using conventional conditions[26,28,,53,88] and by utilising microwave irradiation to facilitate ion exchange[89,90] of carbonate intercalated LDH.

Traditionally, LDH syntheses involving complex anions, such as terephthalic acid[26] or polyoxometalates[28,53,88] have been conducted in the absence of tenaciously held anions. Polyoxometalates and the hydroxide layer itself are sensitive to both high temperature decomposition and severe chemical environments. It is generally accepted[26] that small anions with high charge density, such as carbonate, hold great affinity for the positively charged LDH layer. This electrostatic attraction is so great that their subsequent removal requires conditions sufficiently severe, both chemically and thermally, as to be detrimental to both the layer structure and intended intercalate. It is therefore necessary to ensure complete exclusion of such anions and their precursors during both synthesis and subsequent processing.

The conventional preparation of layered double hydroxides including polyoxometalate species has therefore required an elaborate experimental design to ensure atmospheric carbon dioxide is precluded from the reaction vessel throughout.

On a laboratory scale the most reliable way of excluding unwanted atmospheric contaminants is by use of a Schlenk line. This apparatus is routinely used in the field of organometallic synthesis when reactants and/or products are sensitive to atmospheric moisture and/or oxygen. The basic concept involves use of two reservoirs, one filled with an inert gas at slightly elevated pressure, the other maintained under vacuum. These reservoirs are protected by a system of traps to ensure water does not enter. The reservoirs are connected to the reaction vessel *via* a tap that allows either to be accessed without disrupting the integrity of the now closed system. Prior to the introduction of sensitive reactants, the reaction vessel undergoes evacuation and purge cycles, by alternately accessing the two reservoirs. When the use of a closed system is not possible, i.e. when using reflux condensers etc., the slight positive pressure of the gas line is utilised to provide a constant cushion of inert gas over the reaction mixture.

Subsequent addition of liquid reactants to the reaction mixture is achieved by cannulation- syringe needles are used to remove reactant from rubber sealed vessels, the pressure drop due to loss of volume being compensated for by inert gas delivered from a source kept at a slight positive pressure. These reactants are then delivered by piercing rubber seals on the reaction vessel. The thickness and elasticity of the rubber, combined with the small bore of the needle ensures that integrity is re-established once the needle is removed.

Alternative methods of preparation are subject to uncertainties regarding reliability and reproducibility. The successful reproducible synthesis of layered double hydroxides is reliant on manipulation of this apparatus and careful handling of reactants. Whilst this facilitates absolute control over the chemical composition of the final material, such experimental complexity renders the syntheses somewhat inconvenient and time consuming.

3.2.2.1 Synthesis of LDH Using Conventional Methods

The following is a sample procedure for the preparation of a terephthalate intercalated Mg/Al LDH, subsequently exchanged to prepare polyoxomolybdate LDH, this procedure has also been used to prepare terephthalate, decavanadate and heptamolybdate intercalates of Zn/Al, Ni/Al and Zn/Cr layered double hydroxides. Certain catalysts have been further modified using hydrogen at elevated temperature *vide infra.*

Coprecipitation of the hydroxide layers around the organic acid is achieved by adding an aqueous mixed nitrate solution of the desired metal composition to a solution containing the sodium salt of the acid at high *p*H, followed by "digestion" at elevated temperature. The polyoxometallate-intercalated product is obtained by introducing aqueous metal oxoanion to the double hydroxide suspension at room temperature, followed by subsequent acidification. Concomitant protonation and exchange of the organic acid accompany hydrolysis of the oxoanion to the anionic oligomer.[28] Carbon dioxide was excluded from the system by use of Schlenk methodology.

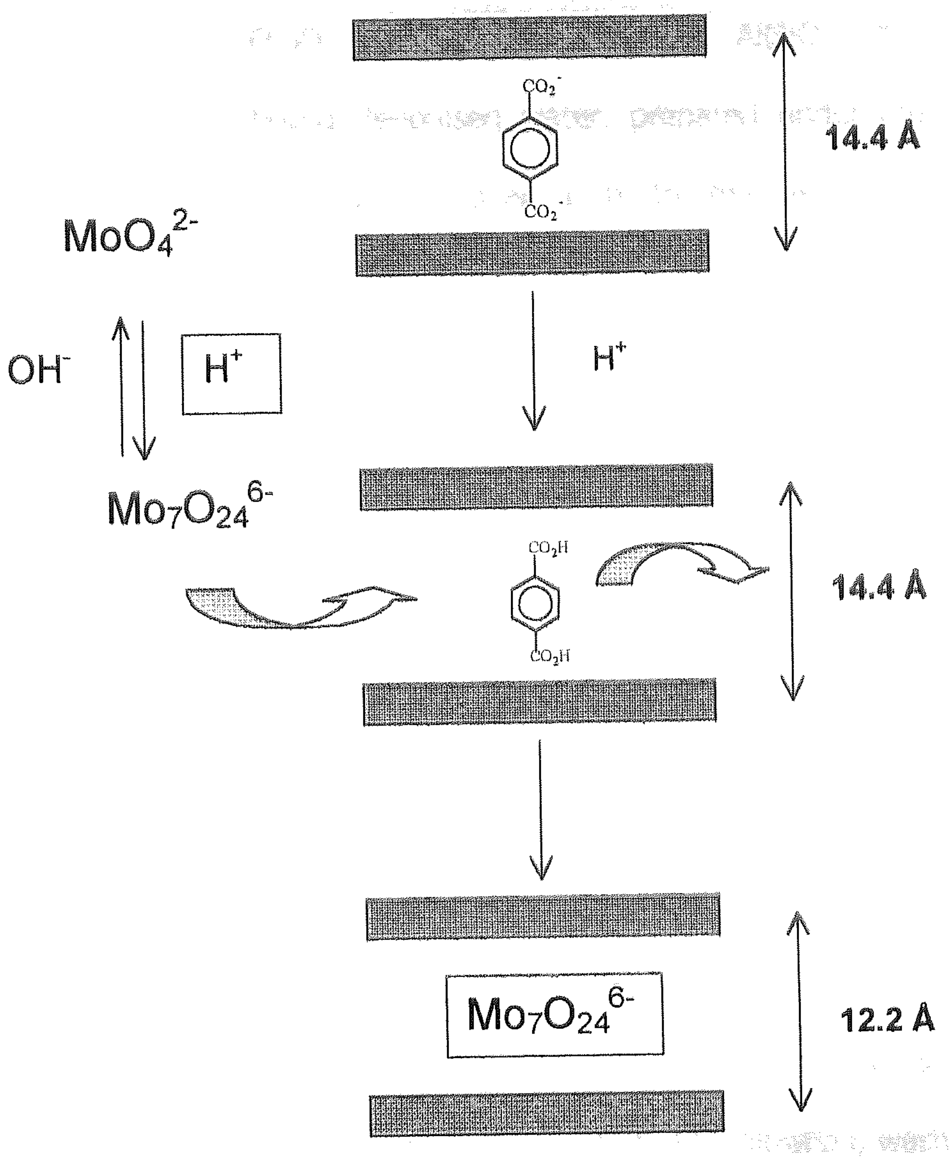


Figure 8 Overview of chemical processes involved during the preparation of polyoxometallate intercalated LDH

A 1 L round bottomed flask equipped with a mechanical stirrer, reflux condenser, *p*H probe and heating mantle was charged with terephthalic acid (26.6 g, 0.16 mol). Following evacuation/purge cycles, boiled de-ionised water (320 mL) was added by cannulation, followed after a brief period of cooling by dropwise addition of NaOH solution (50 %, 115 g, 1.44 mol) to the stirred terephthalic acid suspension. A separately prepared solution containing $Mg(NO_3)_2.6H_2O$ (82.02 g, 0.4 mol) and $Al(NO_3)_3.9H_2O$ (60 g, 0.2 mol) in 320 mL boiled de-ionised water, prepared under argon, was added drop-wise by cannulation over 1 h to the vigorously stirred terephthalate solution at room temperature. Once the addition was completed, the resulting slurry was heated to 75 °C and stirring continued for 18 h. The product was isolated by repeated washing with boiled de-ionised water, followed by filtration. This slurry was suspended in 500 mL boiled de-ionised water. (The terephthalate intercalated material can be isolated by drying *in vacuo* at 75° C).

To a 50 g portion of this slurry was added a solution of $Na_2MoO_4.2H_2O$ (25.4 g, 0.2 mol) in 50 mL boiled deionised water. After 10-15 minutes stirring, 4 M HNO_3 was slowly added with vigorous stirring, *via* cannulation until a *p*H of 4.5-4.7 was achieved and maintained for 10 minutes. After a further 10 minutes stirring the product was isolated by filtration, washing and drying *in vacuo* at 70 °C overnight.

3.2.2.2 Preparation of Ni/Al Layered Double Hydroxide Using Microwave-Enhanced Ion Exchange.

The use of microwave irradiation to enhance ion-exchange in clays has previously been observed.[89]

A solution was prepared containing $Ni(NO_3)_2.6H_2O$ (37.2 g, 0.128 moles) and $Al(NO_3)_3.6H_2O$ (24 g, 0.064 moles) made up to 100 mL with de-ionised water. A 40 mL portion of the turquoise mixed nitrate solution (Ni:Al = 2:1, *p*H 1.5) was added drop-wise over 2 h *via* a burette to a vigorously stirred solution (100 mL) containing NaOH (14.34 g, 0.36 moles) and Na_2CO_3 (5.43 g, 0.05 moles) in de-ionised water at *p*H 12.7. Stirring was continued for 90 minutes after addition was complete. The final *p*H of the solution was 12.7. A 50 mL portion was transferred to a sealed Teflon vessel and irradiated in a 1000 W microwave oven at 3% for 4 hours, maintaining a temperature of 64 – 70 °C.

The turquoise, carbonate intercalated LDH slurry was filtered under vacuum and washed three times with *ca.* 50 mL de-ionised water. Both filtrate and washings were colourless, indicating that all nickel present was taken up in the solid, and that none was leached during washing. The resulting turquoise solid was dried *in vacuo* at room temperature. The remaining slurry was aged in a water bath at 65 °C for 18 h, prior to washing and drying in the same way, *vide supra.*

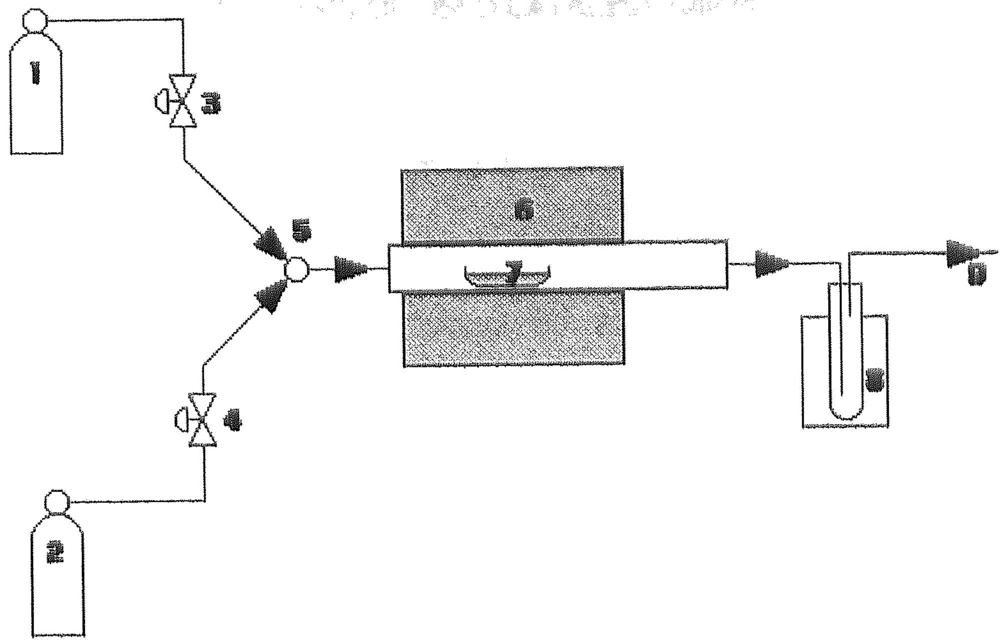
The second series of microwave experiments involved microwave irradiation assisted ion-exchange. To 20 mL of a solution containing 1.07 g terephthalic acid, adjusted to *p*H 12.5, in a Teflon vessel was added 1.1 g of the previously prepared Ni/Al LDH. The Teflon vessel was sealed and transferred to the microwave digestion oven and subjected to a power of 250 W at 2.45 GHz for 5 minutes. The vessel was allowed to cool to room temperature before filtering and drying the product as previously described.

Further exchange reactions were conducted to generate a molybdate intercalated species, intended to act as an analogue of the alumina supported Ni/Al catalysts.

3.2.3 CATALYST MODIFICATION

A number of catalyst samples, both clay and LDH based have been modified using hydrogen at elevated temperatures. This has been employed in two ways; either as a secondary modification following calcination under argon, or as a replacement for argon in the calcination step. In both cases the intention is to assist hydrocracking at lower pressures (*cf* conventional hydrocracking) by hydrogen sorption / pre-reduction of the catalyst.

Following placement of the sample within the reaction zone, the reaction vessel was first sealed and then purged with argon for 20 minutes at *ca.* 30 mL/min. The supply was then switched to 10 % H_2 in argon, and purged for a further 20 minutes at the same rate. The furnace was then used to heat the sample to the appropriate temperature, at which it was held for 60 minutes. Cooling was carried out under constant flow of 10% hydrogen/ argon. The reaction vessel was finally purged with argon and the sample extricated under a flow of argon and stored *in vacuo* prior to analysis.



1. 10% H_2 / Ar cylinder ***2.*** Ar cylinder ***3.,4.*** manual screw valves

5. Manual, 3-way uni-directional valve ***6.*** tube furnace

7. ceramic sample boat ***8.*** Cold trap @ -78 °C ***9.*** vent to atmosphere

Figure 9 Schematic representation of the hydrogen pre-treatment apparatus.

CATALYST ID	**DESCRIPTION**
BOD60	Uncalcined chromia montmorillonite
BOD63	Chromia montmorillonite, calcined under Ar, 500 °C
BOD62	Chromia montmorillonite, calcined under Ar, followed by H_2, 500 °C
BOD64	Chromia montmorillonite calcined under 10 % H_2/Ar, 500 °C

Table 3 Summary Of Chromia-Montmorillonite Catalysts

3.2.4 XPS ANALYSIS OF USED CATALYST SAMPLES

The hydrocracking of coal derived liquids is heavily catalyst dependent. Alumina supported nickel/molybdenum catalysts currently in use are sensitive to poisoning caused by carbonaceous and metal deposition on the surface.[91,92] It is these materials with which the novel catalysts must compete. By means of a comparison, XPS analysis of fresh and used proprietary catalysts was conducted, to determine the effect of hydrocracking on them. Initially a standard ESCA scan was used to analyse surface coking. Later, spectra were obtained for various take off angles, in an attempt to obtain depth resolved data.

3.3 MICROWAVE HYDROTREATMENT EXPERIMENTS

3.3.1 EQUIPMENT

All microwave irradiation was conducted using a CEM MES 1000 microwave digestion oven, using sealed Teflon vessels, whose operating limits are outlined below.

- Pressure 200 PSI
- Temperature 200 °C
- Sample volume 50 mL

3.3.2 EXPERIMENTAL PROCEDURE AND RELATED CONSIDERATIONS

As this is a completely new application, both for the vessels and the microwave oven itself, a number of operational problems had to be addressed. These include;

- Introduction of hydrogen; For safety and practical reasons, air must be excluded from the hydrogen system prior to microwave driven hydrocracking being conducted. A number of modifications have been made to the equipment to allow hydrogen to be introduced in a controlled manner. A system of Teflon valves has been obtained, allowing purge cycles and introduction of hydrogen to be conducted with minimal aerial contamination.

- Hydrogen flammability; The use of hydrogen in this type of system is untested. Due to safety considerations associated with the high flammability of hydrogen, the vessels have been used with the stepwise introduction of reaction components. Experimental runs involving different solvents and model compounds were conducted under argon, to ensure the integrity of the system before introduction of hydrogen and catalyst. Once these experiments were completed, runs using a mixture of hydrogen (10%) in argon were conducted. Subsequent experiments involved an increase in hydrogen content, once the reliability and safety aspects of the system had been assured.
- Successful heating of the target compounds requires a suitable receptor. Various candidates for this role have been appraised. A number of criteria must be fulfilled;
    - i) The chosen receptor compound must mix with the coal derived liquid.
    - ii) In order to act as a receptor to microwaves, the compound must be polar.
    - iii) The receptor must exhibit thermal stability.
    - iv) The receptor must remain substantially in the liquid phase at the temperatures and pressures used, such that thermal transfer to the target molecules can be achieved.
    - v) The receptor must be stable to reaction with starting materials/products.

Various compounds have been investigated, N-methyl-2-pyrrolidone (NMP) proved to be the most suitable. This solvent was observed to be an exceptional microwave receptor, in addition to its good solvent properties. NMP remains largely in the liquid phase and does not decompose at the temperature and pressure used.

- Prior to experimental runs involving actual primary extracts, the viability of the process must be appraised. A number of model compounds have been selected and used in initial runs, these include; pyrene, dihydroanthracene, dibenzothiophene and dibenzofuran, which model certain moieties within the coal matrix.

A number of the catalysts described above have been used in microwave driven attempts at hydrocracking model compounds. These experiments have utilised pure hydrogen at pressures not in excess of 160 PSI. The resultant products were analysed using GLC.

50 ml of model compound mixture *vide infra* was transferred to a Teflon vessel in air. *ca.* 0.1 g of catalyst was added and the mixture agitated to provide suspension. The vessel was transferred to a cold bath at -78 °C. Once the mixture had frozen, the Teflon vessel was sealed in an outer pressure housing fitted with a system of valves and a thermowell. The vessel was then evacuated and charged with hydrogen of varying composition and pressure. The vessel was then transferred to a 1000W-

microwave digestion oven, and fitted with pressure and temperature monitoring equipment. The vessel was then irradiated to achieve and maintain the selected pressure/temperature.

The product mixture was extracted using cannulation following argon purge and stored under argon prior to analysis by GLC

4 RESULTS

4.1 CATALYST PREPARATION

4.1.1 CATALYST CHARACTERISATION

4.1.1.1 Characterisation of Pillared Clays

4.1.1.1.1 *Solution NMR*

Pillaring solutions containing aluminium were analysed using ^{27}Al NMR, with chemical shifts quoted relative to the octahedral hexaquo-aluminium cation.

Conventionally prepared Keggin Ion solutions

Keggin ion solutions prepared in the conventional manner are characterised by a sharp, intense resonance at 62.5 ppm and a broad, weaker peak around 0 ppm, both of variable intensity (Figures 12 and 13).

Microwave aged samples

Analysis of ^{27}Al NMR spectra corresponding to samples of hydrolysed aluminium trichloride exposed to microwave irradiation contain a broad weak peak, centred at *ca.* 60 ppm which partially obscures a sharp peak at 62.5 ppm, relative to $Al(H_2O)_6^{3+}$. The intensity of the latter reduces as irradiation time is increased. A sharp, intense peak at 0 ppm develops following exposure to microwave irradiation, the intensity of this resonance increases with longer irradiation times (Figure 14).

The spectrum for fresh aluminium trichloride is composed of a sharp, intense line at 0 ppm, corresponding to octahedral $Al(H_2O)_6^{3+}$ and a very broad weak resonance centred at 60 ppm (Figure 15).

4.1.1.1.2 *MAS NMR*

Starting materials and pillared clays were analysed using ^{27}Al, ^{29}Si, and ^{23}Na as appropriate. The major resonances are presented below. In all cases there is slight disparity with literature values. This is a result of the presence of isomorphously substituted iron in this montmorillonite that contributes to the variation between naturally occurring clay minerals and causes broadening of the resonance linewidth.

Sodium montmorillonite

^{27}Al resonances are observed at *ca.* 0 ppm and 60 ppm (Figure 16), corresponding to octahedrally and tetrahedrally coordinated aluminium nuclei respectively. Both suffer slight, additional broadening as a result of asymmetric environments, this being most apparent for tetrahedral aluminium. The relatively low shift of the tetrahedral peak indicates that each aluminium atom is associated with three nearest neighbour Si atoms. This, coupled with the low intensity of this peak reflects the low concentration of aluminium in the tetrahedral layer.

A single resonance is observed in the ^{23}Na spectrum at *ca.* –17 ppm relative to NaBr/D_20 (Figure 17), corresponding to the hydrated charge balancing cations.

The ^{29}Si spectrum contains two resonances, one at *ca.* –93ppm (Q^2), generated by particle edges, the second is observed at *ca.* -108 ppm (Q^4) (Figure 18), which reflects the high degree of polymerisation. The latter, highly negative signal is associated with the high degree of shielding of the silicon nuclei (and hence a very negative isomer shift relative to TMS).

Each tetrahedral silicon is associated with three vacancies in the octahedral layer. Montmorillonite is a dioctahedral smectite and as such only 2/3 of the available octahedral sites are occupied. Ideally then, each silicon has a maximum of two next nearest neighbour aluminium atoms. Isomorphous substitution of iron in the octahedral layer and aluminium and/or iron in the tetrahedral layer, coupled with an overall randomness of the layer composition and edge effects result in the possibility that any number between none and four could occur. As previously mentioned the resonances are rather broad in fact they are observed to overlap slightly. The whole range of shifts expected for two or less next nearest neighbour aluminium atoms is covered by this envelope, reflecting the layer composition.

Al pillared montmorillonite

The ^{27}Al resonances are the same as above, however the tetrahedral peak (*ca* 60 ppm, (Figure 19)) is of greater intensity than for sodium montmorillonite, as a result of the pillaring species containing tetrahedrally coordinated Al nuclei.

No ^{23}Na resonance is observed, indicating the completion of ion exchange in favour of aluminium species.

The ^{29}Si spectrum is unchanged (Figure 20), indicating that the layer is unchanged by the pillaring process and calcination procedures.

4.1.1.1.3 *UV/VIS*

Visual inspection and UV/VIS spectrometry were used to follow the action of base on the aqueous chromium(III) solution. Hydrolysis of the aqueous chromium(III) nitrate solution (violet in colour, maxima at λ = 574 and 408 nm (Figure 21)) produces the expected polymeric species (green in colour, maxima at λ= 580 and 414 nm (Figure 22)). The Diffuse reflectance UV/VIS spectrum of the treated clay includes a maximum at *ca.* 610 nm (Figure 23), revealing the presence of pseudo octahedral geometry of oxygen bearing ligands about a chromium(III) centre.

4.1.1.1.4 *XRD*

X-Ray Diffraction data obtained for Aluminium pillared montmorillonite, Chromia pillared montmorillonite and Tin pillared Laponite indicate that large basal spacings were reproducibly obtained by the methods outlined above *vide supra.* Sample spectra, corresponding to the starting materials, are presented in appendix 2 (Figures 24 and 25).

Sample	d(001) (Å)
Sodium montmorillonite	12.7
Laporte Laponite	13.8
Al-montmorillonite	17.1
Calcined Al-montmorillonite	16.3
Cr-montmorillonite	27.5
Calcined Cr-montmorillonite	24.2
Sn-Laponite	21.5

Table 4 Summary of basal spacings of prepared catalysts

These results are consistent with the literature, given that each clay mineral sample is unique, and properties such as layer thickness exhibit some variance depending on the source.

Data for the laponite based materials are less reliable than those for the montmorillonite based clays, due to the nature of the material (small particle size), and the size of the pillars. Very small particles are known to generate poor quality diffractograms due to the limited extent of order within the crystal array. The amount of coherent reflections corresponding to a given feature is therefore reduced resulting in a low intensity signal, and a comparatively noisier trace. These features exacerbate the problem of analysing peaks, particularly those generated by basal spacings at the upper limit of the technique's sensitivity.

4.1.1.1.5 *XPS*

Samples of sodium montmorillonite (starting material), alumina pillared montmorillonite and chromia pillared montmorillonite have been analysed by XPS, for comparison with used catalyst samples. A selection of data indicating surface species present and their relative concentrations is presented below, spectra appear in appendix 2 (Figures 26-31).

Sample	Calcination Temp (°C)	Element (%Abundance)				
		Na	O	C	Si	Al
Na-mont	N/A	0.8	50.8	15.2	22.6	10.6
Na-mont	525	1.4	57.2	6.0	24.8	10.6
Al-mont	N/A		57	8.9	20.2	13.9
Al-mont	525		58.8	5.2	21.9	14.1
Cr-mont	N/A		50.1	17.7	21.4	10.2
Cr-mont	600		53.1	12.8	22.7	10.9

Table 5 Summary of catalyst surface analysis

XPS analysis reveals the presence of the expected species at the surface of the montmorillonite samples, reflecting the composition of the bulk material i.e. primarily oxygen, aluminium and silicon. Some carbon is expected as this is a common contaminant in the XPS apparatus and is often utilised as an internal standard. The reduction in carbon content for the calcined samples indicates the possibility of some intrinsic carbonaceous material being present after clay pre-treatment.

The most apparent omission occurs in the analysis of the chromium montmorillonite samples, as no surface chromium is detected. The UV/VIS data, coupled with the increased basal spacing, indicates the presence of a chromium oligomer between the layers. The fact that the pillaring species is confined to the interlayer region should not preclude its detection, as the depth of penetration of this technique is in excess of the sum of the alumino-silicate layer thickness and chromia pillar (24-27.5 Å). This apparent contradiction is explored further in the discussion chapter.

4.1.1.1.6 *D/TGA analysis of chromia montmorillonite exposed to hydrogen.*

Sodium montmorillonite

The sodium montmorillonite was analysed for purposes of comparison (Figure 32). The profile is composed of a 4% weight loss occurring below 150 °C, accompanied by a sharp endotherm, corresponding to loss of absorbed moisture and loosely bound molecular water from between the clay layers. During the 200-600 °C region weight is stable, but the DTA profile is composed of a large broad exotherm, or series of overlaid exotherms corresponding to structural changes within the layers. A final endotherm is observed, associated with 5% weight loss, starting at 650 °C, indicating a degree of calcination of the layer itself.

Chromia pillared montmorillonite

The uncalcined material produces a profile indicating a large initial weight loss (13%) below 200 °C, accompanied by an endothermic peak at *ca.* 130 °C, associated with absorbed moisture and/or loosely bound interlayer water (Figure 33).

Subsequent materials (Figures 34-36), that had all experienced a calcination step, experienced a much smaller weight loss (1.5-5%) in this region, the endotherm intensity is adjusted correspondingly. A weight loss of *ca.* 2% occurs just above the calcination temperature (530-550 °C), accompanied by a well defined exotherm relating to structural changes within the pillaring material. Following this region, a further 1% is lost in the >600 °C region. These features represent structural changes occurring first within the interlayer oligomer and secondly changes within the clay layer, which continue up to *ca.* 700 °C, as observed with the unmodified material.

The uncalcined material contains extra features between 200 and 500 °C, which do not appear in the calcined samples. An ensemble of overlaid exotherms accompanies a 7% weight loss in this region, representing structural changes occurring to both the pillar and layer during calcination.

4.1.1.2 Layered Double Hydroxides

A number of layered double hydroxides were synthesised, these are summarised below.

Sample ID	M(II)	M(III)	Pillar	Modifications	APPEARANCE
BODLDH1	Mg	Al	CO_3^{2-}		White
BODLDH2	Mg	Al	Terephthalate		White
LDH1	Mg	Al	Terephthalate		White
LDH2	Mg	Al	Decavanadate		Yellow
LDH 4	Mg	Al	Decavanadate	Partial dehydration followed by H_2 calcination	Purple
LDH3	Mg	Al	Heptamolybdate		White
LDH5	Ni	Al	Terephthalate		Turquoise
LDH9	Ni	Al	Decavanadate		Yellow/grey
LDH6	Ni	Al	Heptamolybdate		Turquoise
LDH7	Zn	Cr	Terephthalate		Lilac/grey

Table 6 Composition Summary For Selected LDH Materials

Analytical data confirm the formation of layered mixed hydroxide structures of the desired composition. Thermal analysis has revealed thermal stability exceeding expectations.

Catalyst ID	Idealised Composition	Basal Spacing (Å)	Element %							Principal Features (Temp, °C)	^{27}Al NMR δ ppm, (assign)	^{13}C NMR δ ppm, (assign)
			Al	Mg	O	Ni	Mo	N	C			
BODLDH1	$Mg_4Al_2(OH)_{12}.(CO_3^{2-}).xH_2O$	7.9	10.2	17.9	51.0				17.6		9, Al_{OCT}	170 (CO_3^{2-})
BODLDH2	$Mg_4Al_2(OH)_{12}.(TA).xH_2O$	14.6	10.4	15.7	48.5				20.8		9, Al_{OCT}	200 (COO^-), 174 (CO_3^{2-}) 136, 129 (C AROMATIC)
LDH1	$Mg_4Al_2(OH)_{12}.(TA).xH_2O$	13.7	18.6	13.5	32.8				35.2	550-600 (combustion of terephthalate) 610-700 structural disruption of layer.	8, Al_{OCT}	170 (COO^-), 130 (C AROMATIC)
[a]LDH2	$Mg_{12}Al_6(OH)_{36}.(V_{10}O_{28}).xH_2O$	14.3	16.2	10	28.7				45	550-700 (structural changes)	8, Al_{OCT}	184 (CO_3^{2-}), 174 (COO^-), 130 (C AROMATIC)
[b]LDH4		13.8								550-700 (structural reorganisation)	9, Al_{OCT}	174 (COO^-), 139,130 (C AROMATIC)
[a]LDH3	$Mg_{12}Al_6(OH)_{36}.(Mo_7O_{24}).xH_2O$	11	8.6	7.2	29.7		2.4	4.5	47.6	600 (phase change of intercalate)	9, Al_{OCT}	173 (COO^-), 130 (C AROMATIC)
LDH5	$Ni_4Al_2(OH)_{12}.(TA).xH_2O$	7.6	3.9		36	5.2			54.9			
[c]LDH9	$Ni_{12}Al_6(OH)_{36}.(V_{10}O_{28}).xH_2O$									500-650 (structural collapse)		

Table 7 Summary of analytical data for selected LDH materials

[a]Prepared by ion exchange of LDH1. [b]Prepared by H_2 treatment of LDH 2 [c]Prepared by ion exchange of LDH5

It is clear that the XRD data obtained are in good agreement with the literature[13-15]. In both the carbonate intercalated LDH (BODLDH1) and terephthalate LDH (BODLDH2) peaks are narrow, indicating good crystalline order, and indicate basal spacings of 7.8 and 14.6 Å respectively (Figures 37 and 38). The latter indicates orientation of the terephthalate anion perpendicular to the layer. Similarly ^{13}C MAS NMR (appendix 2) reveals a single peak (δ = 170 ppm) attributed to CO_3^{2-} in the spectrum for LDH1 (Figure 39), and a range of peaks (δ = 174 ppm, COO^- and δ = 136 ppm,129 ppm aromatic carbon), indicating the terephthalate intercalate is present in LDH2 (Figure 40). Both samples give a single peak (δ = 0ppm) in the ^{27}Al MAS NMR (Figures 41 and 42) indicating octahedrally co-ordinated aluminium in the layer.

