UNCLASSIFIED

BREU -0480 BE-4057

AEAT-0032

AEA Technology

SYNTHESIS, CHARACTERISATION AND EVALUATION OF MULTI-LAYERED AND PILLARED MATERIALS FOR PROCESS CHEMISTRY AND THE ENVIRONMENT

SYNTHESIS REPORT

J O W Norris
February 1996

AEA Technology

429 Harwell, Didcot
Oxfordshire OX11 0RA
United Kingdom
Telephone: +44 1235434618
Facsimile; +44 1235432278

SYNTHESIS REPORT

FOR PUBLICATION

CONTRACT **No:** BREU-CT91-0480

PROJECT No: BE-4057

TITLE: Synthesis, characterisation and evaluation of multi-layered and pillared materials for process chemistry and the environment.

PROJECT
CO-ORDINATOR: UKAEA, AEA Technology, Harwell

PARTNERS:

United Kingdom Atomic Energy Authority AEA Technology, Harwell	GB
BP International Ltd., Sunbury	GB
Eniricerche SpA	Italy
Süd-Chemie AG	Germany
University Blake Pascal Clermont-Ferrand II	France
University degli Studi di Perugia	Italy

REFERENCE PERIOD
From 17th November, 1991 To 17th November, 1995

STARTING DATE: 17th November, 1991 DURATION: 48 MONTHS

PROJECT FUNDED BY THE EUROPEAN
COMMUNITY UNDER THE BRITE/EURAM
PROGRAMME

DATE 9 February 1996

BREU-CT91-0480 - Synthesis Report

FOR PUBLICATION

Synthesis, Characterisation and Evaluation of Multi-Layered and Pillared Materials for Process Chemistry and the Environment (contract no. BREU-CT91-0480) is a collaborative project, part funded by the Commission of the European Community's BRITE/EURAM Scheme. The partners in the collaboration are AEA Technology, BP Research, Eniricerche, Sud-Chemie AG, University di Perugia and University Blaise Pascal.

APPROVAL FOR PUBLICATION AND DISTRIBUTION

		Signature and date
Issued by	Dr. J. O. W,Norris	
Approved by.	Dr. 1. H. Balchin	26/2/96

Technical Enquiries:

Dr J O W Norris
AEA Technology
551 Hz-u-well
Oxfordshire
OX11 0RA

Tel: -t-44 1235434618
Fax: -I-44 1235432278

Commercial Enquiries:

Ms V S Scanlan
Commercial Department
AEA Technology
329 Harwell
Oxfordshire
OX1 1 0RA

Tel: +44 1235433208
Fax: +44 1235436657

BREU-CT91-0480 - Synthesis Report

Title: Some observations on the synthesis, characterisation and evaluation of multi-layered and pillared materials for process chemistry and the environment.

Authors:

Dr J O W Norris
AEA Technology, 551 Harwell Laboratory, Didcot
Oxfiordshire,OX11 0RA, UNITED KINGDOM

Dr M P Atkins
BP International Ltd., BP Chemicals, Research and Engineering Centre, Chertsey Road,
Sunbury-on-Thames, Middlesex, TW16 7LN, UNITED KINGDOM

Dr P Zappelli
Eniricerche SpA, Via Ramarini 32, 00016 Monterotondo Scala
Rome, ITALY

Dr T Engelhardt
Süd-Chemie AG, Forschung und Entwicklung, Ostenrieder Str. 15
8052 Moosburg, GERMANY

Dr C Forano
University Blaise Pascal, Laboratoire de Physico-Chimie des Materiaux
BP 45-24 Avenue des Landais, 63177 Aubiere Cedex, FRANCE

Professor G Alberti
University di Perugia, Instituto di Chimica Inorganic, Via Elce di Sotto 10
06100 Perugia, ITALY

1. ABSTRACT

Processes for the reproducible and predictable preparation of pillared layered and multi-layered materials with regular interlayer spacings were developed. Three different types of layered materials were studied, namely pillared and layered clays, zirconium phosphates and phosphonates and layered double hydroxides. Many novel materials were synthesised and characterised. The successful laboratory syntheses were refined and, for representative materials, scaled up to produce several kilograms per batch.

Materials were tested for catalytic behaviour towards a range of industrially important processes including the etherification of olefins, catalytic cracking, isobutane alkylation, ethylene hydration and glycol ether synthesis. Clay based catalysts performed very well for the production of the gasoline components MTBE and TAME, whilst chromium-copper based LDH's pillared with vanadate or molybdate polyoxomettalate anions have been found to be very selective catalysts for the synthesis of glycol ethers.