The characterisation data for the remaining LDH materials is self-explanatory, and repetition here would not be beneficial (NMR: Figures 43-50, XRD: Figures 51-55, D/TGA: Figures 56-60, XPS: Figures 61-66)

In the context of potential catalyst applications, XRD data (basal spacing and phase distinction) and TGA analysis provide the best screening procedures.

XRD has been discussed previously, and the property of interest here is thermal stability. TGA has been utilised to infer expected stability under hydrocracking conditions. These analyses were conducted on a STA 1500 thermogravimetric analyser. Thermographs were obtained in air at atmospheric pressure.

LDH1 (Figure 56)

Between 100-180 °C a 12% reduction in weight is observed, associated with a small endotherm, resulting from the loss of interstitial water and sorbed aerial moisture. This is followed by a corresponding exotherm as the metastable phase restructures to compensate before further weight loss occurs. From 300-450 °C a 21% reduction in weight occurs, associated with a second asymmetric endotherm resulting from superimposition of loss of more strongly bound layer water and sorbed CO_2. This is similarly followed by an exotherm due to restructuring, slightly overlapped by a sharper exotherm due to combustion of the terephthalate intercalate (550 °C). The combustion exotherm is accompanied by a weight loss feature on the thermogravimetric trace (*ca.* 18%). A final broad exotherm is observed between 600-700 °C, with no associated weight loss as the thermally stable anhydrous oxide phase is established.

LDH2 (Figure 57)

A similar profile is observed, with the absence of a combustion exotherm/weight loss feature. The absence of this feature reduces the definition of the penultimate and final endotherms. A sharp feature can be observed on the first exotherm, which is almost totally obscured in LDH1. This feature is most likely caused by metal mobility.

LDH4 (Figure 58)

The profiles are basically the same as for LDH1 and LDH2. The weight loss feature associated with loss of loosely bound water is less apparent due to partial dehydration during hydrogen treatment. The corresponding exotherm is consequently less prominent.

LDH3 (Figure 59)

Again, the same features are observed, however the DTA trace is less well defined and of far lower intensity. This suggests that the material as synthesised is less well ordered than those above (the XRD diffractogram is similarly poorly defined).

LDH9 (Figure 60)

The same transitions are observed, however shifted slightly to lower temperatures.

4.1.1.3 Surface Coking Analysis of Used Catalysts by XPS

Sample	Composition (atm %)						
	Ni	O	C	Mo	Cl	S	Al
Fresh PCB-90D	0.5	47.6	11.8	2.4		4.1	33.6
PCB-90D, following 60 min hydrocracking, standard ESCA scan (TOA 0°)	1.0	51.1	25.2	1.5	2.0	4.2	15
PCB-90D, following 60 min hydrocracking. TOA 70°	1.2	52.6	24.6	1.5	2.1	4.3	13.7

Table 8 Used catalyst surface analysis

4.2 MICROWAVE HYDROCRACKING

In order to assess the ease with which hydrogenation or hydrocracking could be achieved, operating conditions were progressively intensified. Headspace composition, headspace pressure and internal temperature were increased toward the safety tolerances of the available equipment (Table 9). Microwave power was adjusted to reduce temperature fluctuations during operation. The final reactions were conducted using vessels charged with 100 % hydrogen at 160 PSI, irradiated at 5% microwave power (~50 W). Under these operating conditions, reaction conditions of *ca.* 200 PSI and 200 °C were safely achieved and maintained.

NMP was finally selected as the solvent of choice due to;

- Thermal stability.
- Exceptional microwave receptor properties.
- Use in ICSTM bomb hydrocracker.

Use of minimal power was necessitated by the exceptional response of NMP to microwave irradiation. At higher power, fluctuations in maximum temperature and pressure were deemed unacceptably severe.

Under all conditions utilised to date GLC analysis of the product mixtures have revealed no significant reaction.

It is clear from the failure of all catalysts to achieve any alteration of the organic mixtures that current operating pressures and temperatures are unsuitable for the hydrocracking of coal maceral extracts, at the catalyst loadings used.

Particularly receptive solvents such as NMP were observed to heat to temperatures approaching the boiling point in less than one minute, even at high headspace pressure, and were maintained at these temperatures with minimal irradiation.

Recent advances in commercially available microwave technologies will provide a means to generate more acceptable pressures/temperatures in the region of 200 bar/350 °C. It is also clear from the thermal analysis that many of the LDH based catalysts may be stable at such temperatures.

Solvent	Receptor	Model	Headspace Gas	Charged Pressure (PSI, @ room Temp)	Catalyst	Exposure time (min) @ 5% power
Tetralin	DMF Acetonitrile None	None Dibenzofuran Dibenzothiophene Pyrene Dihydroanthracene	Air Argon 10% H_2/Ar	15	None Laponite Sn-Laponite Montmorillonite Cr-Montmorillonite	10
NMP	None	None Dibenzofuran Dibenzothiophene Pyrene Dihydroanthracene	Air Argon 10% H_2/Ar 30% H_2/Ar	15 15 15 15 50 100 160	None Laponite Sn-Laponite Montmorillonite Cr-Montmorillonite	10 20 30
NMP	None	None Dibenzofuran Dibenzothiophene Pyrene Dihydroanthracene	100% H_2	50 100 160	None Laponite Sn-Laponite Montmorillonite Cr-Montmorillonite H_2 Treated Cr-Montmorillonite Mg-Al (TA) LDH Mg-Al (V_{10}) LDH	10

Table 9 Summary of Hydrocracking Conditions Employed.

5. CONCLUSIONS

The targets of the work undertaken within the remit of this thesis are essentially two-fold;

- Reproducible preparation of materials suitable as potential catalysts for the hydrocracking/ hydrotreatent of coal derived and similar liquids. The preparation of these materials has involved the modification of naturally occurring clay minerals, synthetic clay minerals and synthetic clay-like materials, using both conventional and novel experimental processes.

- Initial experiments utilising microwave irradiation as a source of energy for the hydrocracking/ hydrotreatment of coal model compounds. This work has utilised a commercially available microwave digester, and modified reaction vessels.

5.1. DEVELOPMENT OF CLAY BASED POTENTIAL CATALYSTS

- A range of catalysts derived from commercially available naturally occurring and synthetic clays, modified by inclusion of inorganic "pillars" and subsequent heat treatment, have been successfully and reproducibly prepared for the first time.

- Improved reproducibility has been achieved because of advances made in the understanding of the chemistry of the pillaring solutions and their interaction with the clay materials. This, coupled with application of the existing knowledge of the clays used, has resulted in improved experimental design

- Evaluation of these materials by the Imperial College group has revealed a number of catalysts that exhibit greater hydrocracking reactivity and longevity, under comparable conditions, than conventional supported Nickel/Molybdenum based hydrocracking catalysts. In particular, tin pillared laponite and chromia pillared montmorillonite performed extremely well.[78]

- These catalysts have also been evaluated using petroleum-based liquids and display encouraging activity.[78]

- A range of synthetic clay like materials have been prepared and characterised. These materials have undergone similar modifications as the clay based catalysts. The thermal stability of these materials has been investigated, and results suggest stability is maintained at temperatures necessary for hydrocracking reactivity.

- Microwave enhanced chemistry provides a more facile route for the preparation and modification of layered double hydroxides, obviating the need for exclusion of air.

5.2. DEVELOPMENT OF MICROWAVE METHODOLOGY

The bulk of the work conducted involved the procurement, modification and commissioning of equipment to allow the safe operation of microwave irradiation experiments at elevated temperature and under pressure of hydrogen and exclusion of air at all stages of operation and sampling.

- Apparatus for the microwave assisted hydrocracking of coal derived liquids has been assembled, and preliminary investigations attempted using model compounds. Following minor modifications to allow safe operation and the exclusion of air, the apparatus functioned well in terms of integrity, safety, reliability and reproducibility. Maximum hydrogen pressure of 200 PSI and internal reaction temperature of 200 °C were routinely and reproducibly obtained, without compromising the integrity of the reaction vessel or microwave oven assemblies.

- Within the available time span over which the work described in this thesis has been conducted, no hydrocracking of these model compounds has been achieved. The work conducted has established that such reactions are feasible, however operating conditions have been limited by commercially available equipment to those well below conventional bomb hydrocracking equipment.

- Further work utilising purpose built high-pressure microwave reactors is required to determine whether microwave irradiation offers any advantages over conventional heating. The possibility of energy benefits derived from the targeted heating inherent to microwave irradiation have already been indicated by the response of NMP and other solvents to irradiation of this type. The discriminating nature of the energy imparted by microwave irradiation offers possibilities for more efficient use of hydrogen, at reduced operating pressures and/or temperatures when compared to conventional hydrocracking procedures.

Operating conditions were limited by commercially available equipment and fell short of those utilised in the conventional bomb hydrocracking experiments conducted by counterparts at Imperial College to evaluate catalysts.

In no experiments were significant, observable changes observed in the coal model compounds or solvent.

The possibilities offered by microwave driven hydrocracking are explored in the Further Work section.

6. DISCUSSION

6.1 SUMMARY OF CATALYST PERFORMANCE

Catalysts prepared from both montmorillonite and laponite display impressive activity when used to promote hydrocracking of coal derived and petroleum liquids. Catalyst samples were appraised by workers at ICSTM. A brief overview of the methods used, along with extracts of their reports relating to the catalysts are presented in appendix 1. A summary of the catalyst performance, based on their conclusions is presented below.

Catalyst performance is judged on how effectively the following criteria are met;

- Reduction of high molecular mass material (analysis by size exclusion chromatography (SEC)).
- Effective reduction of aromatic ring structures and removal of heteroatoms from heterocyclic rings (synchronous Ultra Violet Fluorescence (UV-F) spectroscopy.
- Conversion of high boiling material to lighter oils.
- Sensitivity to deactivation (repeat exposure of catalyst to fresh feed samples, analysed as above).

The catalysts produced during this thesis have consistently out-performed established catalysts in the upgrading of coal derived liquids by hydrocracking, exhibiting greater efficiency in the reduction of high molecular masses, reduction of aromaticity and heteroatom content, increased conversion from heavy to light materials and improved catalyst lifetime.

In addition to their activity toward coal extracts, the best of the catalysts were used in hydrocracking experiments with heavy petroleum crudes, where they also demonstrated impressive activity.

The most effective catalysts were the chromia pillared montmorillonite and tin laponite. Their performances in terms of boiling point conversions are outlined below;

6.1.1 ACTIVITY TOWARD COAL EXTRACTS

- Tin laponite shows highest activity at both short (10 min, 70 % conversion) and long reaction times (120 min, 67 %), with little overall deactivation on repeat exposure (7% reduction over 3 exposures at 120 mins).
- Cr montmorillonite shows disappointing activity (41 %) at very short reaction time, but is comparable with tin laponite at longer exposure

(67%), with less overall deactivation on repeat exposure (16%, but improved product quality)

- Other catalysts are less impressive but are at least as good as the proprietary catalysts.

6.1.2 ACTIVITY TOWARD PETROLEUM CRUDES

- Tin laponite performs best at short reaction times (65%).
- Tin laponite improved comparably (*cf* best dispersed catalyst) at longer reaction times (91%), suggesting some initiation process.
- Cr montmorillonite very poor at short reaction times (27.5%), but shows remarkable improvement on extended exposure, becoming most effective after 120 minutes(97%)

The experiments conducted by ICSTM have required multiple samples of each of the catalysts to be supplied. Reliable results have only been possible due to the consistently high reproducibility of performance of the materials prepared for their tests.

6.2 STRUCTURAL AND CHEMICAL FEATURES AFFECTING CATALYST ACTIVITY

Despite similar activity observed in both the chromium montmorillonite and tin laponite catalysts, the source of this activity in the two catalysts is likely to be very different, due to intrinsic differences in the starting materials.

6.2.1 COMPARISON OF MONTMORILLONITE BASED CATALYSTS

Montmorillonite is composed of comparatively large clay platelets, which in suspension become almost completely delaminated, displaying little order in relation to each other.[19] Modification by pillaring imposes a degree of order when water is removed and the layer structure of the solid is re-established.[17,18]

Analysis by XRD reveals sharp maxima indicating a consistent spacing of layers within the solid material. The resulting porous solid being composed of aluminosilicate layers held apart by the metal oxide pillars.

Alumina pillared montmorillonite has a greater basal spacing than the parent clay, by virtue of the metal oxide pillar. Catalytic activity is a result of the size of the pores and access to available catalytic acid sites. The pillar itself is composed purely of aluminium and oxygen, and as such exhibits no redox activity. In many ways it behaves as the control in terms of comparative catalytic activity of the new materials toward the coal liquid crudes under hydrocracking conditions.

Chromia pillared montmorillonite is composed in much the same way as its alumina pillared analogue, however its catalytic activity in this application is greater. This increase in activity is largely due to the redox activity of the intercalating polyoxochromia oligomer which promotes reduction of the organic material in the presence of pressurised hydrogen, coupled with the further increased basal spacing which allows improved access to the active sites. That this material behaves poorly at short reaction times indicates an initiation process. This coupled with the response of the material to hydrogen at high temperature suggests that the initiation period corresponds to reaction between the intercalated species and dihydrogen.

6.2.2 LAPONITE BASED CATALYSTS

In the case of tin laponite, the source of catalytic activity is harder to assign, although tin oxide is known not to be innocent, in the redox sense. The starting material itself is composed of much smaller particles, which form a near intractable suspension in water. When suspended in ethanol however, the suspension is far easier to separate and requires constant agitation during intercalation of the metal species. This process results in a less ordered material, in which pore size distribution is much greater.

X-ray diffractograms are composed of much broader maxima, illustrating a greater degree of variation in the layer distribution of the solid. In this case the tin oxide is thought to behave as a link, binding small areas of silicate layer together and generating both meso- and macroporous regions lined with tin oxide, in addition to the micropores that result both from the silicate layers and areas between pillars. In this case it is thought that the catalytic activity is a result of better access to active sites, further enhanced by the presence of tin oxide, promoting the activity of these sites, rather than being caused by any intrinsic activity of tin oxide *per se*.

The two models are illustrated below.[18]

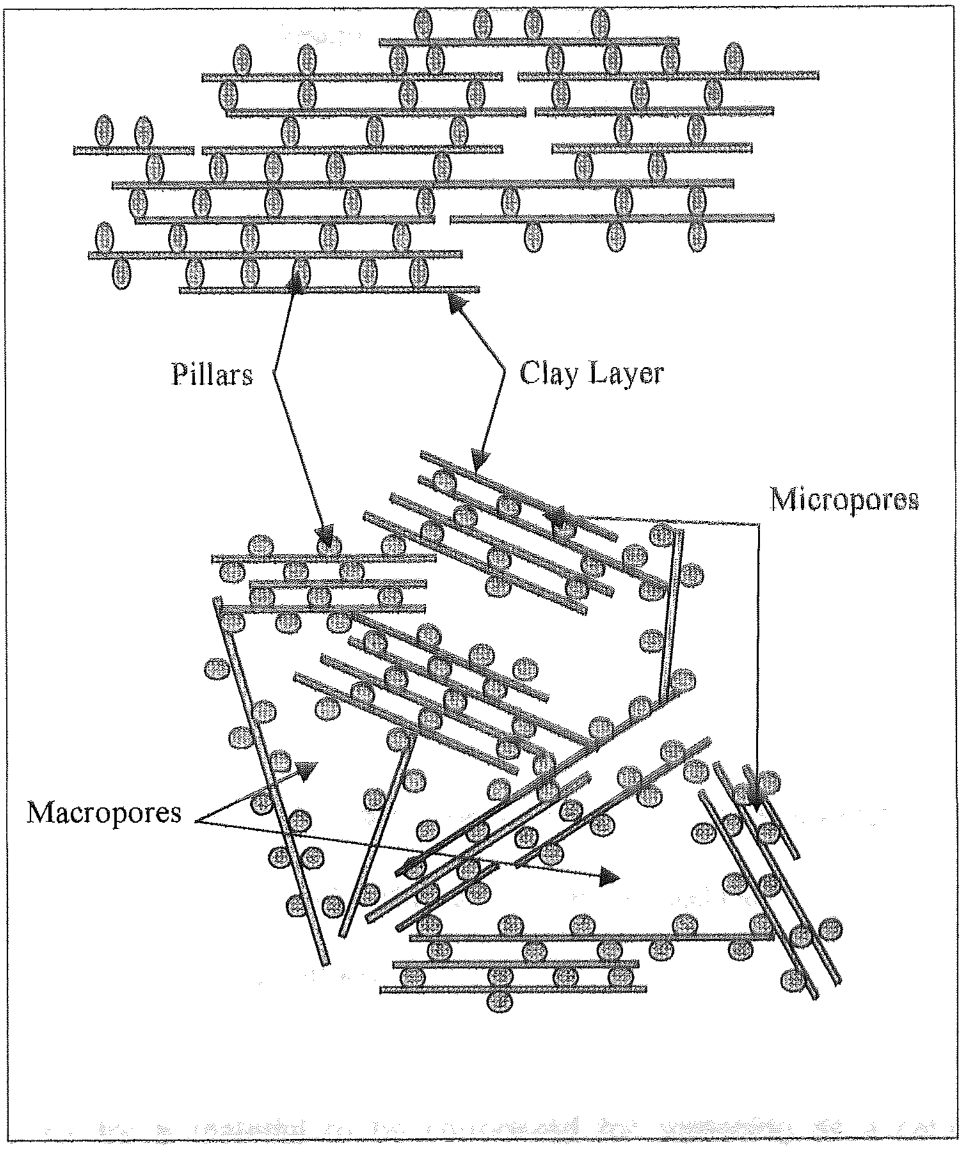


Figure 10 Diagram illustrating the layer stacking proposed for chromia pillared montmorillonite (top) and tin laponite (bottom)

6.3 SURVEY OF NOVEL CATALYSTS

6.3.1 ALUMINA PILLARED MONTMORILLONITE

6.3.1.1 Catalyst Design

A number of experimental variables can profoundly affect the properties of the final product in terms of the macro-porosity, extent of pillaring and thermal stability,[18,93] these include;

- Concentration of Keggin ion in solution, and solution composition in terms of the presence of alternative oligomeric hydrolysis products.
- Presence of competing aluminium hydroxy polymer pillaring species.
- Exchangeable cation within the parent montmorillonite.
- Clay particle size in suspension.
- Pillaring conditions, including method of addition, addition rate, ageing time and presence of competing exchange species.
- Washing and initial drying of the intercalated clay
- Calcination conditions.

In order for a material to be considered for screening as a catalyst for hydrocracking of coal derived liquids, certain criteria need to be met.

- Structural stability at suitable temperature and pressure (in this case 450°C, 150bar).
- Access of the species to be cracked to the catalytic sites.
- Prevention of poisoning or reduced transport by build-up of carbon or trapped products.

The first requirement is favoured by high pillar density, however the latter two are favoured by increased pillar separation, i.e. by minimal pillar density, except when the minimum lateral distance between pillars is greater than the gallery height.

Whilst all these variables must be combined to produce a suitable pillared clay, it is the preparation of the Keggin ion solution which offers the greatest experimental challenge.[94]

In order to control the pillaring process, the composition of the pillaring solution must be known, at least in terms of the concentration of Keggin ion. A number of challenges present themselves.

- The preparation of the Keggin ion solution involves the hydrolysis of a suitable aluminium species, which inherently involves a mixture of products.
- The precise nature of this mixture is affected by the combination of a number of factors including temperature, rate of change of pH, final Al:OH ratio (r), total Al^{3+} concentration and ageing time.
- Not all the species present can be detected by ^{27}Al NMR spectroscopy.[85] The Keggin ion structure can be described as a central, symmetric AlO_4 tetrahedron, surrounded by twelve AlO_6 pseudo-octahedra. Furthermore, many stable asymmetric intermediates exist in the solution. Low symmetry in the arrangement of ligands results in an electric field gradient (EFG)

being established about the complexed metal centre. The ^{27}Al nucleus has a spin of 5/2 and is not spherical, and thus possesses a non-zero quadrupole moment, the axis of which tends to orient perpendicular to the plane of the EFG. Molecular tumbling within the solution causes the nucleus to tumble. Coupling between the nuclear electric moment and electric field gradient is sufficient to prevent coherent alignment of the nuclear magnetic moment with the applied magnetic field. The quadrupolar electric moment supplies an alternative mechanism by which spin relaxation can occur, a given spin state therefore has a much shorter lifetime. The associated broadening of the resonance line results in reduction of the signal intensity such that the resonances from any asymmetric ^{27}Al nuclei are indistinguishable from the baseline. In fact only the hexaquo Al^{3+} species (starting material) and AlO_4 unit of the Keggin species are sufficiently symmetrical to be detected using this technique.

- The absence of signals from such species precludes quantitatively useful analysis, based on integration of the resonance lines obtained, from being conducted.
- Other techniques, including potentiometric titration and turbidity measurements are unsatisfactory.

Whilst there is a wealth of literature relating to the Keggin ion in aqueous solution,[50,85,94-105] the majority is misleading in respect of the simplicity and reliability of its preparation, a situation exacerbated by the fact that each natural clay presents its own behaviour pattern.

6.3.1.2 Hydrolysis of Al^{3+} Solution

The solution chemistry itself is complex and depends on many factors.[50,94-101] Selection of optimum conditions is essential for the generation of solutions suitable for intercalation, as the nature of the pillaring solution is critical to the character of the product. The distribution of products resulting from hydrolysis of aluminium trichloride solution is very sensitive to preparation conditions, and requires careful control. Successful preparation of solutions containing relatively high concentrations of Keggin ions has now been achieved, following a procedure adapted from a literature method,[85] and it is these solutions which were used in pillaring reactions.

The principle method of analysing the Keggin solution is by use of ^{27}Al NMR spectroscopy. In general, a sharp line is visible at 62.5 ppm, relative to $Al(H_2O)_6^{3+}$, accompanied by a broad, weak line around 0 ppm. These are ascribed to tetrahedral Al^{3+} of Al_{13} and octahedral Al^{3+} of the monomeric to pentameric species respectively.[85,95] The broadness of the signal is indicative of the quadrupolar shift caused by increasingly asymmetric environments with oligomer size. Much of the aluminium present, such as that in distorted octahedral environments in the Keggin ion and similar large oligomers, is therefore NMR invisible, producing very broad signals which merge with the background noise.

The concentration of the Keggin ion within hydrolysed aluminium solutions is a fundamental parameter that must be both measurable and controllable for reproducible preparation of pillared clays with thermal stability and consistent basal spacings. Whilst the Keggin ion can be detected, the absence of well defined signals from many of the other aluminium species present precludes a direct measurement of its concentration by ^{27}Al NMR alone. Whilst the high charge of the Keggin ion is likely to favour its preferential exchange into the interlamellar region, this is by no means assured.

6.3.1.3 Pillaring by Hydrolysed Aluminium Solutions

The effect on the final pillared material is unpredictable and further complicated by the acidity of the clay itself, and must in part be responsible for many disparities in the literature relating to thermal stability and other properties. Whilst much of the region between layers will be occupied by the large Keggin ions, which serve to separate the layers on drying, there must be many smaller aluminium based species occupying sites at the expense of Keggin ions. Subsequent calcination is likely, therefore to result not only in aluminum oxide "pillars" but also in stalactite-like internal structures, or entire regions of reduced gallery height.

Analysis of Keggin pillared montmorillonites revealed consistently smaller basal spacings than reported in the literature. Whilst each source of montmorillonite is different, and layer thickness of the starting material will therefore differ from those used by other workers, disparity within the literature can also be explained by processes occurring in addition to exchange and calcination. The acidity of the clay layer itself is known to promote removal of aluminium from the pillars during calcination (*vide infra)*, these mobile aluminium ions can occupy either regions between the layers or leach into the layer, resulting in a reduction of the gallery height.[33] In the absence of Keggin ion solutions of known composition, the significance of this process is unknown.

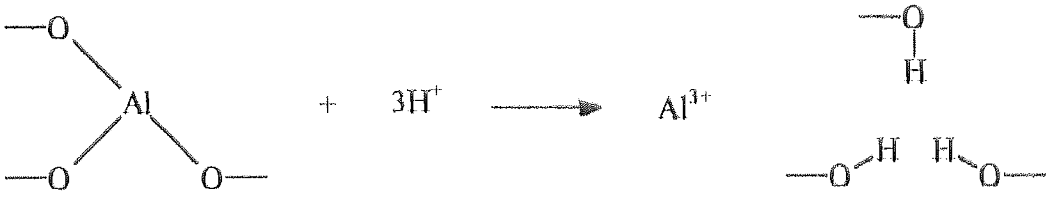


Figure 11 Removal of aluminium ions at high temperature

6.1.3.4 The Experimental Preparation of Alumina Pillared Clays

The consistent generation of Keggin ion solutions must be considered a priority. Simply following experimental procedures outlined in the literature was found to be an unsuitable course of action. In most cases, what were presented as rather facile, if somewhat delicately balanced methods, tended to lack reproducibility. The major observable experimental problem is that of the generation of a permanent precipitate of aluminium hydroxide, as a result of localised increases in *p*H on base addition.

As the amount of base added increases, small quantities of a white precipitate, which quickly dissolve, are observed. As the base addition reaches completion each drop results in increasing amounts of precipitate, which takes longer to dissolve. The formation of any permanent precipitate renders the solution useless, as once present the dynamic equilibrium of the aqueous components is disturbed, producing more precipitate. Removal of such precipitate by filtering is not an appropriate method to salvage the solution as both aluminium concentration is reduced, and the resulting conditions shift the equilibrium in favour of species other than the Keggin ion

It is this observation which underpins objections to the methods reported in the literature. Whilst it is now universally accepted that an Al:base ratio of *ca.* 2.4 maximises yields of the Keggin ion,[85,95-97,100,101,103] the action of base to achieve this is not instantaneous. Increased temperature ageing of solutions is employed to allow equilibrium to be established in favour of the Keggin ion, however no evidence is presented to confirm the success of this method. In fact, experiments conducted using microwave irradiation as a source of rapid ageing suggest a reduction of Keggin ion concentration as heating time increases, the 62.5 ppm line is observed to disappear from the spectrum following microwave irradiation (Figure 14). It is apparent that microwave irradiation accelerates the decomposition of the Kegggin ion to smaller, NMR invisible species, possibly as a result of localised high temperatures.

It is the absence of a suitable analytical technique to probe the NMR invisible portion of the solutions that must draw into question the assertions that

Keggin ion containing solutions can be reproducibly prepared, as no total analysis has been reported. A technique has been reported by Schoonheydt *et al*[100] whereby integrated line intensities of solutions containing known concentrations of octahedral hexaquo Al^{3+} were compared with Keggin ion solutions, as a means of estimating Keggin ion concentrations.

Two main objections to this method present themselves, firstly extrapolation of AAS data to calculate concentrations at the levels used is subject to large errors. Secondly, the integration of peak intensities of the relevant NMR signal is difficult to conduct accurately due to line shoulders. Direct analysis of the Keggin ion solutions by AAS is precluded by the concentration sensitivity of this species in solution, hence dilution to levels at which AAS is an appropriate analytical technique will inherently produce a solution whose composition differs from the stock.

The crystallisation of salts, such as the sulfate, of the Keggin ion and their subsequent dissolution presents a similar problem;[99] once dissolved in aqueous solution there is no reason to expect that the Keggin ion will remain the only species present, thus gravimetric analysis is unsuitable.

The classic method to minimise the deleterious effects of localised concentration gradients is by employing high dilution, however in this case such a solution is inappropriate as the solution chemistry is sensitive to concentration- high dilution favours formation of alternative aluminium bearing anions.

The alternative is to improve mixing. Particularly at the volumes quoted within the literature- typically dropwise addition producing solutions of hundreds of millilitres- efficient mixing can only be achieved locally, if employing standard glassware and ancillary equipment.

After attempting to reproduce many syntheses presented in the standard peer reviewed literature, none of which proceeded with sufficient reproducibility to develop any confidence in the composition of the resulting aqueous solution, a reduced volume method was employed. Using this method, as outlined in the experimental section, it was possible to generate hydrolysed polyhydroxyaluminium containing aqueous solutions without any observable precipitation occurring. The problem of reliable routine analysis of Keggin ion containing solutions however remains unresolved.

A possible course of action to practically control the pillaring of clays with Keggin ion solutions, despite the intractable problem of concentration measurement is outlined below.

- A suitable set of reactions might be undertaken to determine both the diminishing Keggin ion concentration in solution, and expected increase in sodium ion concentration in the liquor above a sodium exchanged clay following fixed aliquot additions. Samples of the suspension, or of isolated mother liquor, taken after aliquot additions and analysed by Na and/or Al NMR analysis combined with AAS to measure the concentration of sodium. This would represent a measure of the change in Al loading of the clay, assuming the replacement of seven sodium ions by each Keggin species, and the absence of any other exchange reactions.. In this case dilution for AAS analysis offers none of the previously stated disadvantages. This would require a rigorous Keggin preparation procedure to ensure near identical solutions for subsequent runs.

- Such an approach MAY result in both a measure of maximum loading, and minimum loading which prevents collapse of the layers at 450°C, using TGA, or by XRD analysis on the heated samples.
- Such a process also assumes that the Keggin ion would be equally distributed throughout the clay, even at low concentrations, rather than collecting to generate areas of greater thermal stability.

Although not producing a value for the Keggin ion concentration, this route may provide a method to empirically relate catalytic activity to aluminium loading.

Due to preliminary results suggesting greater activity of the chromium and tin based catalysts, no experiments were actually conducted to pursue this line of investigation.

6.3.2 CHROMIA MONTMORILLONITE

Preparation of chromia pillared montmorillonite is essentially the same as that of the alumina pillared material, however the solution chemistry of the aqueous chromium (III), or chromic, ion is less complex. Hydrolysis of the acidic solution by base results first in the dimeric $Cr_2(OH)_2^{4+}$ and $Cr_2(OH)^{5+}$. The hydroxide ion(s) act as bridges thought to form by the deprotonation of the coordinated water followed by coordination of the hydroxide ion to a second cation. Further deprotonation and polymerisation occur as the *p*H is raised, formation of larger polymeric species being favoured by the increased temperatures of reflux.

No chromium nucleus can be probed using NMR spectroscopy due to paramagnetism of Cr(III). Ultimately then, the exact nature of the pillaring species is open to conjecture.

Analysis of the chromium(III) nitrate solution by UV/VIS spectrometry produces a spectrum characteristic of the octahedrally coordinated hexaquo Cr^{3+} cation. The characteristic violet colour results from the three spin-allowed d-d transitions, whose absorption bands are observed at 17400, 24500 and 37800 cm^{-1}. The third, high-energy band, is partially obscured by more intense charge transfer features. Hydrolysis of this solution results in replacement of some of the coordinating water by bridging hydroxide ion(s). The resulting aqueous polymeric species are green in colour as a result of distortion to a pseudo-octahedral geometry. The observed bands are slightly shifted to lower energy, commensurate with OH^- appearing lower in the spectrochemical series than water i.e. coordination by hydroxide ions generates less crystal field splitting. The high-energy band is completely obscured by the more intense charge transfer absorption. This distortion is accentuated by constrictions imposed by the clay lattice on intercalation, with an associated shift to lower energy.

It is apparent that intermediates on the reaction pathway toward the oligiomeric species do not exhibit the same sensitivity, in terms of solubility, as experienced during the aluminium hydrolysis. No equivalent gelling process to that observed during base treatment of aquo-aluminium complexes is observed, with solubility maintained over the *p*H and concentration range used. With this in mind, it is reasonable to suspect that the range of stable polymeric species present in the final solution are more limited than experienced in the hydrolysed aluminium, or so called Keggin ion solution.

Calcination results in dehydration of the water/hydroxide species to give the oxide pillared montmorillonite. This material outperformed the aluminium intercalated montmorillonite in all experiments conducted by the ICSTM group, in terms of initial activity, and continued to offer a higher degree of catalytic activity following repeat contacts.

The failure of XPS analysis to reveal the presence of any chromium in the final material has already been mentioned. The colour of the treated clay persists even following extensive elution by de-ionised water (resulting in a clear solution producing UV/VIS spectra indistinguishable from the baseline). This colouring and the UV/VIS spectrum confirm the presence of chromium(III), particularly given the absence of other coloured species during the pillaring procedure. XRD reveals that clay treatment with the polyoxochromium solution results in an increase in the basal spacing.

Considering this evidence and the observed catalytic activity, only one conclusion is reasonable- that chromia is present in the interlayer region, but remains undetected by XPS.

The XPS technique itself is known to be both depth and concentration sensitive. Photoelectrons from the top 50 Å[107] of the sample (less if the take off angle is increased) reach the detector with diagnostic kinetic energy, those emitted from atoms further below the surface lose energy as they travel through the material. Similarly, atoms present at low surface concentrations release an insufficient flux of electrons to be detectable above background noise and other features. The nature and composition of the bulk material would not appear to fall into either of these categories, although bulk composition is not necessarily representative of the surface. These considerations are valid only for idealised cases in which the plane of the surface is presented to the incident X-ray beam.

It has already been noted that a random, "house of cards" model is in the case of individual layers, equally as valid as one of ordered stacking. Despite the fact that the ordered model has been assigned to the chromia pillared material on the scale of layer stacking, the failure of XPS to detect chromia can be explained by invoking the same logic on a larger scale. The particles resulting from this ordered stacking themselves aggregate in a less ordered manner, thus the "surface" that the X-ray beam is incident on is not equivalent to the surface of the alumino-silicate sheet *per se*, but rather a collection of sheet edges and planes at acute angles. This results in an effective dilution of the surface chromia with which the incident beam can interact, and consequently no chromia is detectable.

Chromium Oxide (Cr_2O_3) has a corundum Al_2O_3 structure. It is likely, therefore that the pillaring species is essentially of the same form in both materials. The observed disparity in catalytic activity is therefore the result of;

- Increased basal spacing
- Redox activity of the cation present in the pillaring species.

Of these factors, the latter is of greatest significance, as it offers the greatest scope for further developments.

Catalyst Modification

The hydrogen pre-treatment process appears to have had little or no effect on the condition of the chromia pillared montmorillonite, *cf* the sample calcined under argon, either used as a replacement for or in addition to the previously employed argon calcination. In both cases, thermal stability exceeds the bomb hydrocracker operating temperature. This suggests that the material is sensitive only to oxidation, which has previously been avoided due to generation of carcinogenic species as a result of oxidation to Cr(VI). However, considering that catalyst activity becomes optimum following a short initiation period under the ICSTM hydrocracking conditions, which employ much higher hydrogen pressure, the effect (if any) of hydrogen pre-conditioning cannot be ruled out.

6.3.3 TIN LAPONITE

The synthesis of Tin laponite is unrelated to the above-mentioned aqueous synthesis. The starting materials and experimental conditions are distinctly different from those employed for the aluminium and chromium materials, and this is reflected in the suggested nature of the final material. The principal differences are outlined below.

- Tin organometallic starting material, hence ethanolic solution necessary
- Microwave irradiation employed

- Rapid, one pot preparation
- No calcination step
- Pillaring species is unlikely to be a metal ion oligomer.
- Role of intercalate likely to be different

These factors result in a material that must be considered to belong to a different class of catalytic material, a metal oxide modified clay, rather than a pillared compound.

Firstly, the nature of the microwave accelerated reaction to produce tin(IV) oxide *in situ* precludes the establishment of an ordered structure *vide supra*. The random connectivity of the laponite platelets is further promoted by the use of ethanolic solution, which prevents complete delamination prior to introduction of the metal oxide, and the nature of the laponite itself- small particle size discourages the establishment of an ordered layered structure, particularly given the reaction time.

Secondly, inclusion of tin(IV) oxide is significant in a number of ways. Whilst the variable oxidation state of tin is significant in catalytic terms, it is unlikely that this is the only source of the observed catalytic activity. This was briefly discussed above, however the actual role of tin(IV) oxide is a matter of pure conjecture at this time.

Leaching of aluminium from oxide pillars into aluminosilicate layers, with a concomitant reduction in gallery height,[33] has been reported in the literature, similarly bond formation has been observed between aluminium oxide pillar and layer when using a synthetic beidellite.[105,106] This has been posited as a reason for the range of basal spacings observed between different montmorillonites pillared following otherwise similar methods.

Catenation is a principal property of group IV compounds. In the case of tin laponite, the silicate layered material is treated with a congener and reaction is observed, promoted by the acidity of the clay. These considerations, when taken together suggest a mechanism by which the tin(IV) oxide intercalate could behave to extend the two dimensional silicate layers into a three dimensional matrix, resulting in the suggested macroporous catalytic material.

The behaviour of this material when exposed to hydrocracking conditions suggests an initiation period, after which catalytic activity towards coal liquids and petroleum residues is optimised, followed by slow deactivation. Preliminary hydrocracking runs using petroleum distillation residue in the presence of calcined tin laponite revealed improved activity after 10 mins than experienced for the uncalcined tin laponite, the best of the fully studied catalysts. Further investigation is required to determine whether the same is true of the calcined material, or if the calcination step reduces or replaces the initiation period.

Experiments conducted using a calcined, chromium treated laponite indicated relatively poor activity, compared to the other novel catalysts previously studied, which supports the theory that catenation to form an extended tin oxide/silicate matrix is responsible in part for the tin laponite activity.

Optimisation of catalyst activity requires still greater understanding of the role of the intercalated metal, its interaction with the layered material and the final thermal treatment of the catalyst. This is explored more thoroughly in the further work chapter.

6.3.4 LAYERED DOUBLE HYDROXIDES

The activity of LDH materials has not been addressed extensively within the thesis, as time constraints have prevented extensive studies of their use with coal derived liquids, however preliminary investigations by ICSTM have revealed that activity towards petroleum crudes has been greater than anticipated, considering the expected thermal stability.

Of the samples synthesised, Ni/Al layered double hydroxide, incorporating heptamolybdate was observed to exhibit initial activity toward coal extracts, comparable to that of montmorillonite and laponite based catalysts, despite its predicted lack of thermal stability.

These materials are known to decompose to form an oxide on heating, following dehydration during exposure to high temperatures. Assuming this to be the case, it is possible that the catalytic activity is not a result of a layered molecular sieve, but that the layered double hydroxide is acting as an *in situ* source of a high surface area oxide material supporting finely dispersed nickel and molybdenum. The analogy with the alumina supported Ni/Mo catalysts, known to be successful when used as hydrocracking catalysts for petroleum crudes supports this theory. It is conceivable that the conditions of high temperature and presence of hydrogen result in reduction of these metal ions to form the zero valent metals on a porous alumina support, and it is the presence of these metals which is the source of the surprising catalytic activity.

6.3.5 ANALYSIS OF USED CATALYST

Varying take-off angle resulted in identical spectra to those obtained from the standard ESCA scan. It was therefore not possible to analyse surface coking of used catalyst samples. The nominally spherical catalyst particles prevented depth-resolved data from being obtained. Variations in detector angle do not in fact reflect variations in mean free path for spheroids as the collection angle remains the same (measured from the normal to the tangent at the point of impact).

6.4 MICROWAVE HYDROCRACKING

Whilst disappointing, the inability to achieve hydrocracking of coal model compounds by microwave irradiation does not represent a total failure. In order to run the experiments it has been necessary to successfully tackle a number of technical problems and it has been demonstrated that such experiments can be conducted safely whilst using high pressure hydrogen in a potentially hazardous environment.

Whilst the maximum operating temperature attained within the microwave bomb apparatus approaches the conditions used for the conventionally heated mini-bomb, the hydrogen pressure possible within the microwave apparatus was *ca.* 15 times less. The lack of reaction serves to demonstrate that experimental requirements exceed the tolerances of commercially available equipment currently available.

NMP exhibited exceptional response to 2.45 GHz microwave irradiation, surpassing the response time of salt water, and reaching its boiling point in under 1 minute, even at low power, compared to the response of water, which requires 560 W to reach 81 °C in the same time.[57] This is not necessarily a surprising result, as discussed below.[57]

The response of a liquid to incident microwave irradiation depends on two properties; the dielectric constant, which describes the ability of a molecule to be polarized by the electric field and the dielectric loss, which measures the efficiency with which the energy from electromagnetic radiation can be converted into heat. Both properties are frequency dependent - dielectric loss goes through a maximum over the range of frequencies where the dielectric constant falls.

The frequency of radiation supplied by commercial magnetrons was selected for use in the domestic microwave oven, and as such heats food via excitation of the water present therein. It is complete, even heating of food, rather than rapid heating, which is the overriding consideration. The optimal response of water is not, therefore a necessity- in fact, the maximum dielectric loss occurs at 20 GHz. The dielectric loss profile for NMP is apparently closer to its maximum at the frequency used, and thus heat is generated more efficiently. Despite this efficient heating being an attractive feature of this solvent, in practice NMP may not be suitable as a microwave receptor/solvent as it is certain to undergo reaction under hydrocracking conditions.

7. FURTHER WORK

It is clear from the catalyst evaluation work that there is much scope for continuing investigation into catalysts based on clay and clay based systems.

Materials derived from both naturally occurring and synthetic clays exhibit improved activity and longevity, in terms of catalytic activity towards coal derived liquids and heavy petroleum fractions, when compared to conventional alumina supported and dispersed catalysts.

7.1 OPTIMISATION OF CATALYST ACTIVITY

It is clear that the catalysts developed to date offer themselves to applications not only in coal liquids but also to petroleum crudes. Of particular interest are heavy resids- the largely intractable, economically unappealing material left following fractional distillation of crude oil. Future development is largely an issue of honing desired catalyst properties by trial and error contact experiments to determine the most efficacious combination of experimental variables both from a scientific and commercial standpoint.

Such evaluation would be tackled in three ways

- Mixing of different catalysts- some have shown greater initial activity, whilst others give better quality products. Mixing catalysts could be used to optimise the system as a whole.
- Multiple modifications- i.e. chromium treatment of a tin laponite. Such a process would achieve the same aim as above, combining the observed properties of the different species, but on a molecular level
- Control of calcination. It is clear that the role of calcination is complex and may be important to at least the initial activity of the catalyst. More in-depth investigation of this process, combined with a redox procedure by introducing either an oxidising or reducing atmosphere will improve design of next generation catalysts.

7.2 CATALYST ANALYSIS

Any future investigation should have at its core a study of the behaviour of these materials under conditions more closely related to those experienced during hydrocracking, to assist catalyst design.

Variable temperature XRD, conducted under pressurised hydrogen should reveal the effect of the hydrocracking environment on the structure of both the material as a whole and phase changes within the layers. Such investigation should result in invaluable information as to the correct course of action to optimise catalytic activity and longevity, for example in addressing the question of whether calcination could be considered an activation process.

Surface area measurements are often used as a method by which catalysts are compared. Standard nitrogen adsorption is of limited use in this application as total surface area is revealed, without revealing much information as to how much surface area is available to molecules of the size encountered in coal liquids. Mercury vapour deposition is more useful, as it provides some information relating to pore-size and distribution.

An alternative method may provide a useful survey of the catalyst/substrate behaviour at a molecular level. Apparatus exists for the testing of cement water permeability that is composed of two glass bulbs sandwiching a compressed cement disc. Adaptation of this apparatus to accept a compressed disc of catalyst is feasible and the bulbs could then be charged with solvent, one side containing a dissolved model compound or mix of compounds. Analysis of the equilibrium mixtures and/or a solvent wash of the disc, by GLC, ^{13}C NMR, ^{1}H NMR and SEC should provide an indication of the size of molecules that are excluded from the catalyst material itself, which are retained within it and which travel through without being adsorbed.

Such a process could be simplified if SEC apparatus could be modified to accept the catalyst as column packing.

7.3 USED CATALYST ANALYSIS

Used catalysts must be successfully characterised to fully understand the catalytic hydrocracking process as a whole. Depth resolved XPS, combined with other surface studies such as SEM (Scanning Electron Microscopy) or AFM (Atomic Force Microscopy) is necessary to understand the nature of surface coking. It has been shown that standard XPS methods fail to produce depth-resolved data. Employing surface ablation by argon, prior to surface analysis will assist analysis of the carbon at a chemical level and could conceivably be used in conjunction with SEM or AFM to observe surface distribution of carbon.

7.4 LAYERED DOUBLE HYDROXIDES

These materials are far less well known than pillared clays, and offer a rich source of further investigation, for example using microwave enhanced ion exchange to avoid the use of Schlenk equipment and, perhaps more importantly, by employing purpose built apparatus to allow controlled synthesis of LDHs.

Whilst it is easy to control the chemistry of system, by controlling the stoichiometric ratio of reactants, and to some degree to control the morphology of the final material by addition rate, the ultimate aim of such preparations must be to achieve systematic and reproducible variation in the final LDH. It is common for chemists to become blinkered when studying materials such as clays, relying on knowledge of the chemical composition of these materials without considering the distribution of chemical moities and morphology of the product, and the resulting effects on it's application.

Use of a purpose built bench top micro reactor will allow complete systematic control of addition rates, rate and type of mixing, headspace atmosphere, pH, temperature etc. and offer a means to finely control and modify crystal size and morphology. Materials generated in this way could be evaluated as catalysts to determine which factors are critical to optimisation.

On a more fundamental level, further work is required to evaluate the existing LDH materials in terms of longevity and catalyst regeneration to assess the effects of the hydrocracking conditions on the material.

7.5 MICROWAVE HYDROCRACKING

It is clear that commercially available equipment cannot currently provide conditions severe enough to promote hydrocracking rections. Assembly of a purpose build reactor able to withstand pressures and temperatures experienced in a conventional hydrocracker would allow the conventional and microwave driven processes to be compared more fairly. Ideally, a variable frequency magnetron would be incorporated to allow specific targeting of functional groups/solvents and/or molecular fragments. This is unlikely to be cost effective due to regulations relating to control of radio frequency emissions.

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9. FIGURES

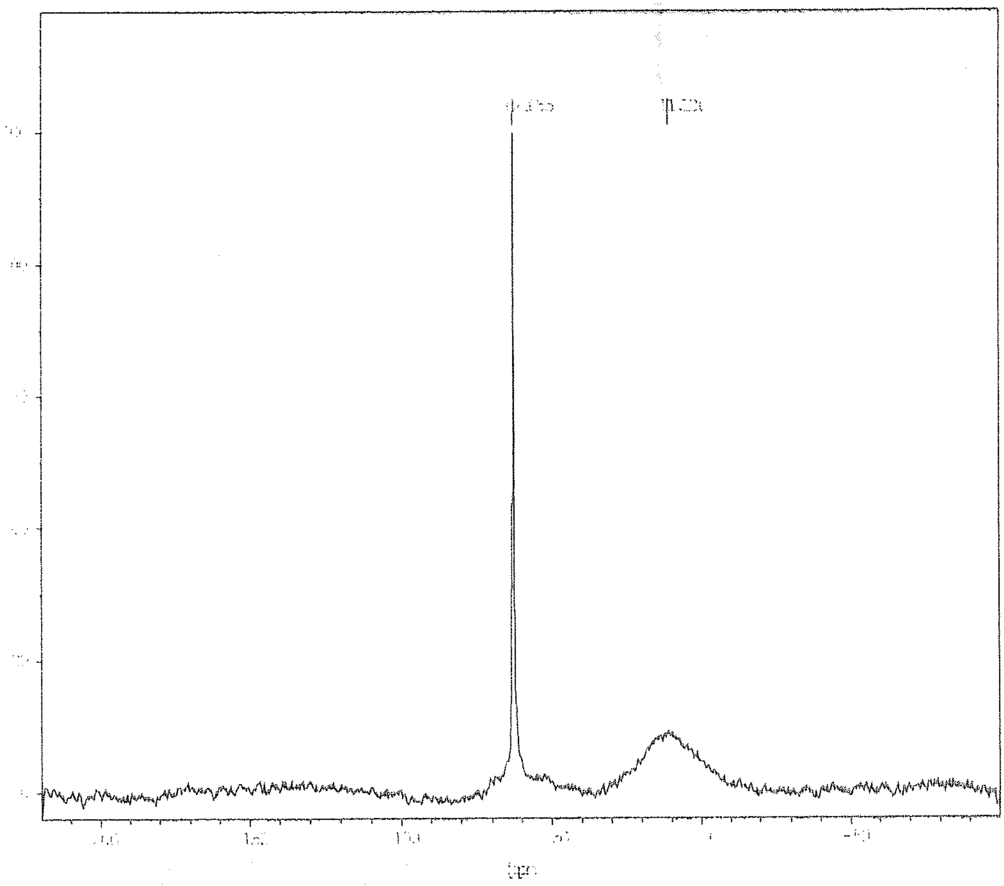


Figure 12 Typical ^{27}Al NMR spectrum of the Keggin ion, prepared in aqueous solution

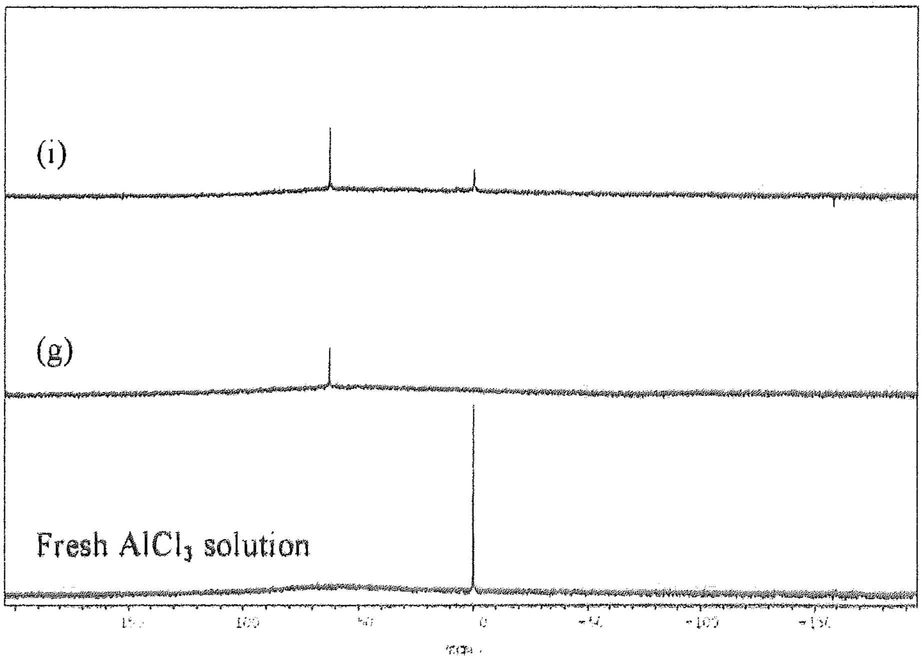


Figure 13 ^{27}Al NMR spectra of (i) incomplete hydrolysis of AlCl$_3$, (g) Primarily Keggin ion and a reference AlCl$_3$ solution

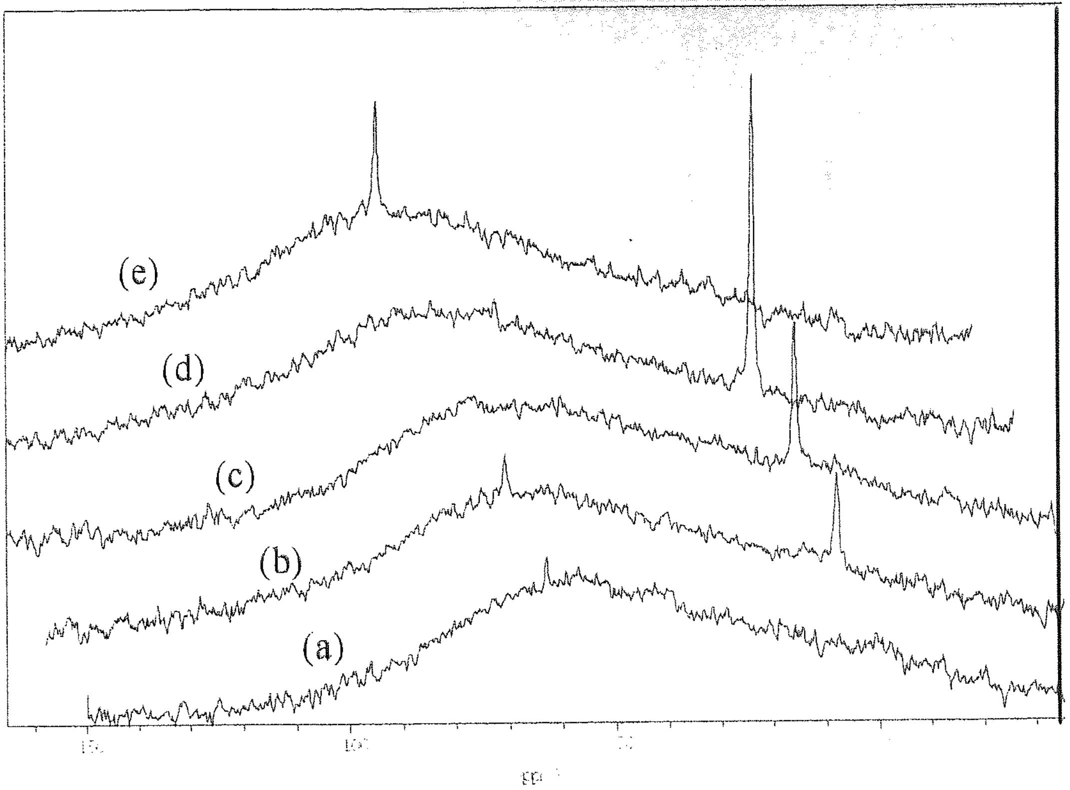


Figure 14 The effect of microwave exposure on the product distribution of hydrolysed $AlCl_3$ solution

(a) immediately after sodium hydroxide addition
(b) after 150 s irradiation
(c) 300 s irradiation
(d) 600 s irradiation
(e) aged at room temperature for 600 s