2. INTRODUCTION

Several research groups world-wide are currently investigating the catalytic and sorptive properties of layered structures such as cationic and anionic clays and zirconium phosphates. However, the field is hampered by a lack of understanding of the basic materials' parameters, such as physical properties and their correlation to reactor performance and difficulties in scale-up. It is known how t o prepare layered solids with well-defined interlayer distances, and that some pillaring reactions lead to microporous materials, but there is no known method for the preparation of regularly spaced pillars giving materials with predictable and desirable pore structures.

In addition, exploitation of many of these materials has in the past been inhibited by their poor temperature stability. Recent advances suggest it maybe possible to prepare materials which address high temperature applications. The materials can also be used in lower temperature processes, where selectivity is the key, or in environmental applications where selectivity and efficiency are important.

The principal economic driving forces arise from the possible use of materials as catalysts, Developments being sought by plant operators include improving process efficiency, using cheaper feedstocks and maximizing the selectivity of catalysts to enable their operation at stoichiometric feed ratios rather than requiring an excess of one reagent. These changes will, in turn, reduce operating costs,

The overall objectives of this project were to develop processes for the reproducible and predictable preparation of pillared layered and multi-layered materials of regular interlayer spacings having desirable physical and chemical properties for use in process chemistry and environmental applications, to scale-up these preparations and to thoroughly evaluate the technology in a laboratory pilot scale plant for the process under consideration.

Three different classes of pillared layered and multi-layered materials were studied and developed, namely:

1. Pillared and layered clays
2. Phosphates and phosphonates
3. Layered double hydroxides.

3. TECHNICAL DESCRIPTION

3.1 PILLARED LAYERED STRUCTURES

Aluminium pillared clays were prepared from both Volclay and a sodium ion exchanged Volclay using aluminium chloride. X-ray diffraction indicated that of the two materials the un-exchanged Volclay gave the more crystalline pillared clay. These experiments show that this pillaring strategy is possible with Volclay despite the impurities known to be present.

For the zirconium pillared clays work was directed towards synthesizing crystalline materials with a reproducible basal spacing. Many authors have reported the preparation of Zr-PILCs by reaction with zirconyl chloride7>(16). In these solutions the pillaring species is usually based on the zirconium tetramer unit, but little quantitative data is available on the size and shape of these species in solution. In this work the use of a zirconia sol, having a narrow particle size distribution, is expected to produce more uniform pillared materials. Therefore, Zr-PILCs were produced using:

1. Zirconyl chloride solution, fresh or aged, was added to Volclay and cation exchanged Volclay
2. An acetic acid stabilised zirconia sol
3. Nitrate stabilised zirconia sols with various ratios of acid: zirconium.

For all three different preparative techniques the clay was first dispersed in a water plus organic solvent solution before mixing with the solution, or sol, containing zirconium. These syntheses produced Zr-PILCs which were moderately crystalline.

The Al-PILCs and Zr-PILCs synthesised were characterised by several techniques. X-ray diffraction was used on the powdered samples to determine the inter-layer spacing, thereby confirming that the product was indeed a pillared layered structure.Nitrogen sorption characterisation was used to determine the materials' surface areas, pore volume and pore size distribution. A summary of the findings is given in Table 1. Key features from the data in the Table are confirmation that the reaction with aluminium or zirconium compounds does cause the interlayer spacing to increase. The reported clay thickness for a bentonite is 9.6Å(4). If the free interlayer spacing is taken as the increase in layer spacing relative to Volclay, then the materials produced had a free interlayer spacing of 9.3 -12.5 Å. The presence of an X-ray diffraction reflection indicates a degree of uniformity in the size of this separation.

Coincident with the increase in interlayer spacing with respect to Volclay, is a large increase in available surface area relative to the unpillared Volclay(37 m^2g^{-1}). The pillared materials had BET surface areas ranging from 200-420 m^2g^{-1}, with the largest surface area being found for the material synthesised using zirconyl chloride. An estimation of pore volume was made from analysing the adsorption isotherm. Values found were in the range 0,086 to 0.169 cm^3g^{-1}, and broadly followed the trends in surface area, with materials having a high surface area also having a large pore volume.

Thermal and hydrothermal stability was assessed using thermogravimetric analysis, X-ray diffraction and surface area analysis after heat treatment at various temperatures, Hydrothermal stability was assessed by exposure to 100% steam at 700 “C for 6 hours. The BET surface area measured after this treatment was strongly dependent on the method of preparation of the PILC. Some materials still had surface areas greater than 100 m^2g^{-1} after this treatment.