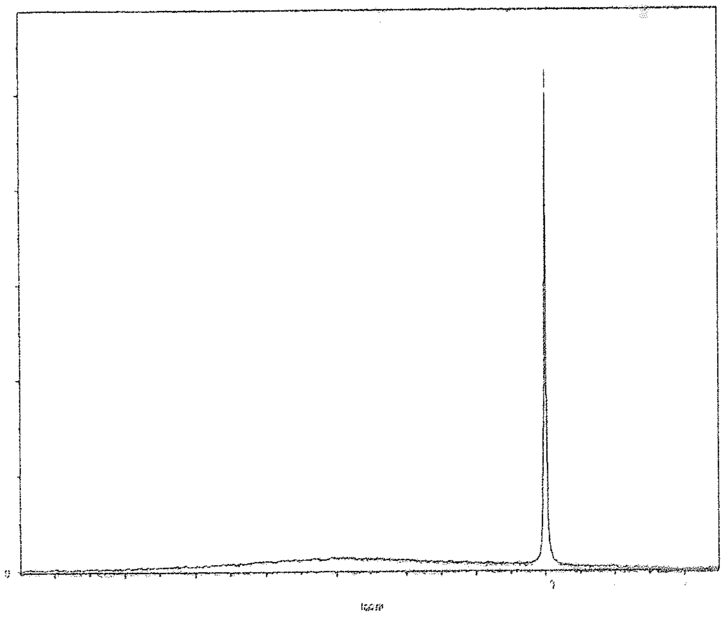


Figure 15 ^{27}Al NMR spectrum of freshly prepared $AlCl_3$ aqueous solution

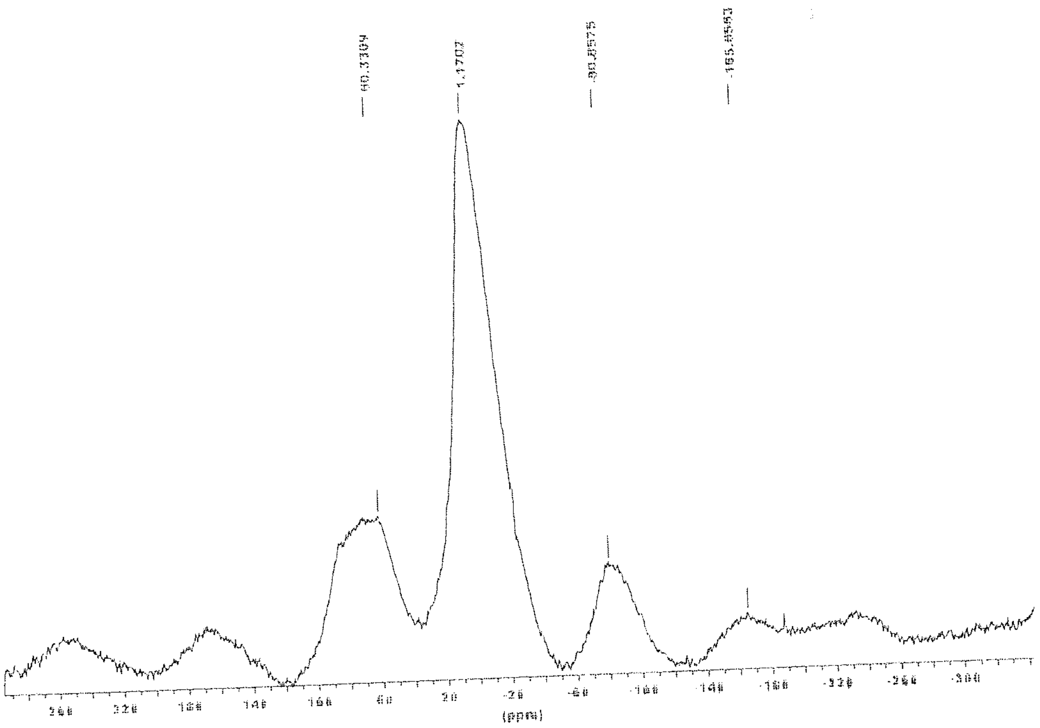


Figure 16 ^{27}Al MAS NMR spectrum of monoionic sodium montmorillonite

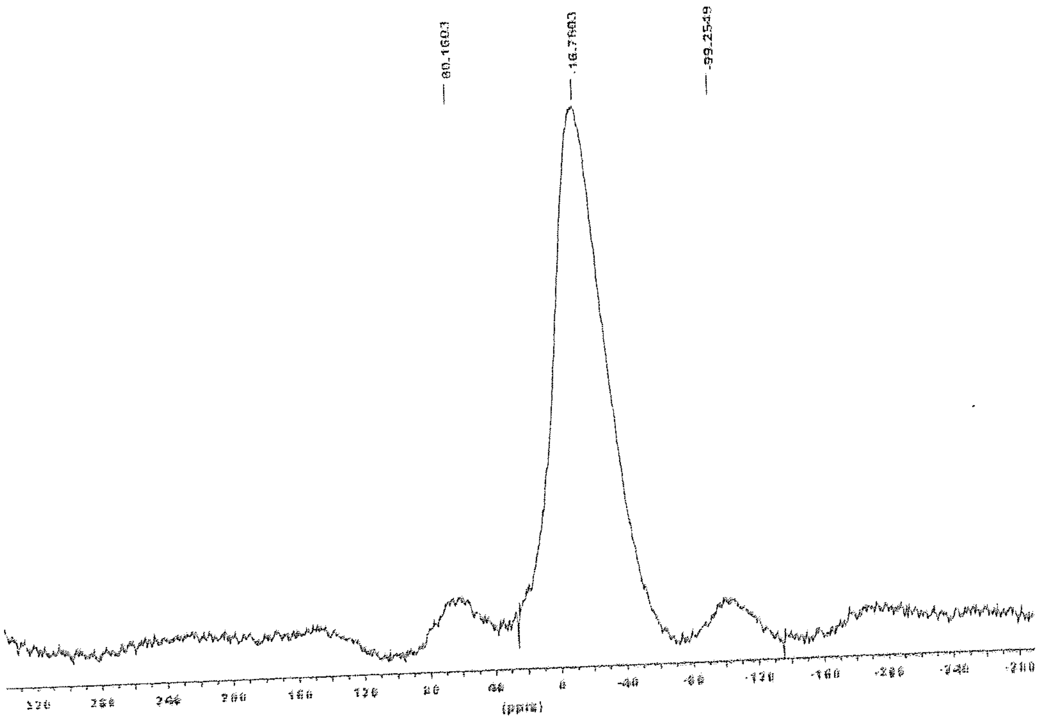


Figure 17 ^{23}Na MAS NMR spectrum of monoionic sodium montmorillonite

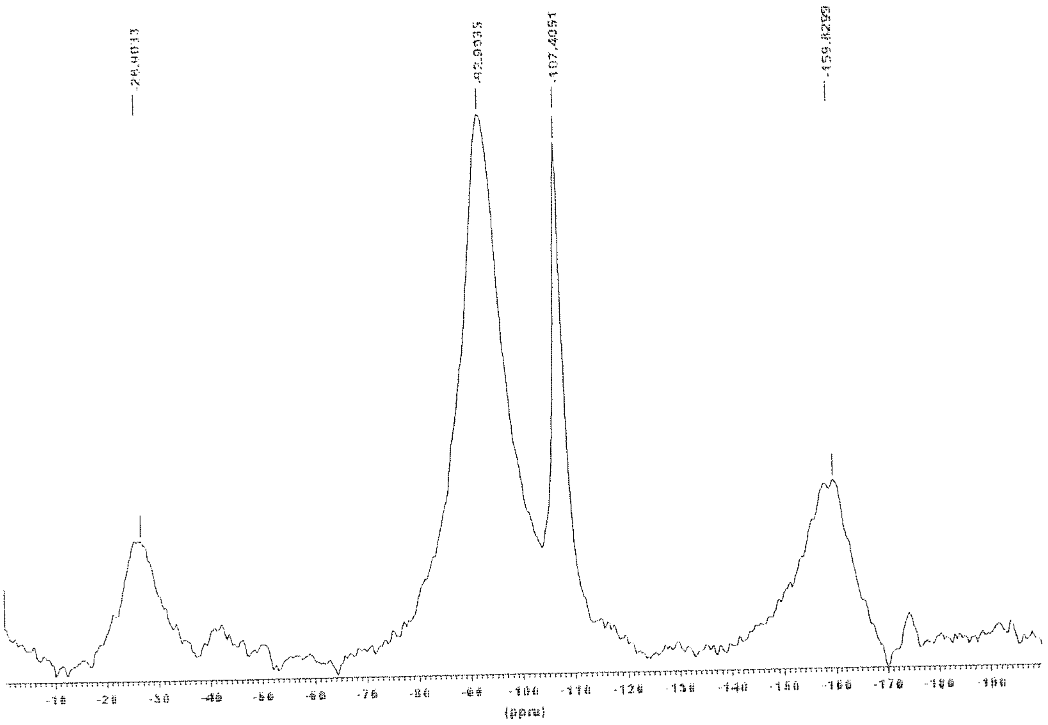


Figure 18 ^{29}Si MAS NMR spectrum of monoionic sodium montmorillonite

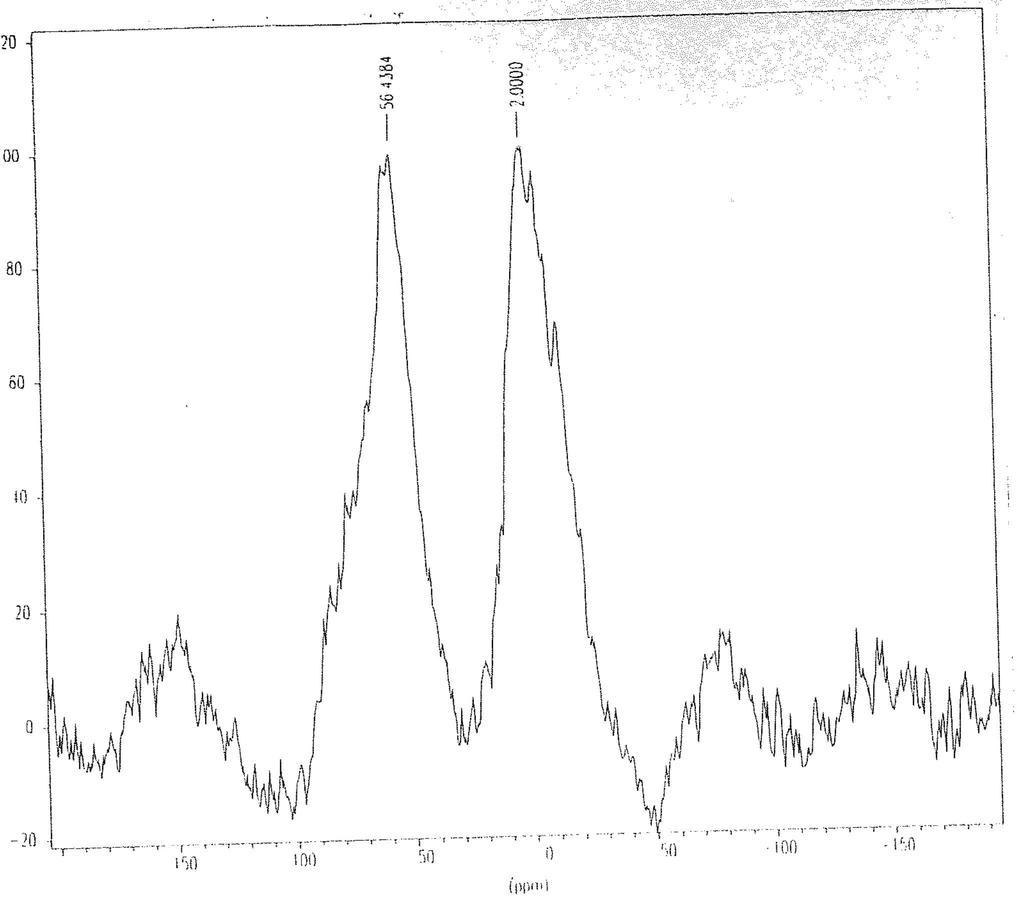


Figure 19 ^{27}Al MAS NMR spectrum of Keggin pillared montmorillonite

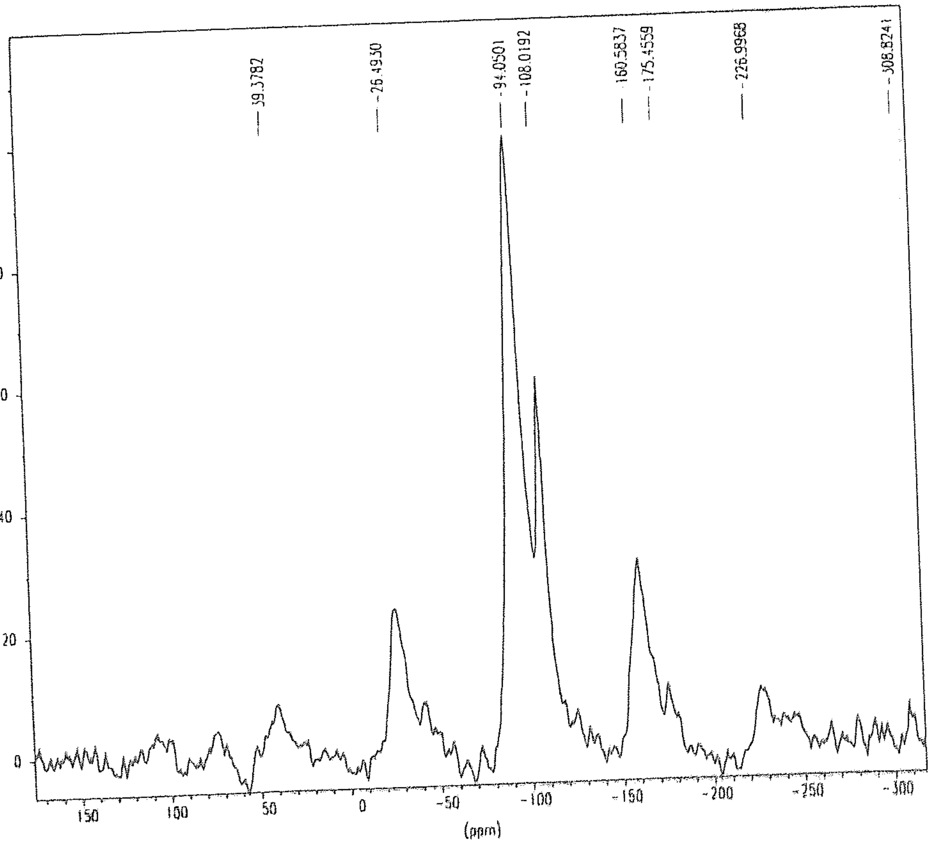


Figure 20 ^{29}Si MAS NMR spectrum of Keggin pillared montmorillonite

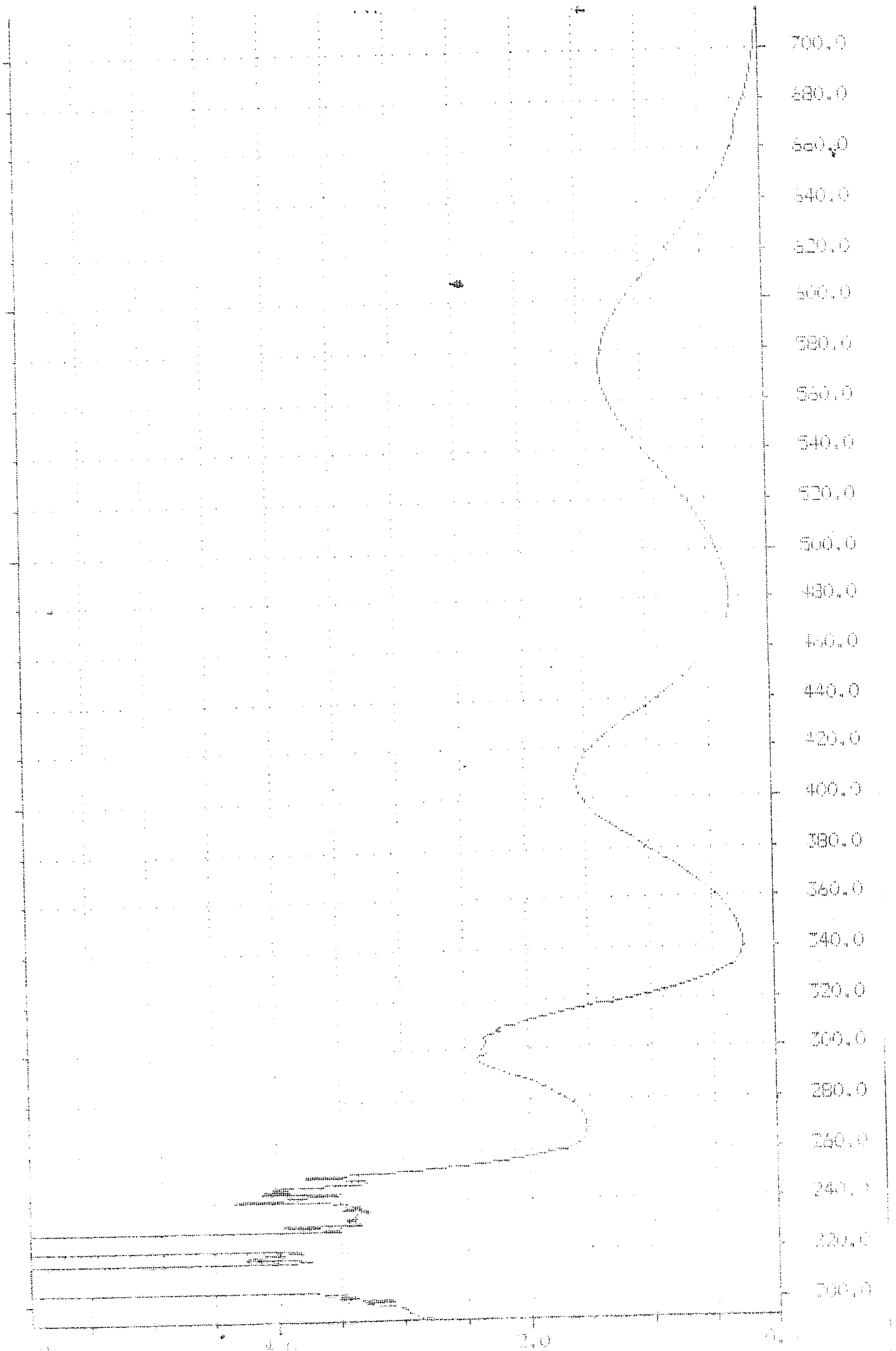


Figure 21 Electronic spectrum of chromium(III) nitrate aqueous solution

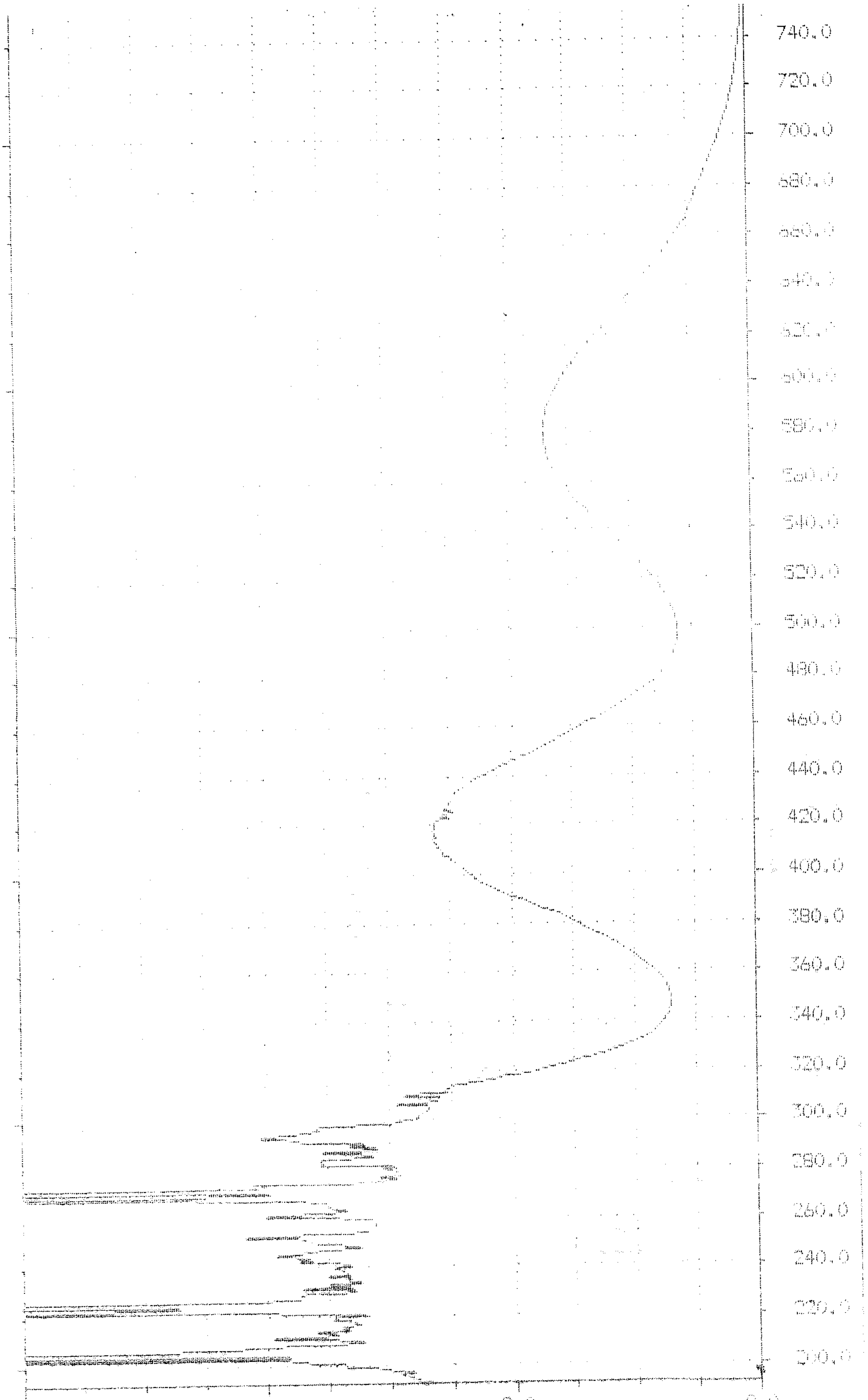


Figure 22 Electronic spectrum of aqueous Cr(III) following base hydrolysis

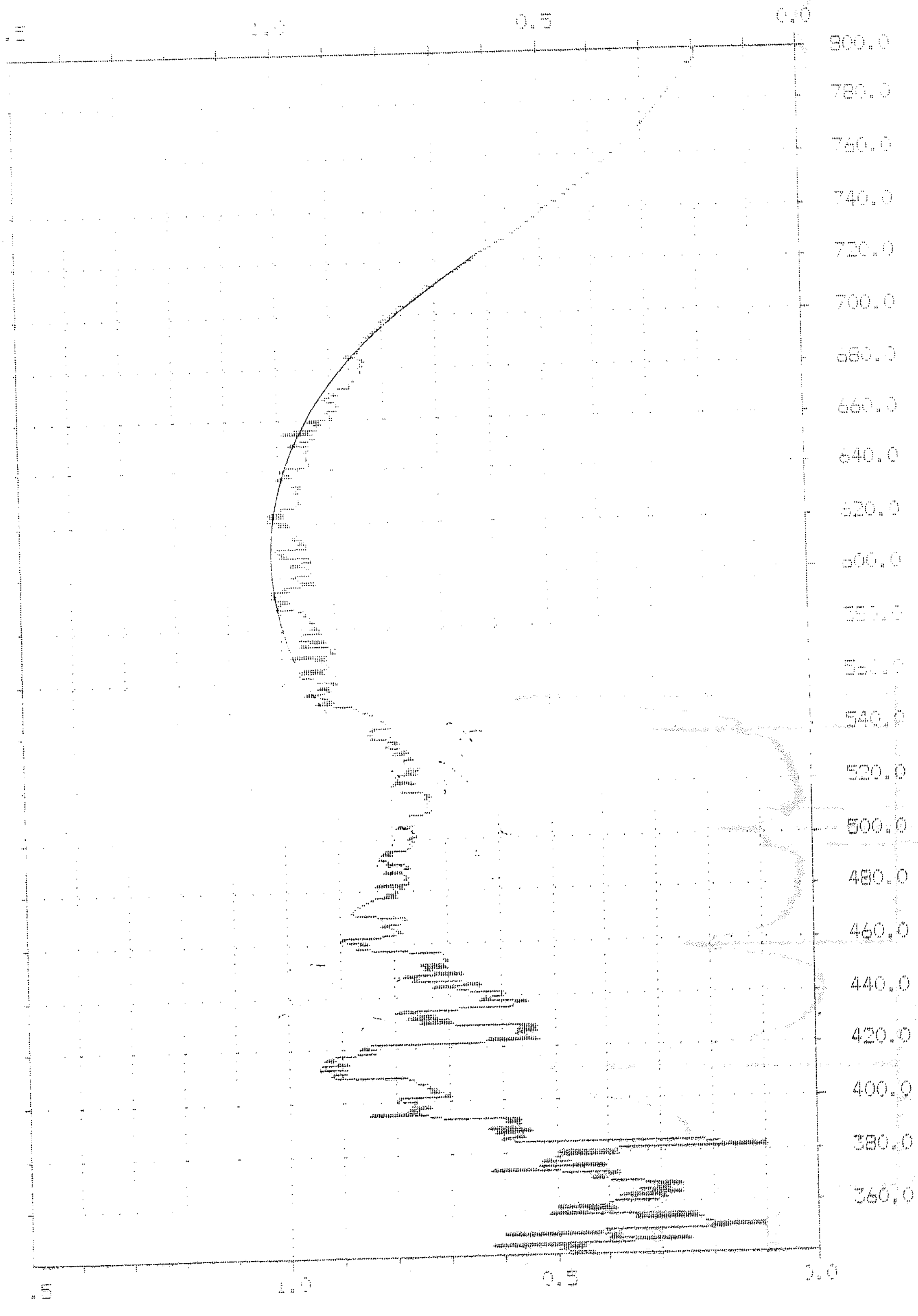


Figure 23 Diffuse reflectance electronic spectrum of chromium pillared montmorillonite

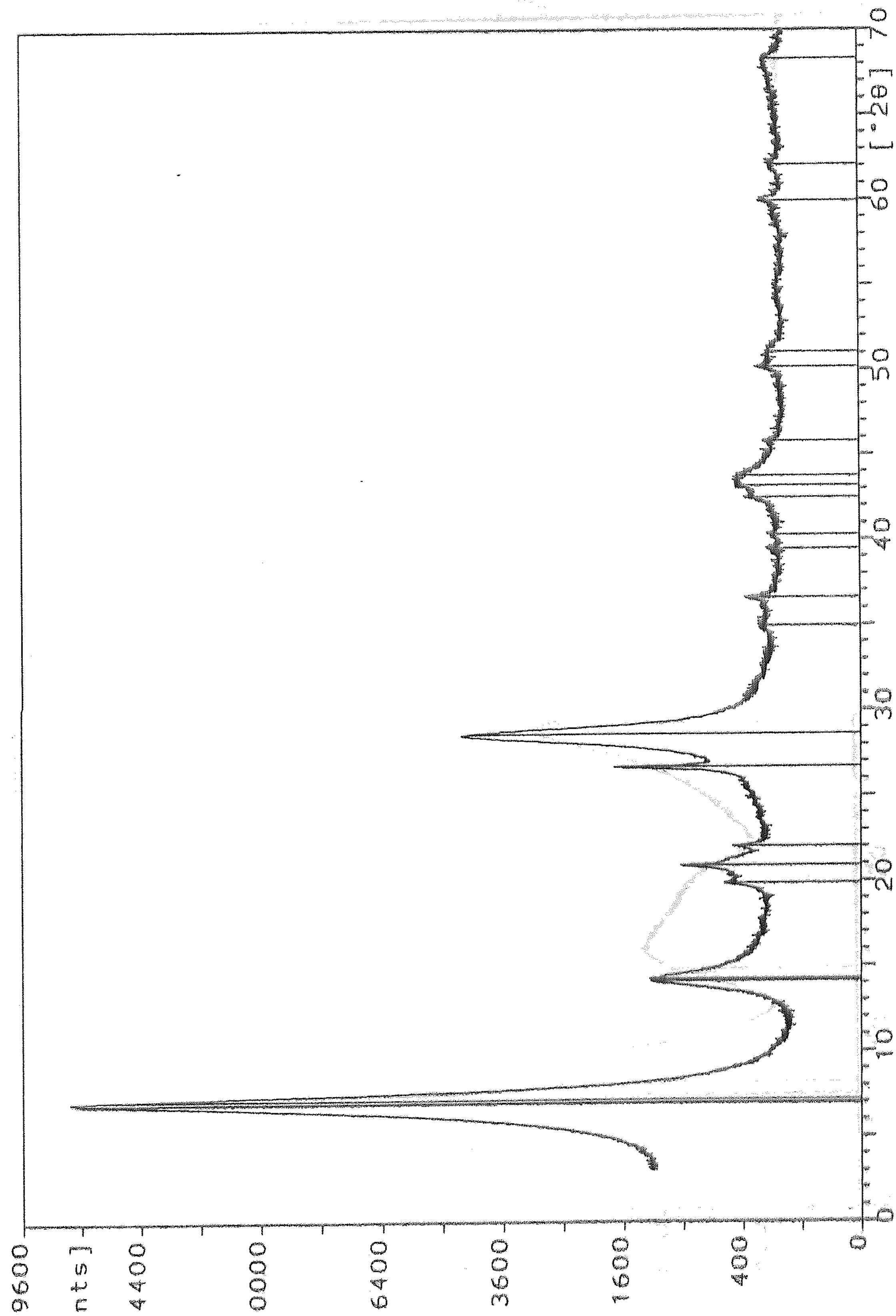


Figure 24 X-Ray Diffractogram of sodium montmorillonite

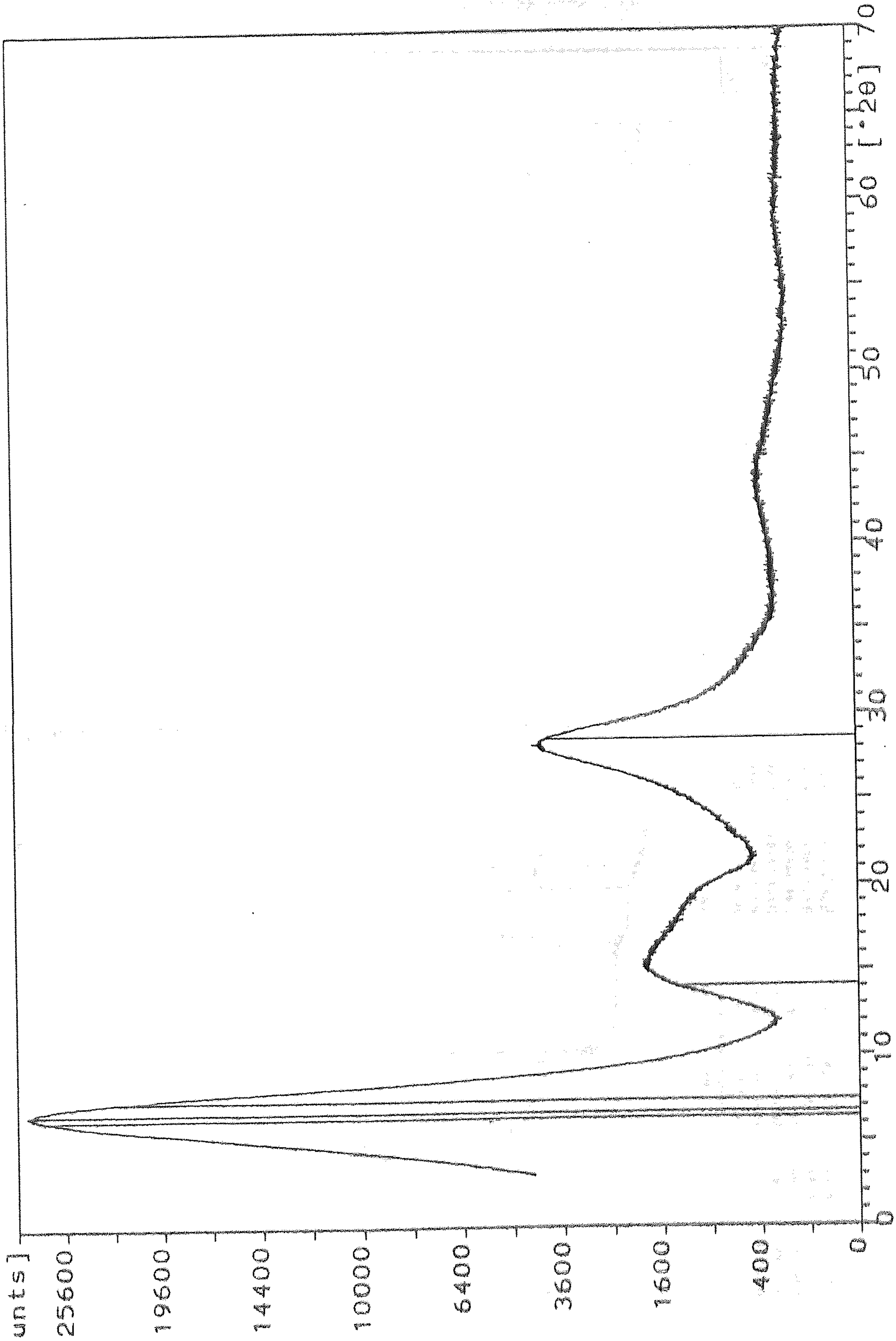
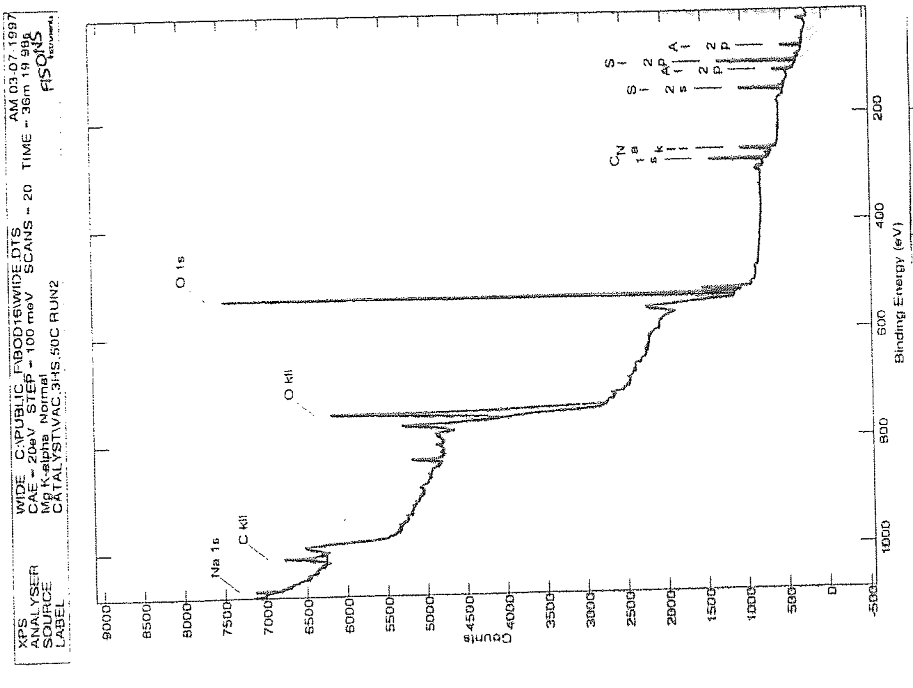
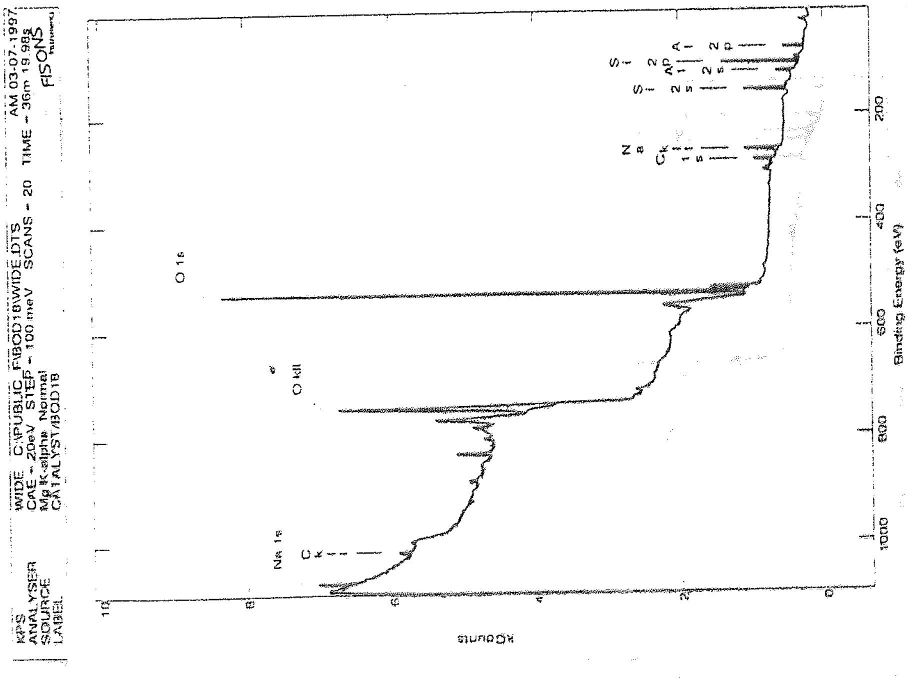