The synthesis of Al-PILCs was scaled Up to produce semi-commercial quantities. Of several bentonite clays investigated, a natural sodium-bentonite from Wyoming was found to be the most suitable for synthesizing pillared clays, having very good crystallinity. Special methods (involving decanting and centrifuging) were developed to remove crystalline impurities which could not be intercalated. However, once demonstrated this expensive purification would only be undertaken for applications requiring high purity pillared clays.

Table 1 Summary of characteristics of some pillared layered clays prepared

Sample Description	X-ray diffraction	Interlayer spacing d_{001} (A)	Nitrogen Physisorption	
	Calcined @ 400 “c	Free Interlayer Spacing	BET Surface Area m^2g^{-1}	Micropore Volume cm^3 $^{-1}$
Volclay	9.72	0.00	3 7	
Al-PILC aluminium chloride route	19.11	9.39	245	0.100
Zr-PILC zirconyl chloride with Volclay	21.93	12.21	421	0.169
Zr-PILC zirconyl chloride with exchanged Volclay	22.26	12.54	223	0.086
Zr-PILC acetic acid stabilised Zr sol, with Volclay	21.05	11.33	385	0.127
Zr-PILC 0.3M nitrate stabilised Zr sol. with Volclay	19.71	9.99	242	0,098
Zr-PILC 0.1M nitrate stabilised Zr sol, with Volclay	19.34	9.62	371	0.143

A study of possible sources of cationic polymeric aluminium hydroxide complexes, showed that the commercial product “Locron” from Hoechst gave the best pillared clays. The concentration of solids in the reaction mixture was increased from 0.5 to 20 g/l for laboratory recipes up to 80 g/1, thereby significantly reducing the production cost. Higher solid contents led to products with much lower specific surface areas. The washing (desalting) of the reaction mixture was also optimised, with the most economical process being the use of a membrane filter press. These last two improvements significantly reduced the quantity of waste water produced per kilogram of pillared clay.

Once produced, the Al-PILC’s were passed through either a reciprocating screw extruder or a granulating mixer to produce cylindrical extrudates or spherical granules that had a high crush resistance. This systematic approach led to the economic production of 20 kg of Al-pillared clay in one batch, a scale up of the original laboratory synthesis by a factor of 1000. The product had a high specific surface area, 310 m^2g^{-1}, and good pore volume and micropore size distribution characteristics.

Similar scale up was undertaken for the Zr-PILCs. A major issue was the use of organic solvents in the preparation, which is undesirable for large scale technical synthesis of Zr pillared clays because of problems related to the disposal of organics and the increase in the production costs. Consequently, the recipes needed to be modified to exclude organic solvents. The nitrate stabilised sol route appeared the most cost effective of the three original preparative routes. Components of the synthesis that were optimised included:

- reducing the Zr:clay ratio,
- the use of fresh zirconia sols, and
- reducing the reaction temperature and/or contact time.

When the optimised parameters were used a material was successfully synthesised whose X-ray diffraction showed it to be amorphous. A detailed pore size and volume analysis showed that the product from the aqueous route had similar pore characteristics to that prepared using organic solvents, despite the difference in X-ray pattern. The optimised and modified aqueous synthesis route was scaled up and used to produce a 6 kg batch of Zr-PILC. This material had a specific surface area of 280 m^2g^{-1} and a pore size distribution where 50°/0 of the pores were within the range O -20 Å.

3.2 PHOSPHATES AND PHOSPHONATES

The preparation and characterisation of zirconium phosphates and phosphonates was driven by interest in their potential as acid catalysts. The materials synthesised can be classified as:

a) Zirconium phosphite diphosphonates (ZPDPs) - Mesoporous materials of an inorganic-organic nature having a narrow distribution of pore sizes, high surface area but only moderate thermal stability (≤ 250 °C)(3,9).

b) Solid dispersions of zirconium phosphate on amorphous porous silica or zirconia that are inorganic, have a broad distribution of mesopore sizes and high thermal stability.

c) Materials based on classes a) and b) that have been functionalised with sulphonic acid (SO_3H) groups to increase their acidity, The low thermal stability of the sulphonic acid group reduces the thermal stability of these materials to around 180 °C(2,10).

The slow decomposition of zirconium fluoro-complexes in a solution containing diphosphonic acids led directly to zirconium phosphite diphosphonates (ZPDPs) which had a high surface area and a sharp distribution in pore sizes.