Figure 25 X-Ray Diffractogram of untreated laponite



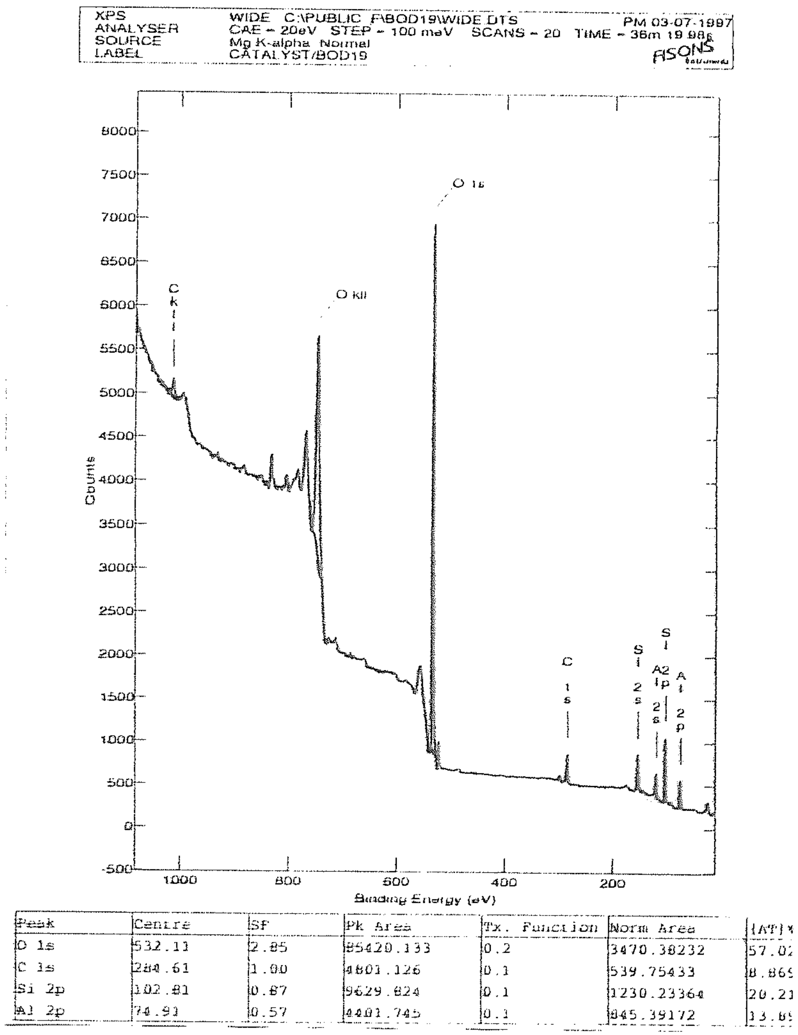
Peak	Centre	SF	Pk Area	Tx. Function	Norm Area	[AT]%
Na 1s	1072.61	7.99	3093.547	0.3	51.47903	0.79
O 1s	532.11	2.85	80746.477	0.2	3280.50610	50.8
C 1s	284.61	1.00	8736.057	0.1	982.12915	15.21
Si 2p	102.91	0.87	11405.780	0.1	1457.12939	22.5
Al 2p	74.71	0.57	3555.242	0.1	682.80237	10.5

Figure 26 X-Ray Photoelectron Spectrum of uncalcined sodium montmorillonite



Peak	Centre	SF	Pk Area	Tx. Function	Norm Area	[AT]%
Na 1s	1072.78	7.99	5726.981	0.3	95.31043	1.444
O 1s	532.08	2.85	92984.672	0.2	3777.69507	57.24
C 1s	284.58	1.00	3511.007	0.1	394.71490	5.98
Si 2p	102.78	0.87	12802.029	0.1	1635.48694	24.7
Al 2p	74.78	0.57	3626.720	0.1	696.53424	10.5

Figure 27 X-Ray Photoelectron Spectrum of sodium montmorillonite, following calcination at 525 °C



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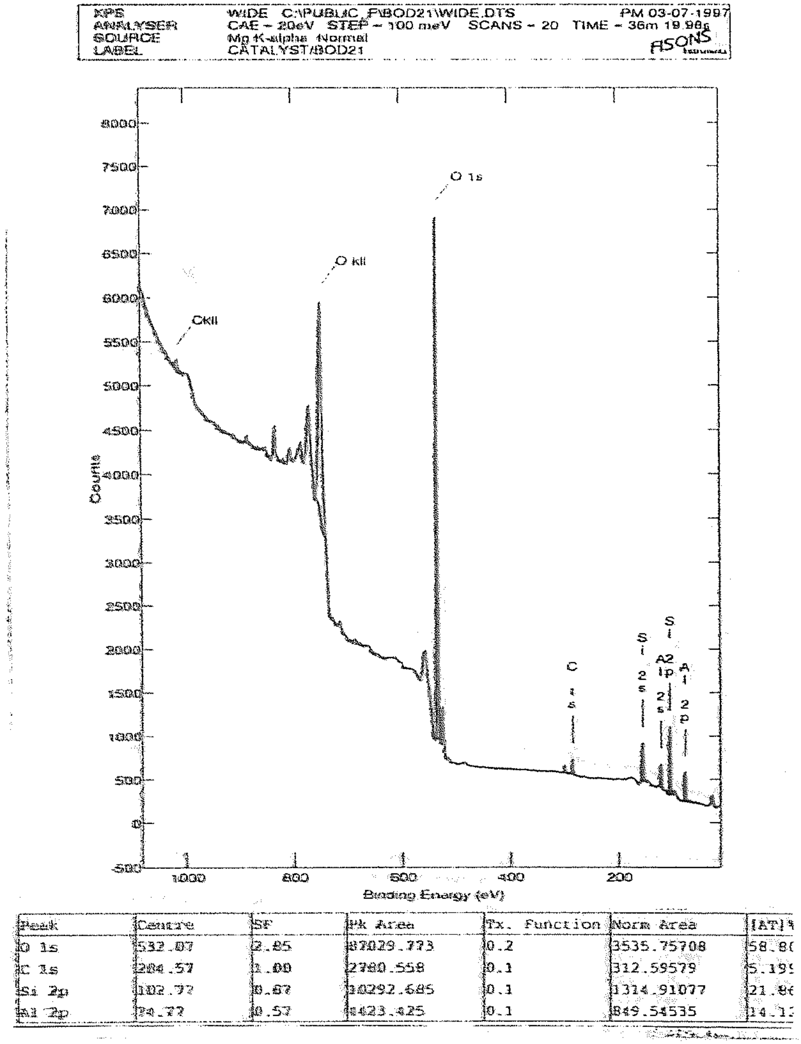
ANALYSER CAE - 20eV STEP - 100 meV SCANS - 20 TIME - 36m 19.98s
SOURCE Mg K-alpha Normal
LABEL CATALYST/BOD19

Peak	Centre	SF	Pk Area	Tx. Function	Norm Area	[AT]%
O 1s	532.11	2.85	85420.133	0.2	3470.38232	57.0
C 1s	284.61	1.00	4801.126	0.1	539.75433	8.86
Si 2p	102.81	0.87	9629.824	0.1	1230.23364	20.21
Al 2p	74.91	0.57	4401.745	0.1	845.39172	13.8

Figure 28 X-Ray Photoelectron Spectrum of uncalcined keggin pillared montmorillonite



XPS WIDE C:\PUBLIC_F\BOD21\WIDE.DTS PM 03-07-1997
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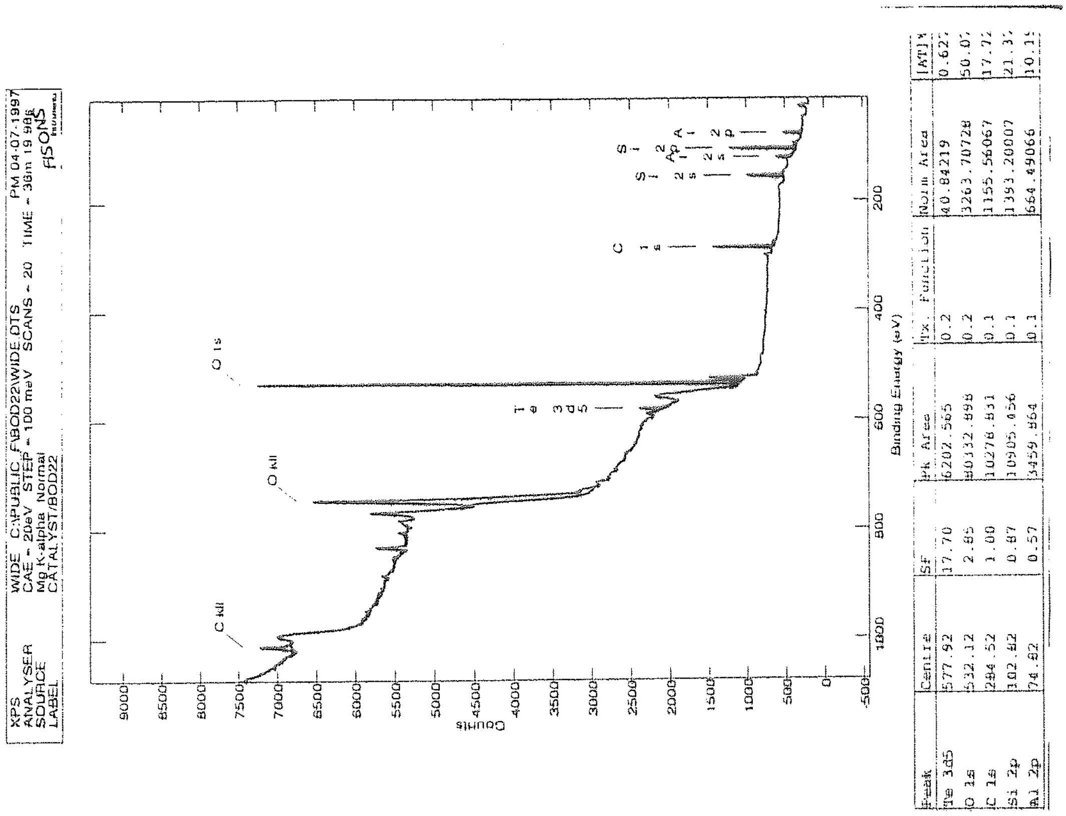
SOURCE Mg K-alpha Normal
LABEL CATALYST/BOD21

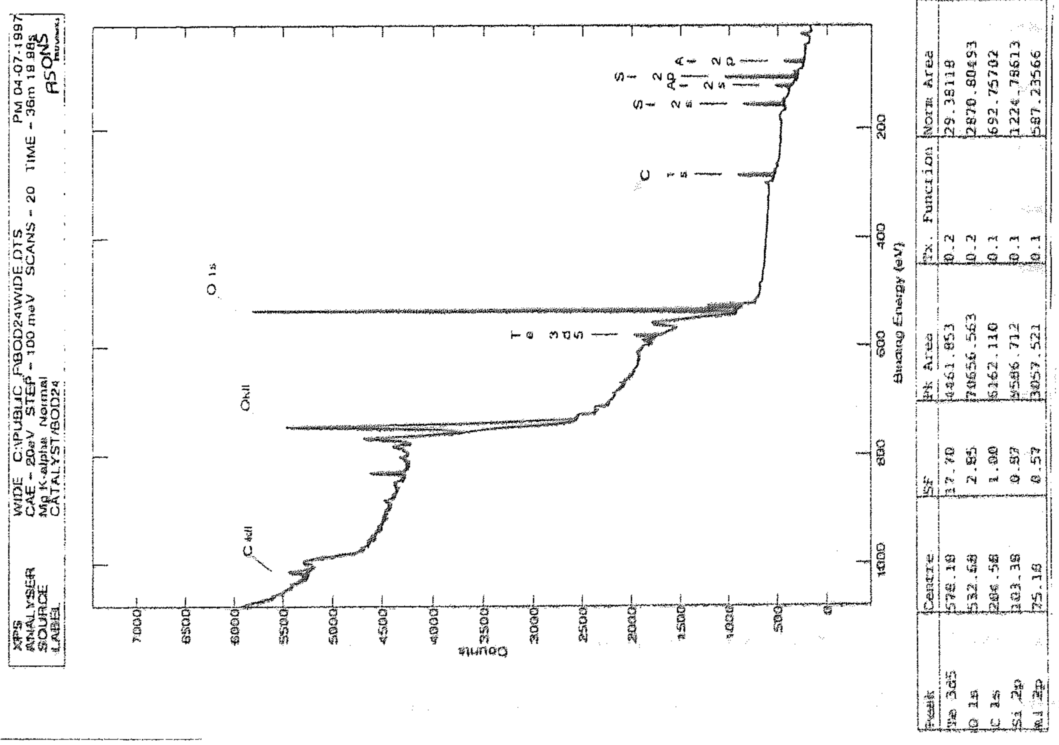
Peak	Centre	SF	Pk Area	Tx. Function	Norm Area	[AT]%
O 1s	532.07	2.85	87029.773	0.2	3535.75708	58.8
C 1s	284.57	1.00	2780.558	0.1	312.59579	5.19
Si 2p	102.77	0.87	10292.685	0.1	1314.91077	21.8
Al 2p	74.77	0.57	4423.425	0.1	849.54535	14.1

Figure 29 X-Ray Photoelectron Spectrum of calcined keggin pillared montmorillonite



Peak	Centre	SF	Pk Area	Tx. Function	Norm Area	[AT]%
Te 3d5	577.92	17.70	6202.565	0.2	40.84219	0.62
O 1s	532.12	2.85	80332.898	0.2	3263.70728	50.0
C 1s	284.52	1.00	10278.831	0.1	1155.56067	17.7
Si 2p	102.82	0.87	10905.456	0.1	1393.20007	21.3
Al 2p	74.82	0.57	3459.864	0.1	664.49066	10.1

Figure 30 X-Ray Photoelectron Spectrum of uncalcined chromium montmorillonite



Peak	Centre	SF	Pk Area	Tx. Function	Norm Area	[AT]%
Te 3d5	578.18	17.70	4461.853	0.2	29.38118	0.54
O 1s	532.68	2.85	70656.563	0.2	2870.80493	53.1
C 1s	284.58	1.00	6162.110	0.1	692.75702	12.8
Si 2p	103.38	0.87	9586.712	0.1	1224.78613	22.6
Al 2p	75.18	0.57	3057.521	0.1	587.23566	10.8

Figure 31 X-Ray Photoelectron Spectrum of calcined chromium montmorillonite

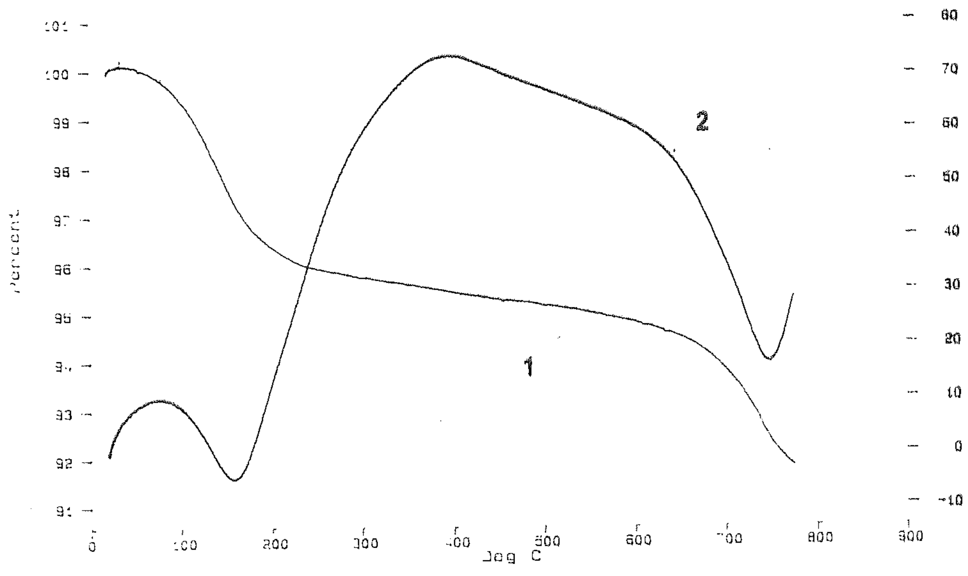


Figure 32 D/TGA Plots for sodium montmorillonite. Shown are the thermal gravimetric (1) and differential thermogram (2) data obtained by heating the sample to 800 °C, in air, at a rate of 20 degrees min^{-1}

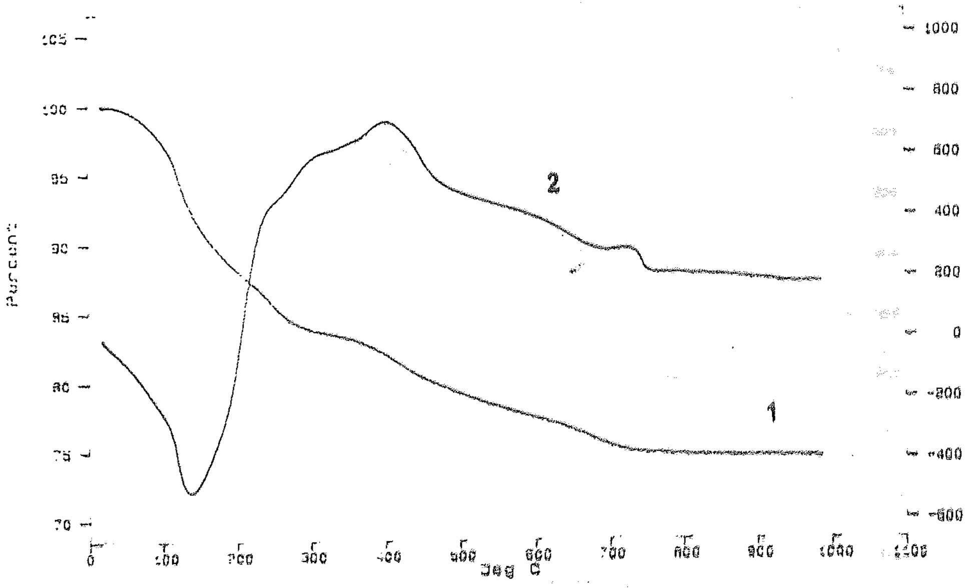


Figure 33 D/TGA Plots for uncalcined chromium montmorillonite. Shown are the thermal gravimetric (1) and differential thermogram (2) data obtained by heating the sample to 1000 °C, in air, at a rate of 20 degrees min^{-1}

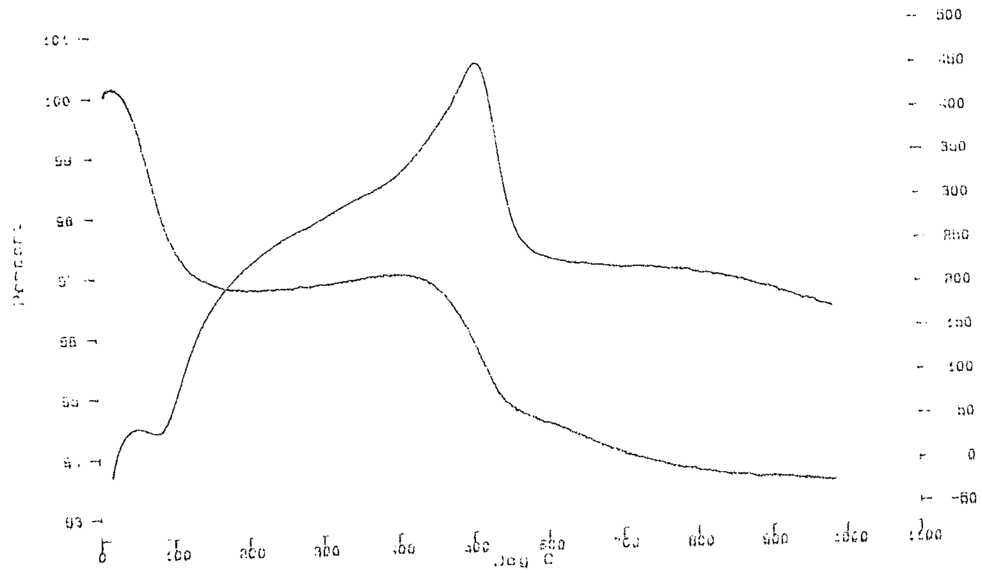


Figure 34 D/TGA Plots for chromium montmorillonite, calcined under argon at 500 °C.

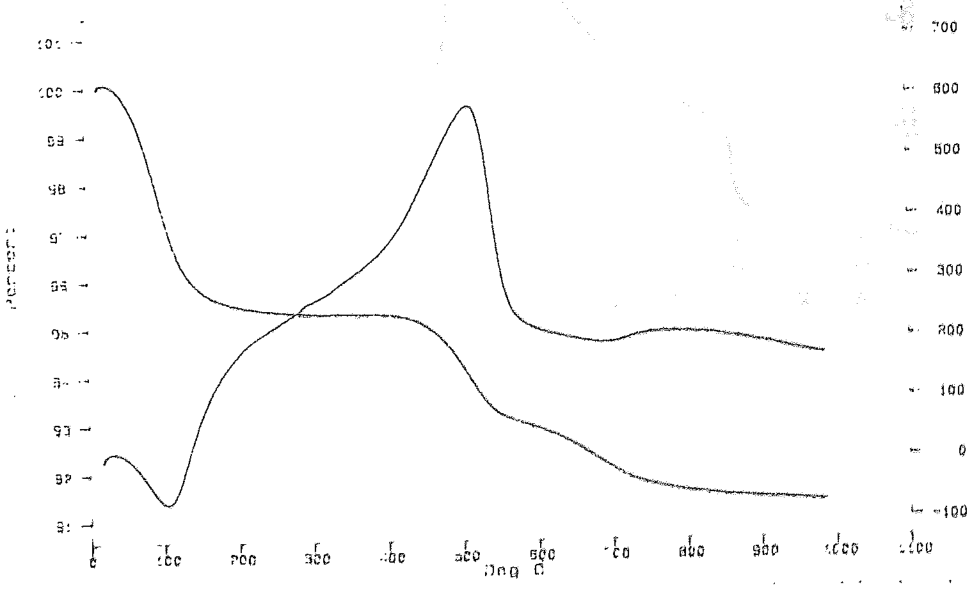


Figure 35 D/TGA Plots for chromium montmorillonite, calcined under argon at 500 °C, then exposed to hydrogen at this temperature

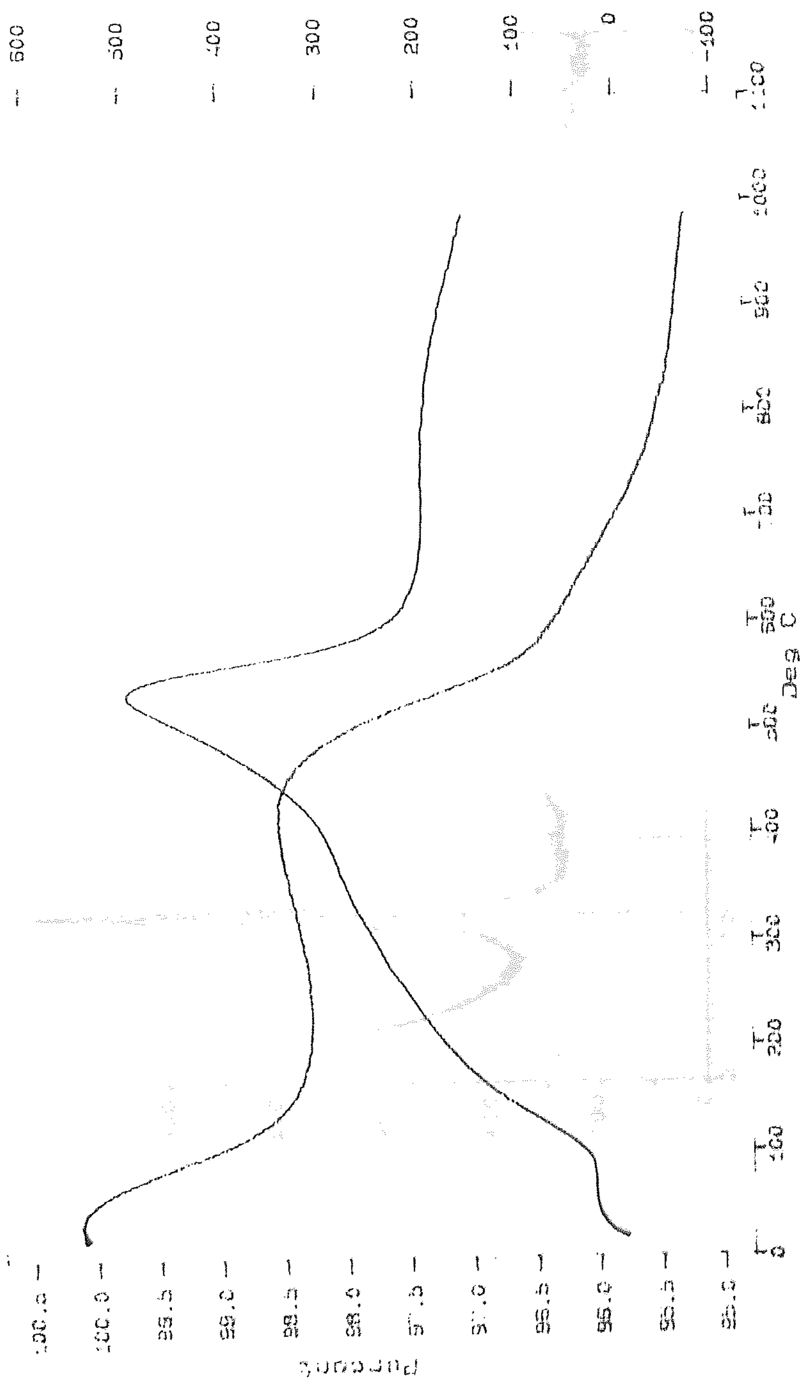


Figure 36 D/TGA Plots for chromium montmorillonite caclined under 10% H_2 in argon at 500 °C

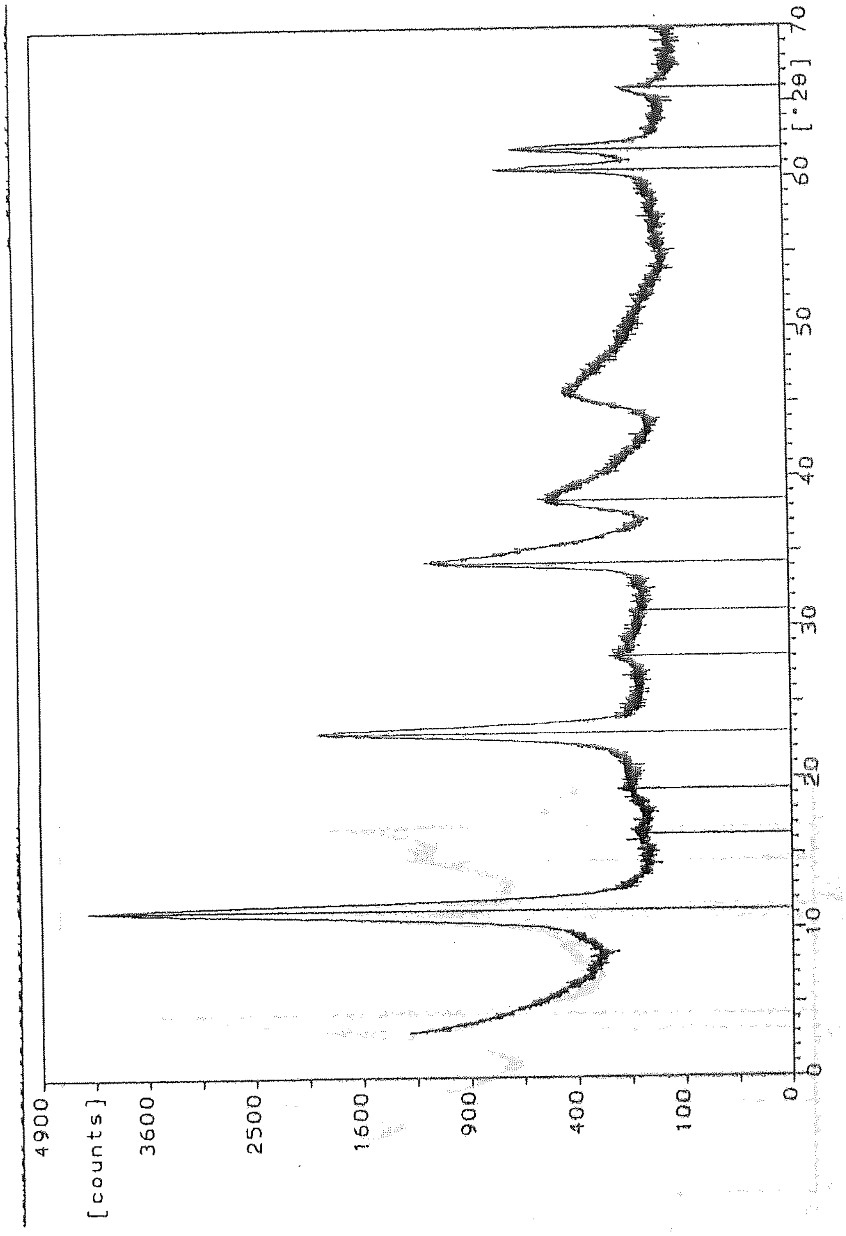


Figure 37 X-Ray Diffractogram of BODLDH1, a carbonate intercalated Al/Mg 2:1 Layered Double Hydroxide

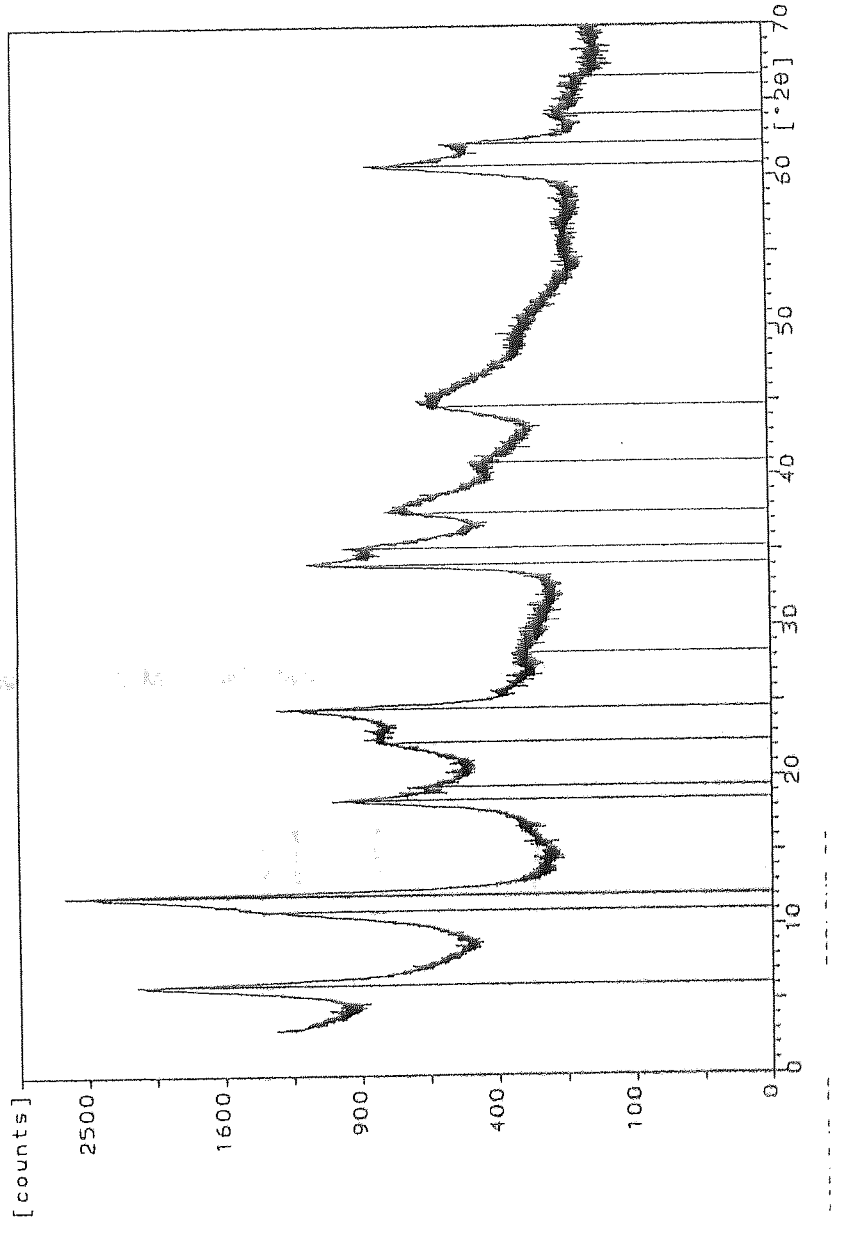


Figure 38 X-Ray Diffractogram of BODLDH2, a terephthalate intercalated Al/Mg 2:1 Layered Double Hydroxide

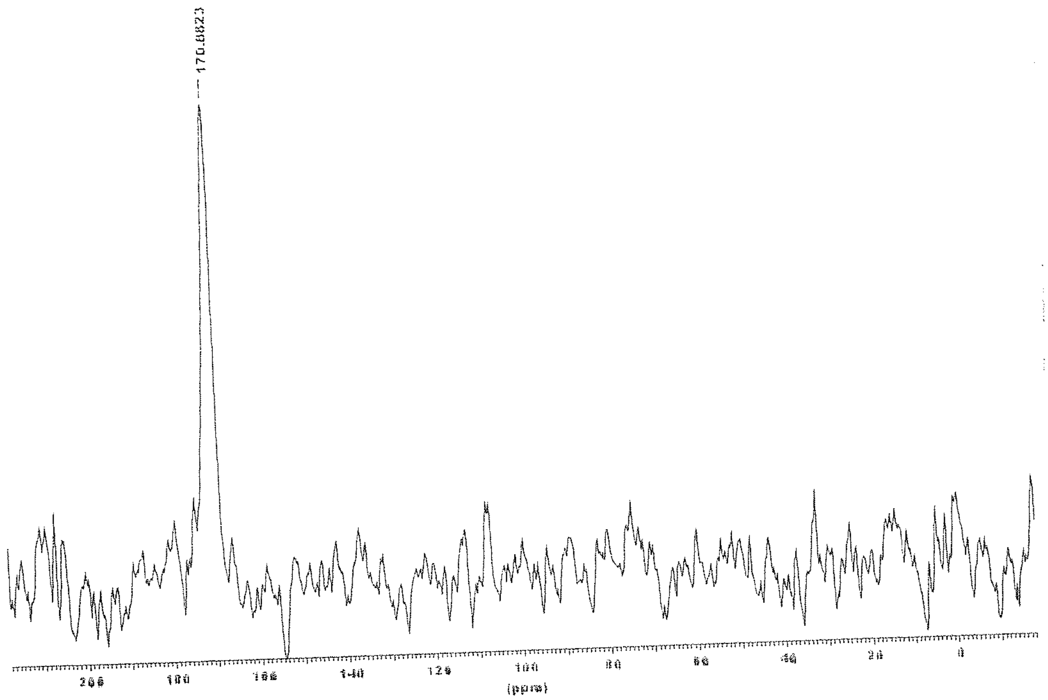


Figure 39 ^{13}C MAS NMR spectrum of BODLDH1

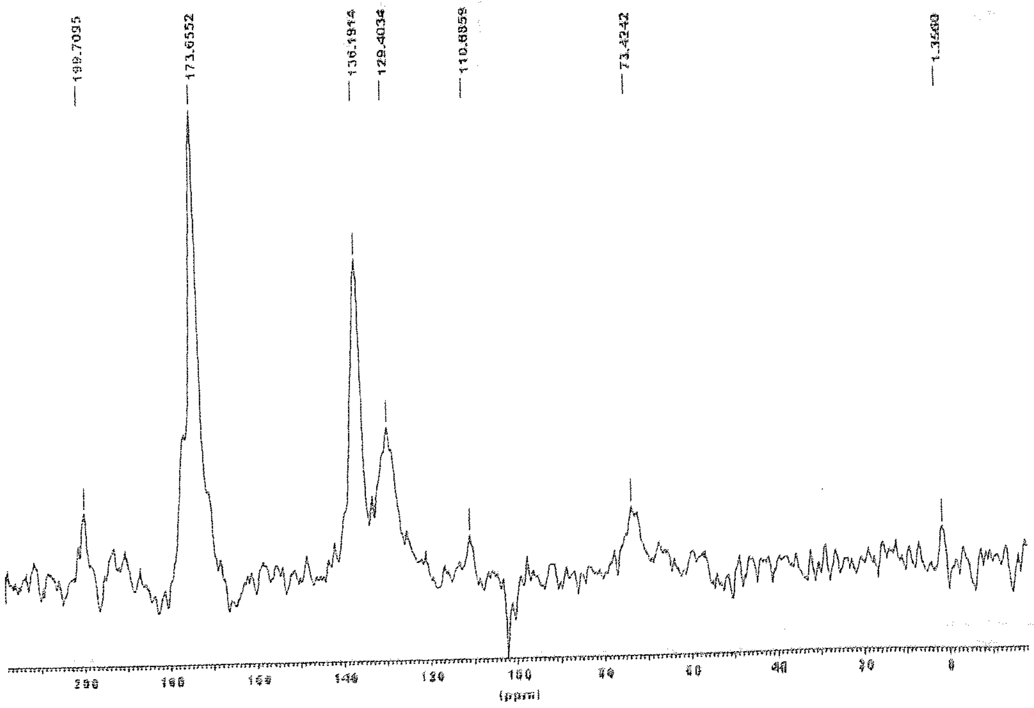


Figure 40 ^{13}C MAS NMR spectrum of BODLDH2

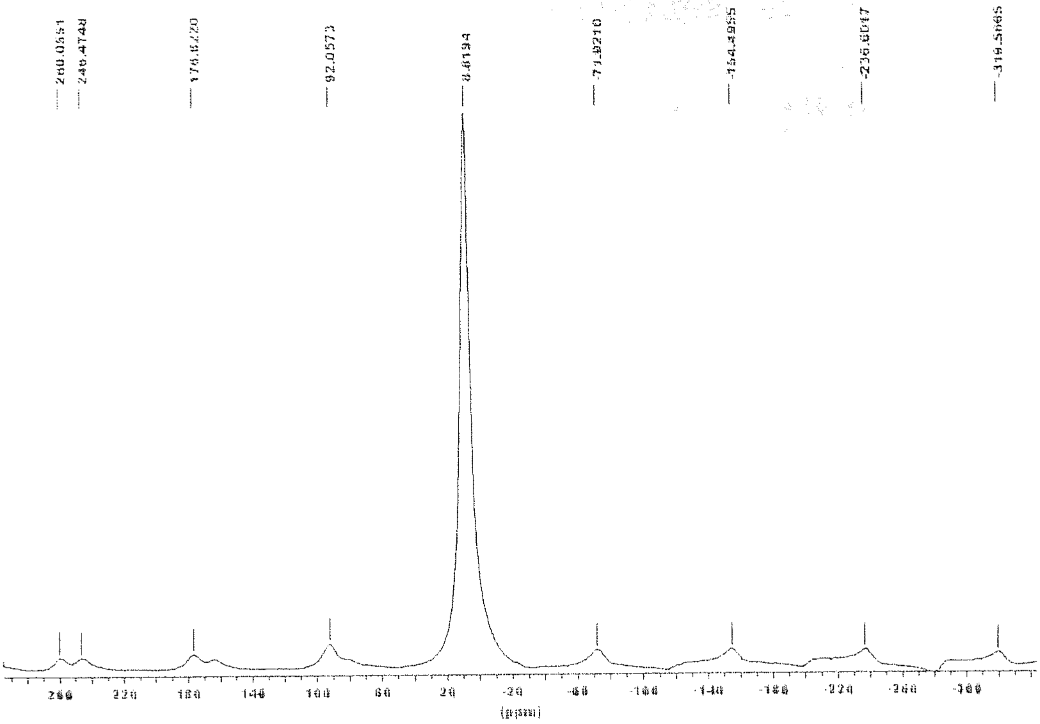


Figure 41 ^{27}Al MAS NMR spectrum of BODLDH1

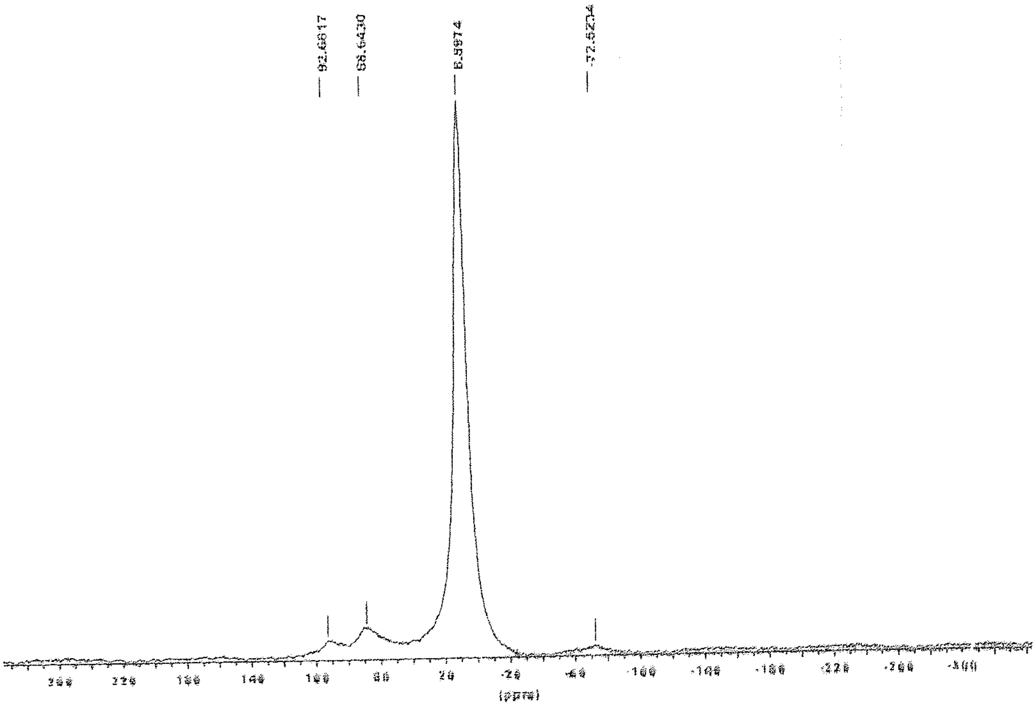


Figure 42 ^{27}Al MAS NMR spectrum of BODLDH2

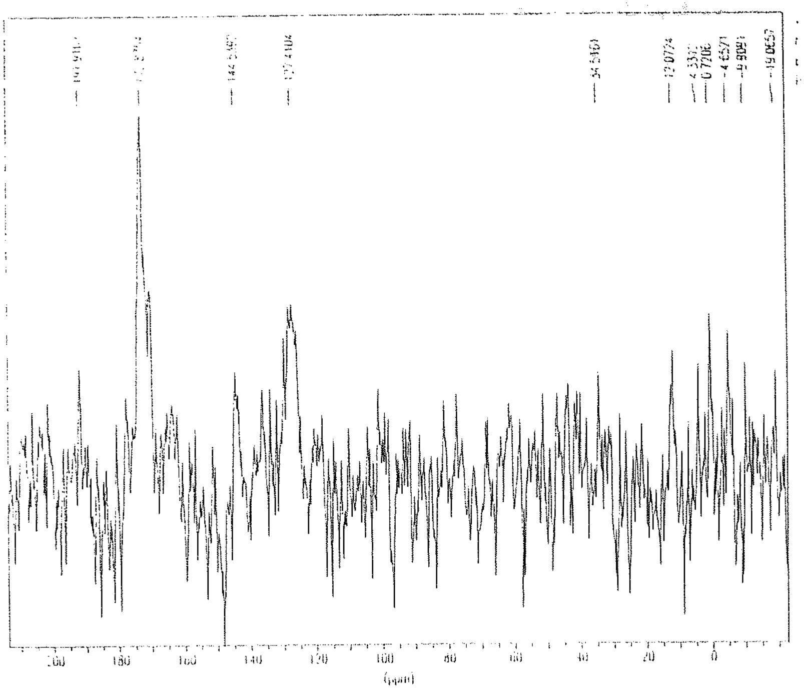


Figure 43 ^{13}C MAS NMR spectrum of LDH1, a terephthalate intercalated Al/Mg 2:1 Layered Double Hydroxide

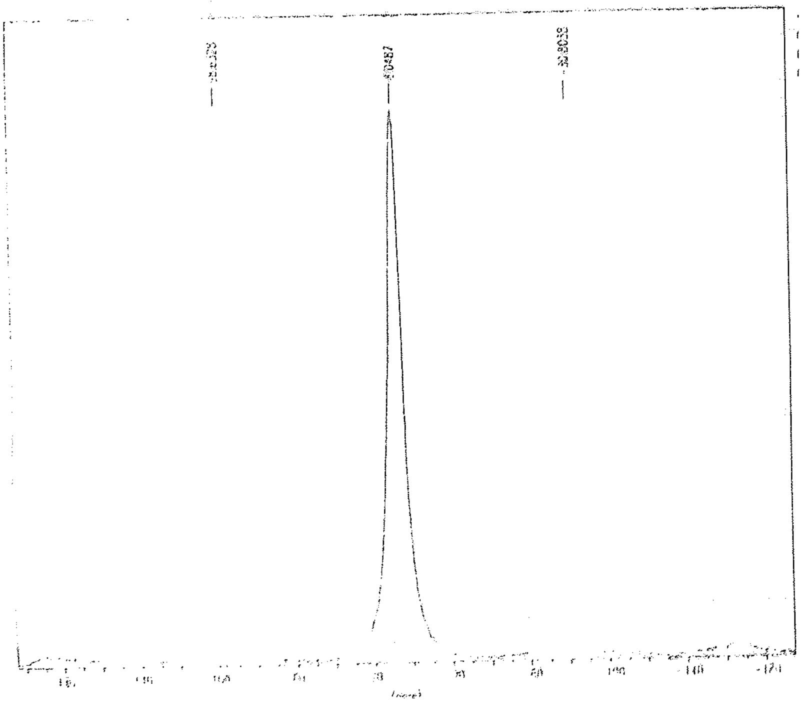


Figure 44 ^{27}Al MAS NMR spectrum of LDH1

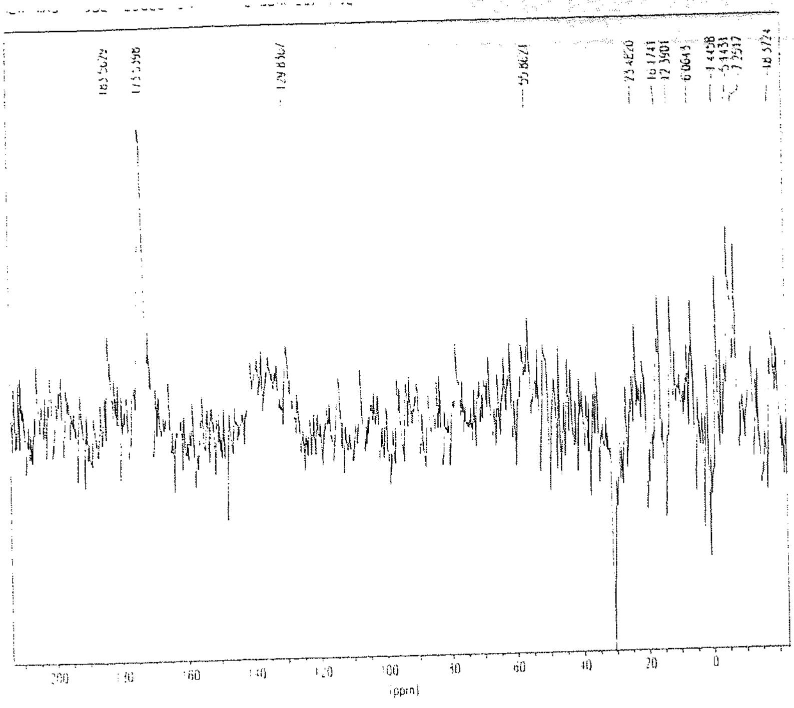


Figure 45 ^{13}C MAS NMR spectrum of LDH2, a decavanadate intercalated Al/Mg 2:1 Layered Double Hydroxide

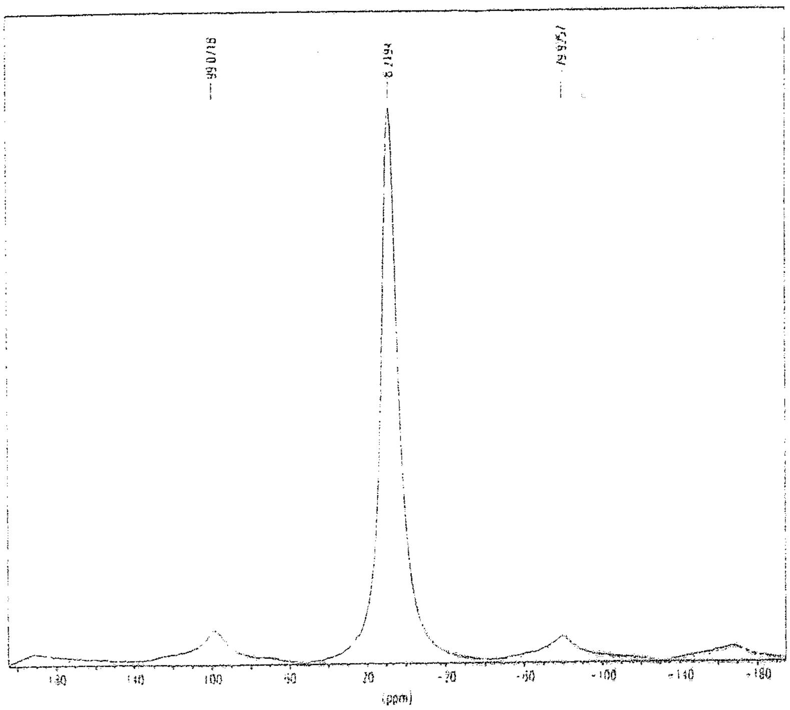


Figure 46 ^{27}Al MAS NMR spectrum of LDH2

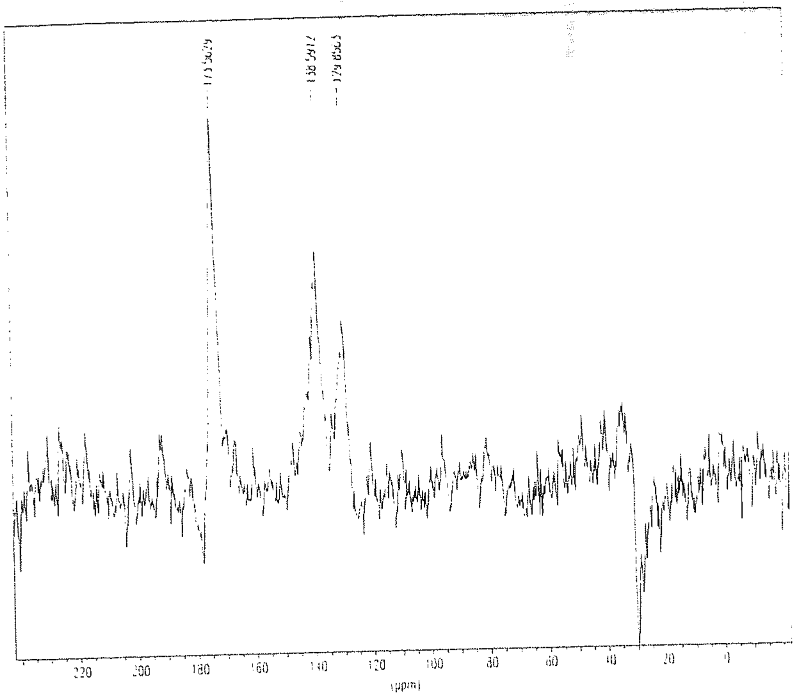


Figure 47 ^{13}C MAS NMR spectrum of LDH4, a decavanadate intercalated Al/Mg 2:1 Layered Double Hydroxide, calcined under H_2

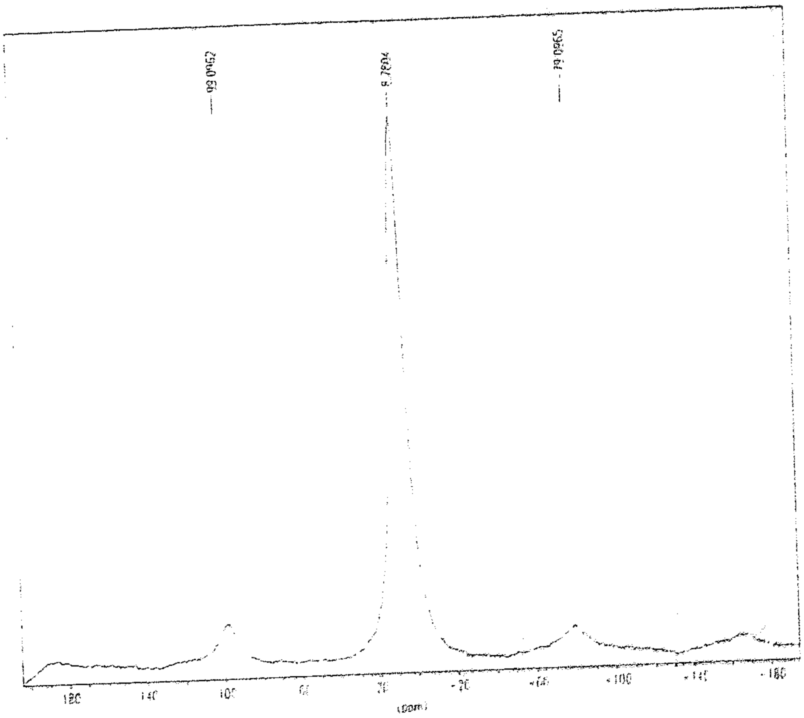


Figure 48 ^{27}Al MAS NMR spectrum of LDH4

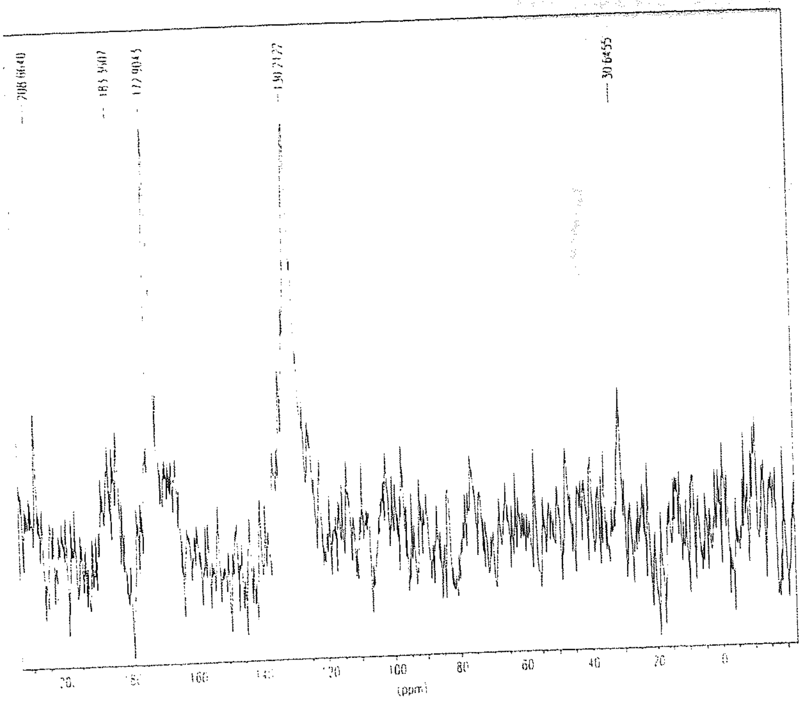


Figure 49 ^{13}C MAS NMR spectrum of LDH3, a heptamolybdate intercalated Al/Mg 2:1 Layered Double Hydroxide

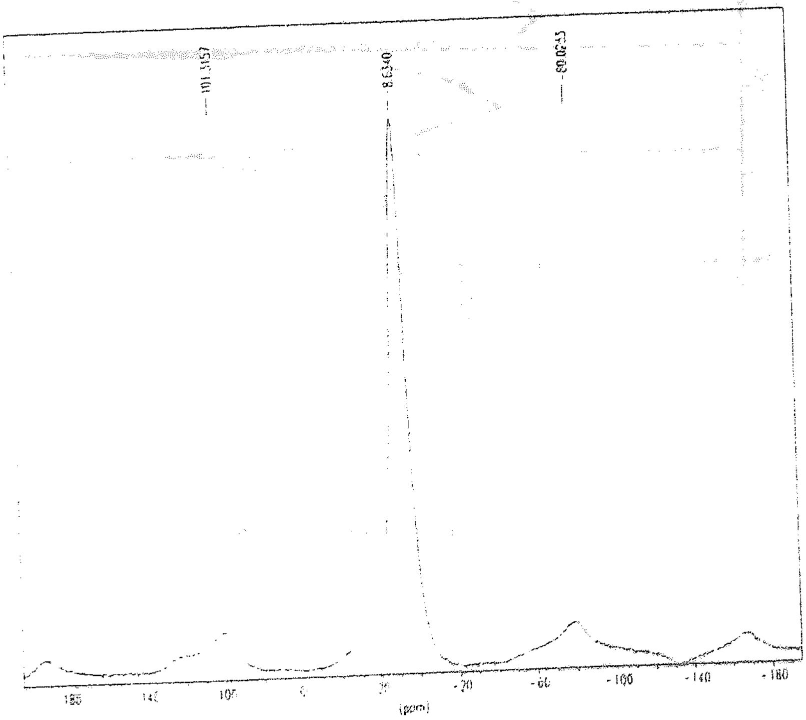


Figure 50 ^{27}Al MAS NMR spectrum of LDH3

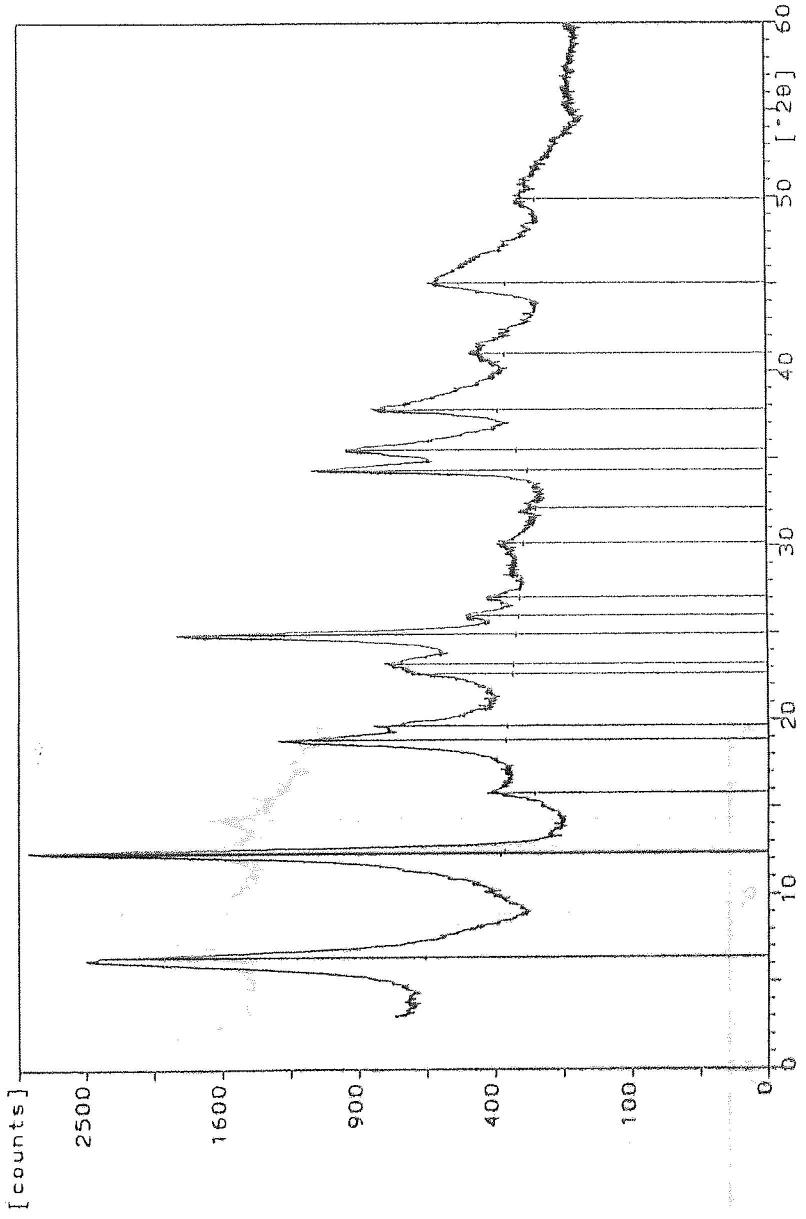


Figure 51 X-Ray Diffractogram of LDH1

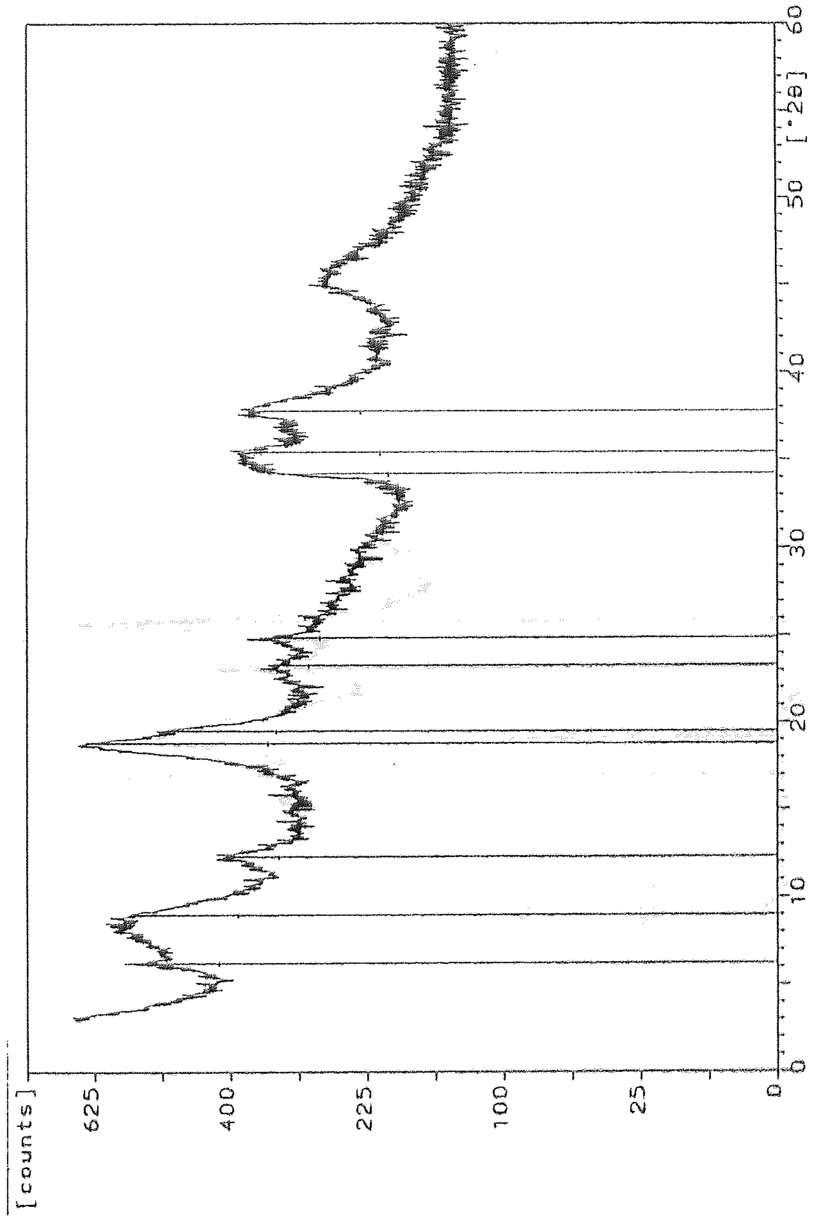


Figure 52 X-Ray Diffractogram of LDH2

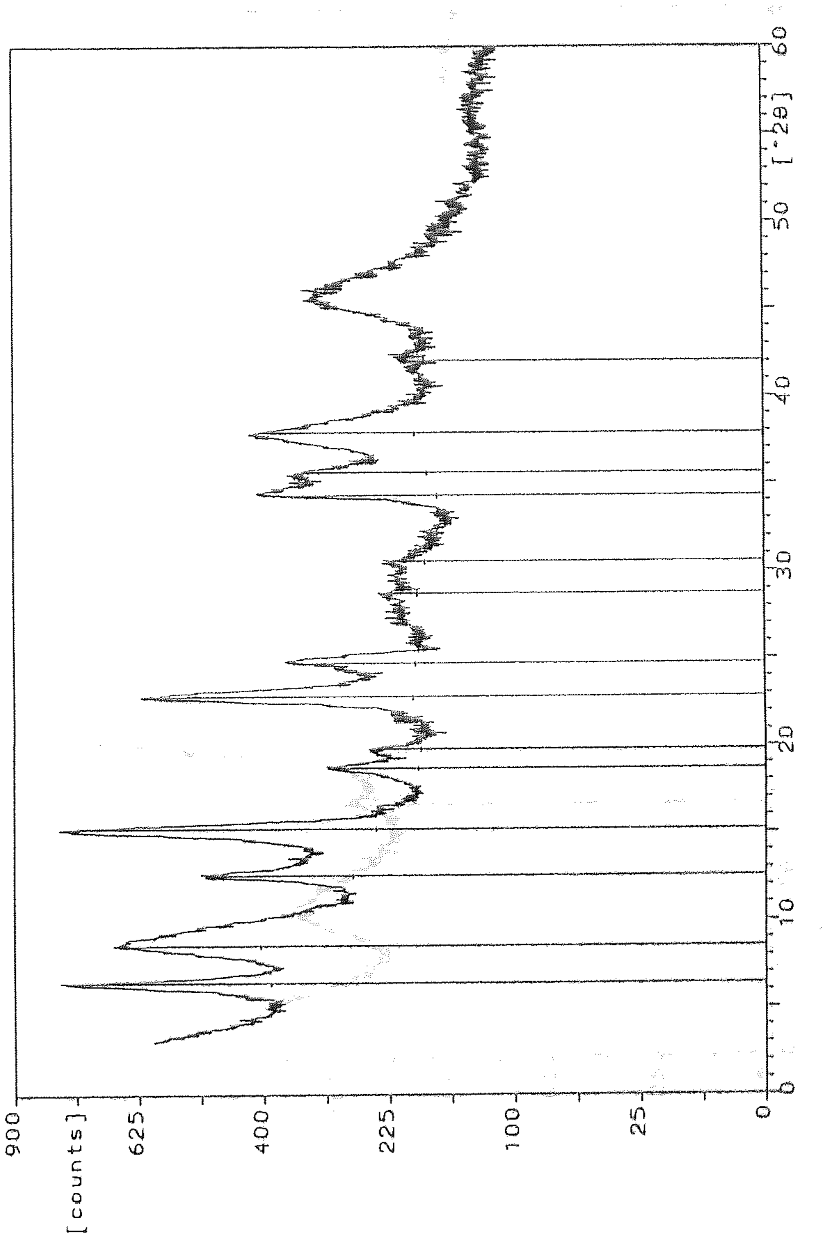


Figure 53 X-Ray Diffractogram of LDH4

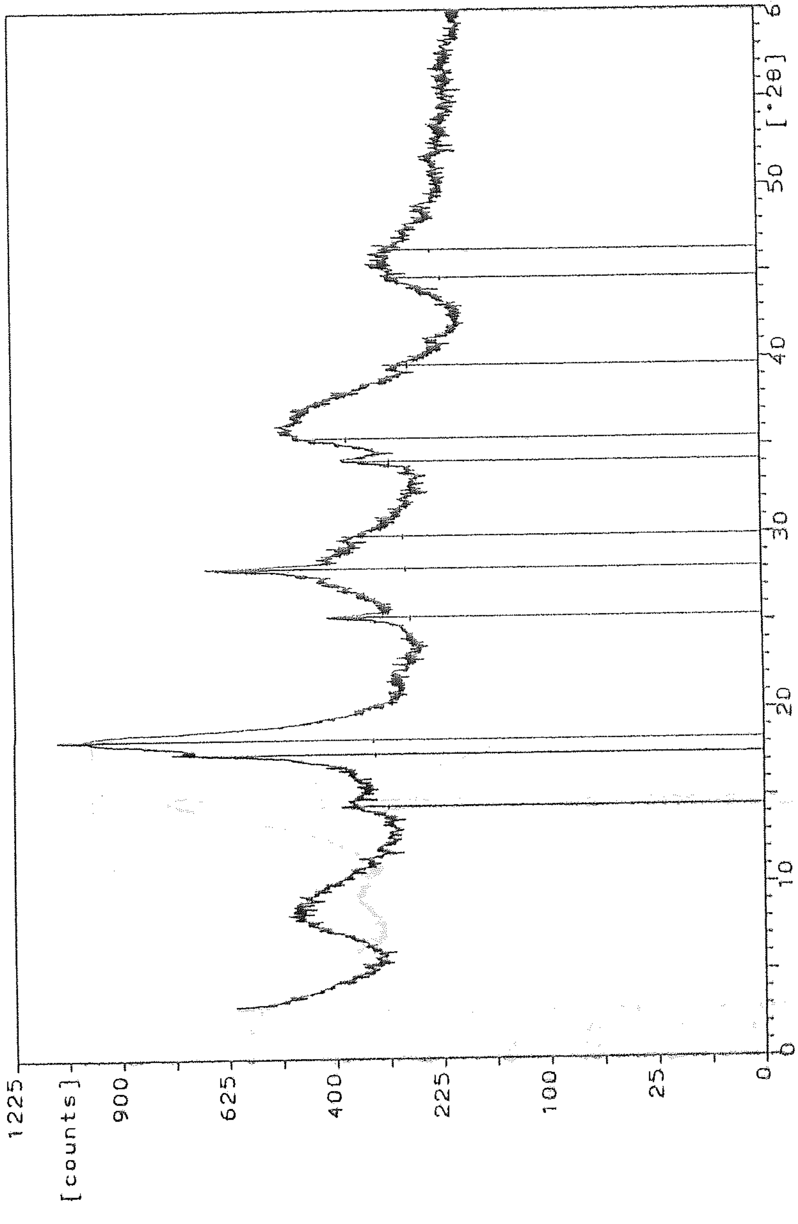


Figure 54 X-Ray Diffractogram of LDH3

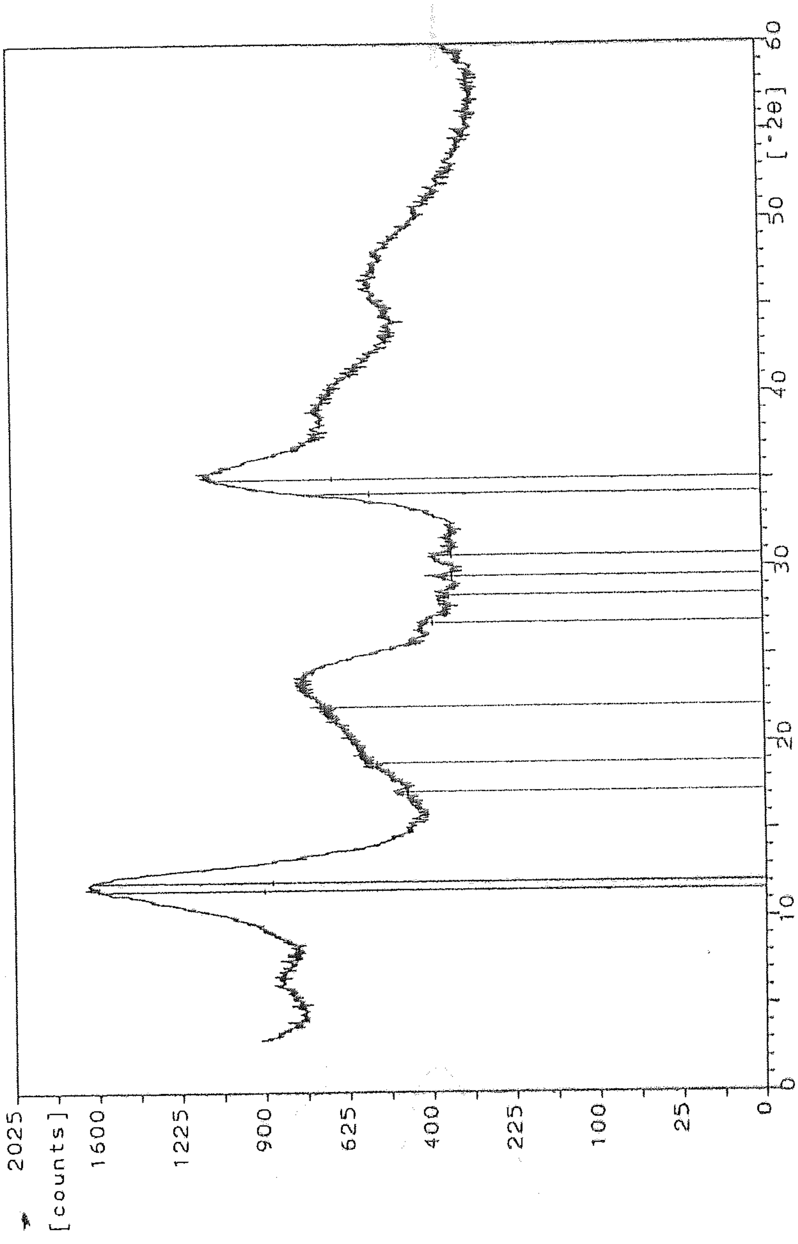


Figure 55 X-Ray Diffractogram of LDH5

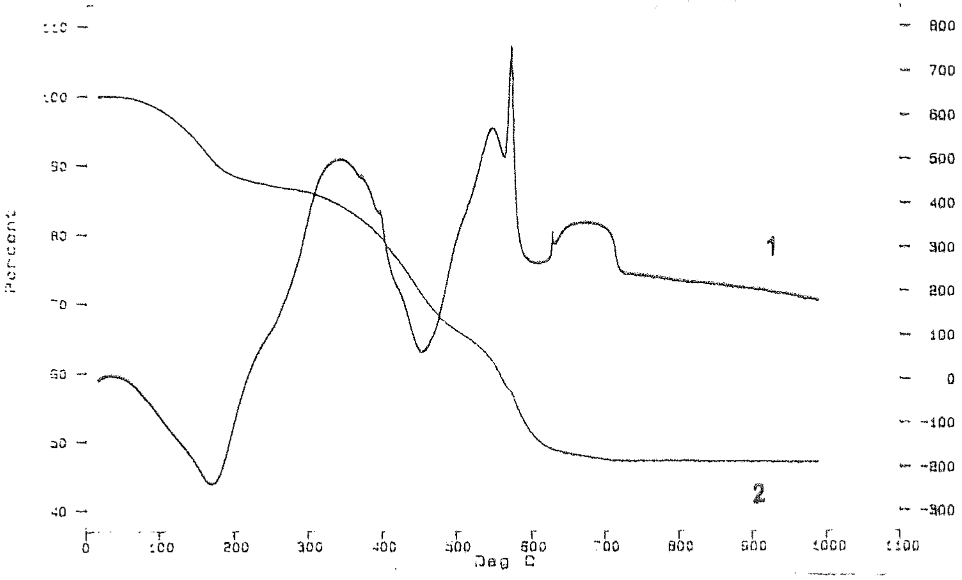


Figure 56 D/TGA Plots for LDH1. Shown are the thermal gravimetric (1) and differential thermogram (2) data obtained by heating the sample to 1000 °C, in air, at a rate of 20 degrees min^{-1}

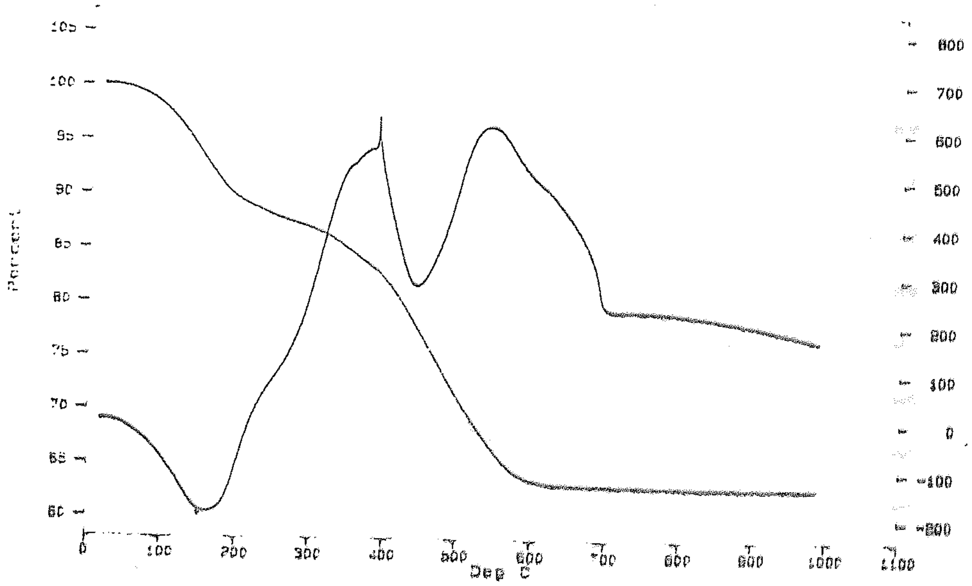


Figure 57 D/TGA Plots for LDH2

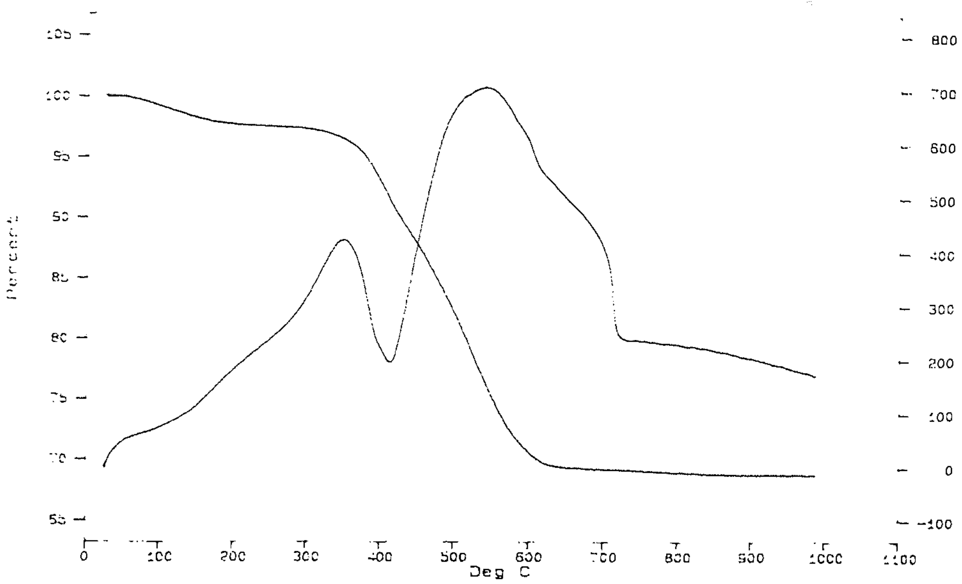


Figure 58 D/TGA Plots for LDH4

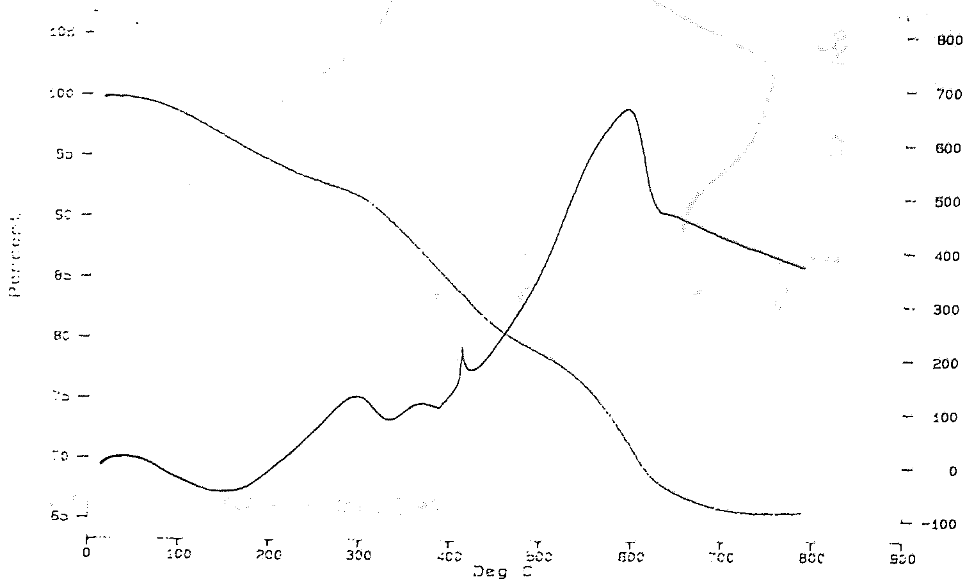


Figure 59 D/TGA Plots for LDH3

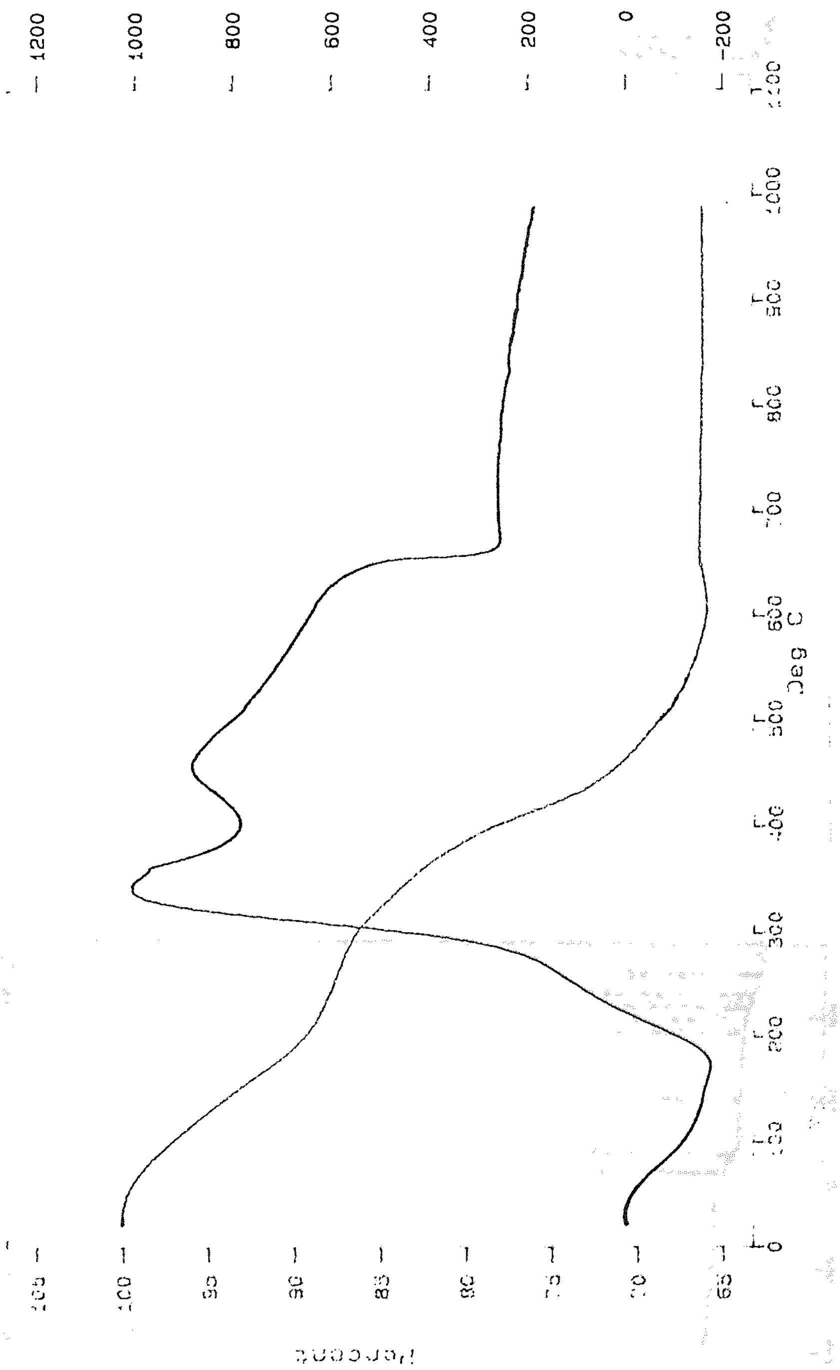
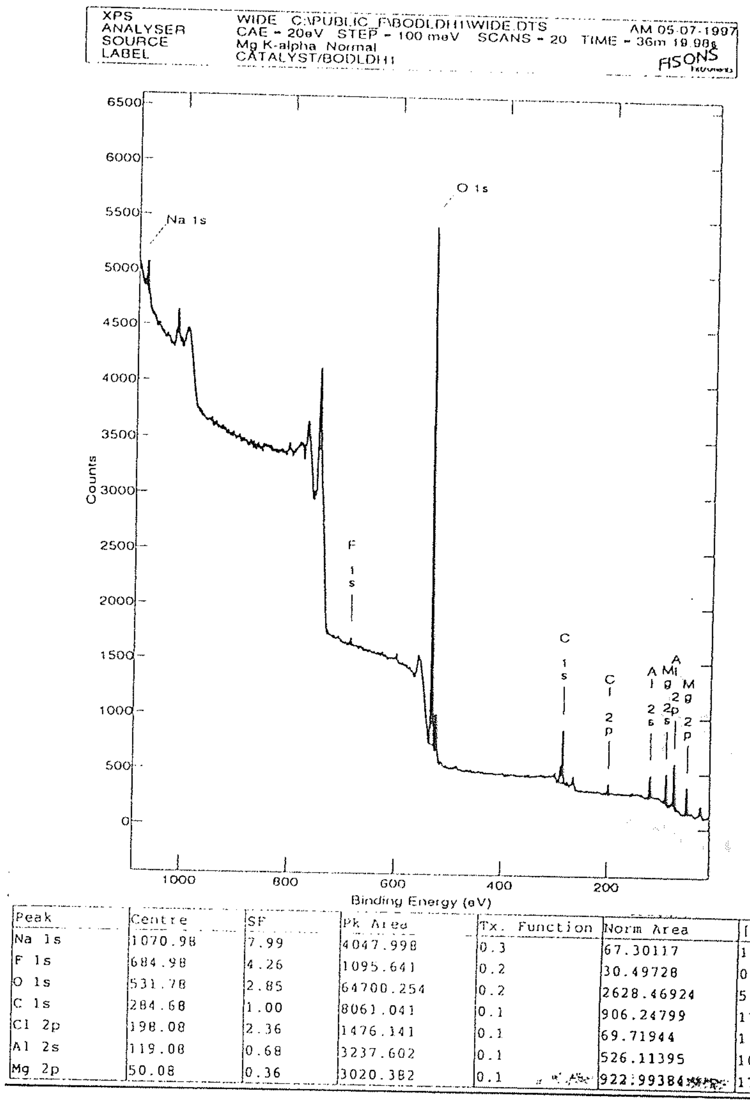
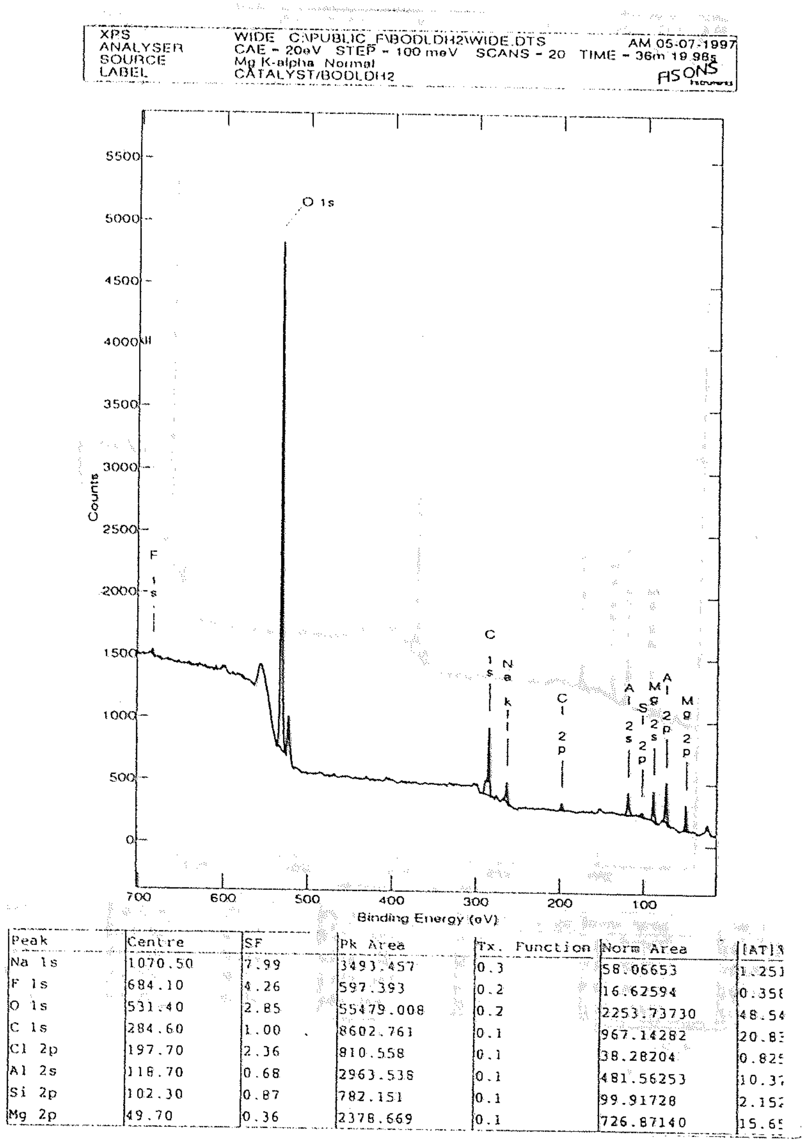


Figure 60 D/TGA Plots for LDH9


XPS WIDE C:\PUBLIC_F\BODLDH1\WIDE.DTS AM 05-07-1997
ANALYSER CAE - 20eV STEP - 100 meV SCANS - 20 TIME - 36m 19.98s
SOURCE Mg K-alpha Normal
LABEL CATALYST/BODLDH1

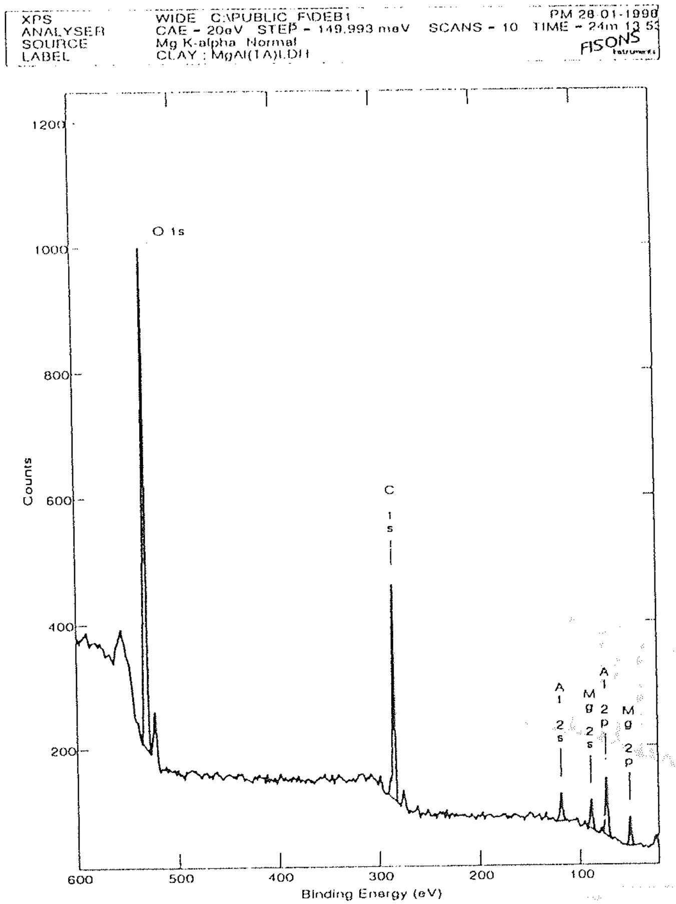
Peak	Centre	SF	Pk Area	Tx. Function	Norm Area	[AT]
Na 1s	1070.98	7.99	4047.998	0.3	67.30117	1.30
F 1s	684.98	4.26	1095.641	0.2	30.49728	0.59
O 1s	531.78	2.85	64700.254	0.2	2628.46924	51.0
C 1s	284.68	1.00	8061.041	0.1	906.24799	17.5
Cl 2p	198.08	2.36	1476.141	0.1	69.71944	1.35
Al 2s	119.08	0.68	3237.602	0.1	526.11395	10.2
Mg 2p	50.08	0.36	3020.382	0.1	922.99384	17.9

Figure 61 X-Ray Photoelectron Spectrum of BODLDH1


XPS WIDE C:\PUBLIC_F\BODLDH2\WIDE.DTS AM 05-07-1997
ANALYSER CAE - 20eV STEP - 100 meV SCANS - 20 TIME - 36m 19.98s
SOURCE Mg K-alpha Normal
LABEL CATALYST/BODLDH2

Peak	Centre	SF	Pk Area	Tx. Function	Norm Area	[AT]
Na 1s	1070.50	7.99	3493.457	0.3	58.06653	1.25
F 1s	684.10	4.26	597.393	0.2	16.62594	0.35
O 1s	531.40	2.85	55479.008	0.2	2253.73730	48.5
C 1s	284.60	1.00	8602.761	0.1	967.14282	20.8
Cl 2p	197.70	2.36	810.558	0.1	38.28204	0.82
Al 2s	118.70	0.68	2963.538	0.1	481.56253	10.3
Si 2p	102.30	0.87	782.151	0.1	99.91728	2.15
Mg 2p	49.70	0.36	2378.669	0.1	726.87140	15.6

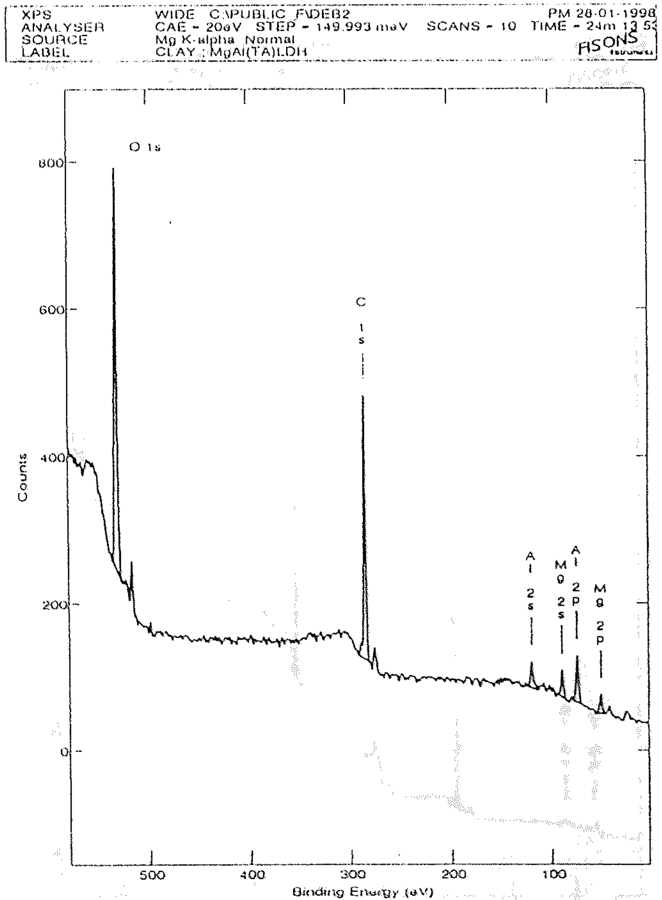
Figure 62 X-Ray Photoelectron Spectrum of BODLDH2


XPS ANALYSER SOURCE LABEL
WIDE C:\PUBLIC_F\DEB1
CAE - 20eV STEP - 149.993 meV SCANS - 10
Mg K-alpha Normal
CLAY : MgAl(TA)LDH
PM 28-01-1998 TIME - 24m 13 53

Quantification Table for Experiment C:\PUBLIC_F\DEB1

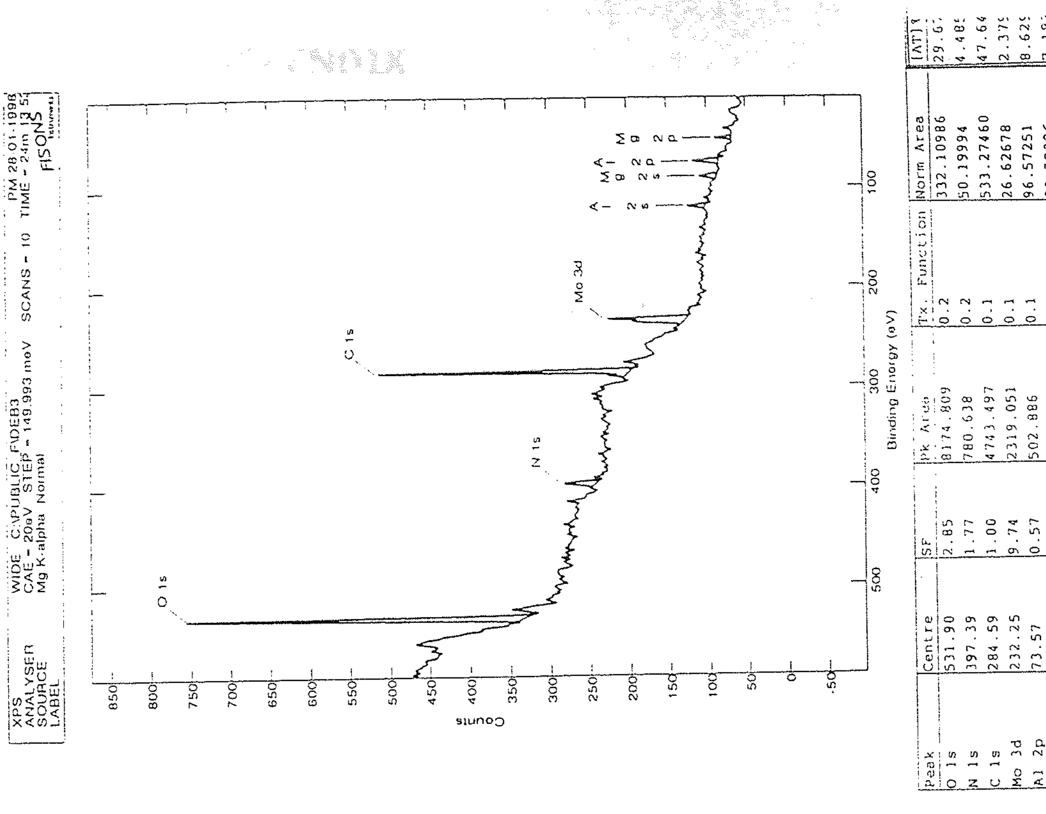
Peak	Centre	SF	Pk Area	Tx. Function	Norm Area	[AT]%
O 1s	532.09	2.85	12381.391	0.2	503.02036	32.7
C 1s	284.59	1.00	4801.454	0.1	539.79022	35.1
Al 2p	73.55	0.57	1483.720	0.1	284.92789	18.5
Mg 2p	50.15	0.36	675.721	0.1	206.49390	13.4

Figure 63 X-Ray Photoelectron Spectrum of LDH1


XPS ANALYSER SOURCE LABEL
WIDE C:\PUBLIC_F\DEB2
CAE - 20eV STEP - 149.993 meV SCANS - 10
Mg K-alpha Normal
CLAY : MgAl(TA)LDH
PM 28-01-1998 TIME - 24m 13 53

Peak	Centre	SF	Pk Area	Tx. Function	Norm Area	[AT]%
O 1s	532.04	2.85	8713.491	0.2	354.00159	28.7
C 1s	284.54	1.00	4936.265	0.1	554.94299	45.01
Al 2p	73.50	0.57	1037.333	0.1	199.20459	16.1
Mg 2p	49.95	0.36	408.164	0.1	124.72887	10.1

Figure 64 X-Ray Photoelectron Spectrum of LDH2



XPS ANALYSER SOURCE LABEL

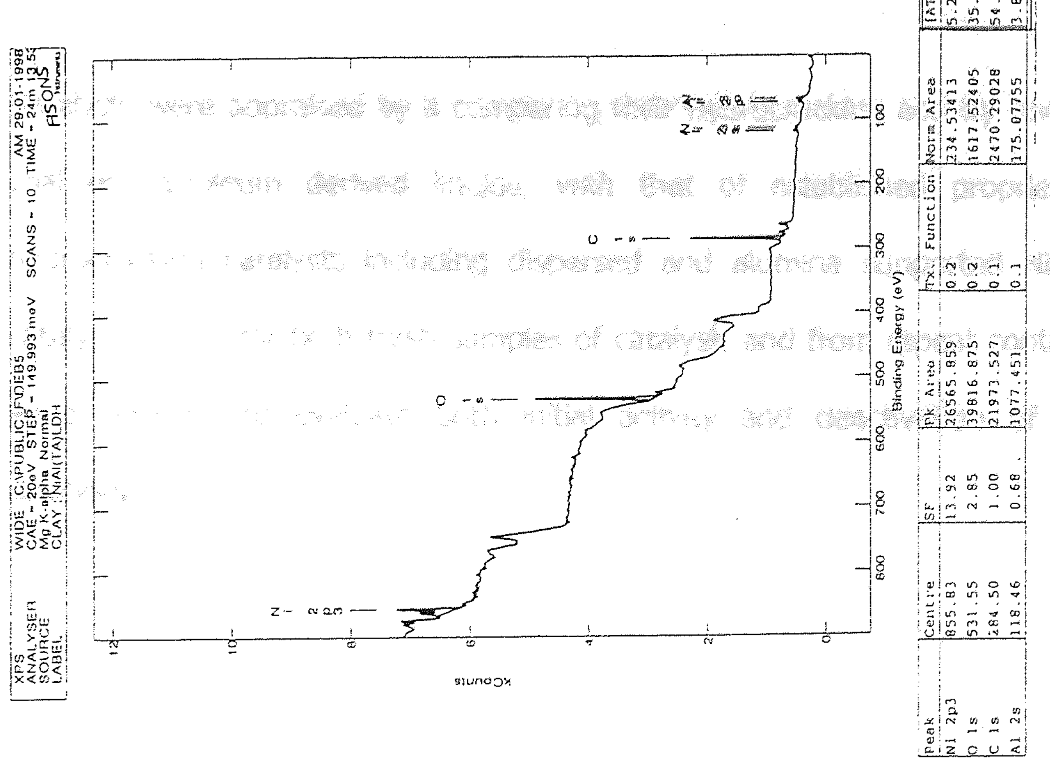
WIDE C:\PUBLIC_FDEB3 SCANS - 10 PM 28-01-1998

CAE - 20eV STEP - 149.993 meV TIME - 24m 13 5

Mg K-alpha Normal

Peak	Centre	SF	Pk Area	Tx. Function	Norm Area	[AT]
O 1s	531.90	2.85	8174.809	0.2	332.10986	29.6
N 1s	397.39	1.77	780.638	0.2	50.19994	4.48
C 1s	284.59	1.00	4743.497	0.1	533.27460	47.64
Mo 3d	232.25	9.74	2319.051	0.1	26.62678	2.37
Al 2p	73.57	0.57	502.886	0.1	96.57251	8.62
Mg 2p	50.02	0.36	263.078	0.1	80.39326	7.18

Figure 65 X-Ray Photoelectron Spectrum of LDH3



XPS ANALYSER SOURCE LABEL

WIDE C:\PUBLIC_FDEB5 SCANS - 10 AM 29-01-1998

CAE - 20eV STEP - 149.993 meV TIME - 24m 13 5

Mg K-alpha Normal

CLAY : NiAl(TA)LDH

Peak	Centre	SF	Pk Area	Tx. Function	Norm Area	[AT]
Ni 2p3	855.83	13.92	26565.959	0.2	234.53413	5.21
O 1s	531.55	2.85	39816.875	0.2	1617.52405	35.9
C 1s	284.50	1.00	21973.527	0.1	2470.29028	54.9
Al 2s	118.46	0.68	1077.451	0.1	175.07755	3.89

Figure 66 X-Ray Photoelectron Spectrum of LDH5

10. APPENDIX

10.1 CATALYST APPRAISAL BY WORKERS AT IMPERIAL COLLEGE

10.1.1 METHODS OF ANALYSIS

Catalysts prepared during the course of this thesis were initially screened for activity toward coal derived liquids by workers at Imperial College, as part of a collaboration funded by BCURA and the DTI. This was later extended to include petroleum derived crudes. Work conducted at ICSTM is the subject of a separate thesis, but a brief overview is presented here for clarity.

Catalysts were appraised by a comparing their hydrocracking activity toward coal or petroleum derived liquids, with that of established proprietary hydrocracking catalysts including dispersed and alumina supported Ni/Mo catalysts. Data for both fresh samples of catalyst, and from repeat contacts were obtained to evaluate both initial activity and deactivation of the catalysts.

The product streams were analysed in a number of ways including, but not restricted to ,

- Synchronous UV-F spectroscopy
- Size exclusion chromatography (SEC), employing an Ultra Violet Fluorescence (UV-F) detector able to detect intensity at various fixed wavelengths.
- Boiling point distribution
- Conversion of high (>450 °C) to low (<450 °C) boiling material.

10.1.1.1 Synchronous UV-F Spectroscopy

The intensity of fluorescence over a range of wavelengths are simultaneously measured. These emissions result from the excitation of polynuclear aromatic ring systems, where wavelength is related to size of the polynuclear aromatic ring system (*i.e.* the extent of conjugation) and intensity reflects the concentration of these structures. Comparison of area normalised spectra obtained from the crude extract and the hydrocracked product reveal changes in the overall composition of the material.

A hyposochromic shift in the overall profile (a reduction of intensity at longer wavelengths, with a complimentary increase at the short wavelength end of the envelope) indicates a general trend toward smaller structures. This results from a reduction in the concentration of larger polynuclear aromatic ring systems, heterocyclic structures, heteroatom elimination and dealkylation. A bathochromic shift is indicative of competing polymerisation reactions prevailing and is symptomatic of reduced catalyst activity.

10.1.1.2 Size Exclusion Chromatography

SEC chromatograms were obtained, using a UV-F spectrophotometer as a detector. Large fragments elute earliest, with the exclusion of very large fragments from the substrate pores resulting in very rapid elution without resolution (the excluded peak). Smaller fragments elute with progressively longer retention times, with very small molecular fragments being retained on the matrix far longer than the rest of the sample, again with loss of resolution (the retained peak).

The spectral envelope reveals variation of intensity of emission with elution time measured at a fixed wavelength and is area normalised. As such it reflects the distribution of molecular mass within the sample as a whole. Up to five wavelengths can be detected simultaneously. Again, comparisons between the chromatograms obtained for liquefaction extracts and hydrocracked products reveal structural changes occurring as a result of the hydrocracking process. Increases in the intensity of the retained peak and toward longer retention time indicate an overall reduction in molecular mass.

10.1.1.3 Boiling Point

Measuring the proportion of material boiling above 450 °C that is converted into lighter materials by the hydrocracking process, expressed as a percentage, allows a quantitative comparison between different catalysts.

10.1.2 COMPARATIVE CATALYST APPRAISAL

The following is composed of extracts from contract reports submitted by the ICSTM group during the course of the BCURA contract.

Extract from periodic report four

Hydrocracking experiments have also been conducted with catalysts provided by Aston University. The effect of catalyst on hydrocracking conversion...for 10 minute reaction time [were compared]. Comparison between the hydrocracking conversions from runs using different catalysts showed that pillared clay catalysts exhibit higher activity than the supported or dispersed catalysts. The highest activity, given by the highest conversion [of the material boiling above 450 °C to material boiling below 450 °C] is shown by the tin pillared catalyst.

Extracts from report five

Coal extract hydrocracking

[A number of catalysts were supplied to ICSTM for hydrocracking experiments, including alumina and chromia pillared montmorillonites calcined at various temperatures, uncalcined tin laponite and an uncalcined layered double hydroxide, composed of Ni/Al layers and an organic intercalate (LDH5)]

[SEC data recorded at 350 and 450 nm, obtained for the feed and its hydrocracking products prepared in the presence of catalysts were used to assess the activity of the catalysts.]

"For all catalysts the excluded peak in the hydrocracking products is much reduced compared to the feed whilst the retained peak is much higher. Both Chromium-Montmorillonite catalysts calcined at 500 and 600 °C, showed the lowest intensity in the excluded peak, whereas the tin Pillared showed the highest intensity in the retained peak. Compared to all the catalysts, the tin Pillared and the Cr-Montmorillonites exhibit the highest activity."

[UV-F spectra obtained from the same system were also analysed.]

"Once again the same trend is observed for all the catalysts with their spectra showing an *(sic)* hypsochromic shift compare to the feed *(sic)*. Not many differences were observed between all the catalysts, except for the Cr-Montmorillonite calcined at 500 °C, which showed the biggest hypsochromic shift. It is followed by the tin Pillared and the Cr-Montmorillonite calcined at

600 °C. Complementary changes were observed at the short wavelength edge of the spectra. The data tend to confirm SEC results and are in good agreement with the results obtained for the first batch of experiments. None of the new catalysts...have shown better results than the Cr and tin-based catalysts."

Extracts from report six

Catalyst deactivation study

"The best catalysts tested so far in the hydrocracking reaction of coal extracts, the Cr montmorillonite calcined at 500 °C and the [uncalcined] Sn laponite have been used in successive 2 hour step experiments in order to assess their resistance to deactivation."

[SEC data recorded at 450 nm, obtained for the feed and its hydrocracking products prepared in the presence of Cr montmorillonite, were used to assess the degree of deactivation of the catalyst with time.]

"The overall extent of the reaction is quite remarkable after 2 hours, most of the excluded peak in the extract have *(sic)* been reduce *(sic)* in the product, leading to a complementary increase in its retained peak. After the 2nd re-use of the catalyst (2 x 2hrs), the chromatogram exhibit *(sic)* the same trend as previously, the intensity of the excluded peak is as low as with the fresh catalyst and the intensity of the retained peak is just slightly lower. After the third re-use, once again the trend is the same. The only difference between the three chromatograms is the slight decrease of the retained peak with time. However, this decrease is very minor compared with that observed for similar experiments performed with the [proprietary] catalyst. The chromatograms recorded at 350 nm exhibit the same trends as described above."

[UV-F spectra obtained from the same system were also analysed.]

"Indications of deactivation is more clearer *(sic)* in the UV-F spectra than in the SEC chromatograms, the largest hypsochromic shift is given by the fresh catalyst, after the second and third re-use the spectra have shifted to longer wavelength. However, this bathochromic shift is smaller than the one observed with [the proprietary catalyst]."

"According to SEC and UVF data, Cr montmorillonite exhibit *(sic)* some signs of deactivation, especially in reducing the number of polyaromatic ring systems, heteroatoms *(sic)*. However, this catalyst seems much more efficient and resistant to rapid deactivation than [the proprietary catalyst]."

Different results have been observed for the tin pillared catalyst. Even though the extent of reaction is still good after the third contact (3 x 2hrs), greater signs of deactivation have been observed compare *(sic)* to the Cr-based catalyst. The SEC data show a clear increase of the excluded peak an *(sic)* a decrease of the retained peak of the products with time. [Analysis of the UV-F data reveals] the profile of the 1st and 2nd contact spectra are quite similar however, after the 3rd contact, the spectrum shows a bathochromic shift, indicating a drop in the efficiency of the reaction. The Sn-based catalyst seems to be less resistant to rapid deactivation than the Cr-based one, nevertheless, both catalysts exhibit better results than the [proprietary] catalyst.

The hydrocracking of petroleum fractions

"The petroleum feed used is a crude oil residue obtained from the bottom of an atmospheric-pressure distillation column of the PETROX oil refinery. The sample is part of the reduced crude which leaves the bottom of the column at *ca.* 330 °C."

"For the PETROX sample, the distillation clearly removed nearly all the lighter components, leaving behind a relatively high content of material boiling >450 °C."

"...SEC chromatograms of the PETROX sample and its hydrocracking products that have been prepared in the presence of the two best pillared catalysts for 10 and 120 minutes [single contact coal hydrocracking runs]. The PETROX shows some excluded materials...and a large broad retained peak. After 10 minutes of hydrocracking, the Cr spectrum do *(sic)* not show any reduction of the MMs, in fact the spectrum has shifted to higher MMs. However, after 2 hours, almost all of the excluded peak has disappeared and the retained peak has more than tripled in intensity and shifted to lower MMs compare *(sic)* to the feed. Comparing to the coal extract hydrocracking results, this Cr-based catalyst exhibit *(sic)* poor results at short reaction time, but remarkable results after 2 hours.

The trend is however slightly different for the Sn laponite catalyst. After 10 minutes the results are much better as the intensity of the excluded peak is much lower and the intensity of the retained peak higher than for the feed. However, after 2 hours, the profile of the spectrum is identical to the 2hrs Cr-spectrum. These SEC data show that both catalysts are efficient for the hydrocracking of petroleum residue at long reaction time. Nevertheless, the Sn laponite seems to give better results than the Cr montmorillonite at short reaction time.

A more complex pattern is observed for the UV-F data. The "envelop" *(sic)* of the three spectra is the same, changes only occur within this envelop *(sic)*. No real shifts are observed at the longer wavelength end of the spectra, instead changes in the shape of the peaks are detectable. The hypsochromic shift occurs for the *ca.* 350 nm peaks. Therefore it seems that the aromatics are not touched during the reaction. It is however worth remembering that the petroleum feed is a residue and have *(sic)* probably been thermally modified during the distillation, so it contains only heavy materials but not necessary *(sic)* large aromatic clusters."

Coal extract hydrocracking, with latest batch of modifications

"Three new pillared clay catalysts have been tested in the hydrocracking reaction of the feed, a Cr laponite calcined at 500 °C, a Sn laponite calcined at 500 °C and another Sn laponite calcined at 500 °C under nitrogen and then calcined at 800 °C under air.

[The five catalysts supplied to ICSTM were compared, based on SEC data recorded at 450 nm and UV-F spectra]

The five [SEC] chromatograms present the same profile, with roughly the same intensity for both the retained and excluded peaks, however, the Sn laponite calcined at 500 °C exhibit *(sic)* the highest intensity in the retained peak and the lowest in the excluded peak. These results show that this catalyst is the best among those five in reducing the high MM materials. Indeed it give *(sic)* slightly better results than the Cr montmorillonite and the original Sn laponite, which where *(sic)* the best catalysts tested so far.

[In the corresponding UV-F spectra] no *(sic)* much differences can be observed between the spectra except the Cr montmorillonite calcined at 500 °C which is shifted to the higher wavelength, and the Sn laponite calcined at 500 °C which shows the largest hypsochromic shift. The UV-F data are in good agreement with the SEC results and confirm that Sn laponite calcined at 500 °C [under nitrogen] is the most efficient catalyst for both reducing the MMs and improving the chemical structure of the products.

Extract from final report

"Catalyst efficiency was also assessed in terms of proportion of high boiling point materials (>450 °C) converted into lower boiling fractions. All the pillared clays exhibit higher conversion than the conventional supported [proprietary] catalyst, which does not become active until after 10 min reaction time. The results were particularly impressive for Sn laponite, with 70.5 % conversion. However, the Cr montmorillonite calcined at 500 °C showed a surprisingly lower conversion than expected (40.6 %). Nevertheless, based on overall SEC UV-F and conversion data, the Sn laponite and the Cr montmorillonite calcined at 500 °C were seen to be the most efficient in terms of molecular mass reduction, and general improvement of hydrocracking product quality."