During the project 5 different diphosphonic acids were synthesised and characterised:

• 1, 2 ethanediphosphonic acid	$H_2O_3PCH_2CH_2PO_3H_2$
• 1, 4 butanediphosphonic acid	$H_2O_3PCH_2CH_2CH_2CH_2PO_3H_2$
• 1, 4 phenyl diphosphonic acid	$H_2O_3P\text{-}\phi\text{-}PO_3H_2$
. 4, 4' biphenyl diphosphonic acid	$H_2O_3P\text{-}\phi\text{-}\phi\text{-}PO_3H_2$
. 4, 4' biphenyl bis methylene diphosphonic acid	$H_2O_3PCH_2\text{-}\phi\text{-}\phi\text{-}CH_2PO_3H_2$

where ϕ = para substituted benzene ring.
Characterisation of these diphosphonic acid precursors included measuring their acidity and confirming their structure (using mass spectrometry).

More than 25 ZPDPS were prepared using different reagents or reaction conditions. Studies showed that the solvent played an important role, with the best results obtained from organic solvents such as dimethyl sulphoxide and n-propanol. It was found that the average dimensions of the pores can be modified by varying synthesis conditions, e.g. the concentration of diphosphonic acid, see Figure 1.

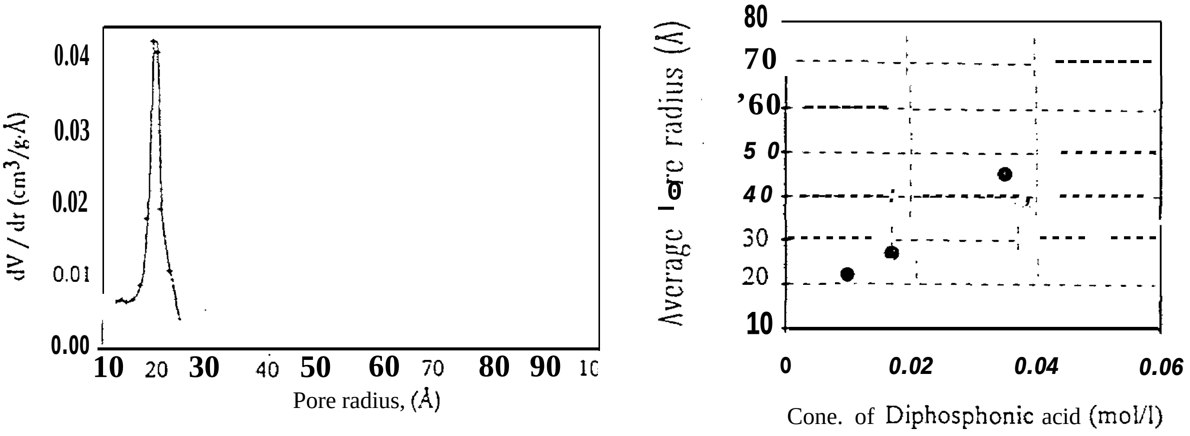

Figure 1 Pore size distribution curve of ZPDP

Dependence of average pore radius vs the concentration of diphosphonic acid in the reaction solution

The materials made were found to have a narrow distribution of pores that was tuneable over the range 20-70 Å, see Figure 1. Their surface areas and pore volumes were consistently quite high, ranging from 230 to 400 m^2g^{-1}, and 0.3 to 0.7 cm^3g^{-1}, respectively. ^{1}H and ^{31}P NMR analyses were performed on liquid phase ZPDP materials. This enabled quantitative evaluation of the materials' structures to be established. Thermo-gravimetric analysis showed the thermal stability of the materials was around 250 to 300°C. X-ray diffraction analysis of powder samples showed a low degree of crystallinity with the first reflection at 9.6 Å.

It had been shown that it is possible to exfoliate cc-zirconium phosphate (et-Zr(HP04),) microcrystals by the intercalation of some ties into the layer structure$^{(8)}$. This forms stable aqueous colloidal suspensions of single, or packets of a few, layers, which can then be dispersed on a porous substrate, e.g. porous silica, The organic bases are then removed by pyrolysis at 650°C. Optimal surface and ion exchange characteristics were reached when 36% w/w zirconium phosphate was used$^{(1)}$. Material with this composition was prepared' together with a formulation containing 60°/0 w/w zirconium phosphate on amorphous silica.

The material containing 36% w/w ZP had specific surface areas around 400 to 460 m^2g^{-1}. After pyrolysis a significant number of surface acid phosphate groups remain active, characterised to be around 0.4 meq g^{-1}. For the material containing 60 '/0 w/w ZrP the surface area was around 240 m^2g^{-1}. X-ray diffraction showed products to be amorphous. TGA showed that the materials were stable to 700-900°C and maintained their surface -P-OH group Up to 650°C.

This approach was broadened to investigate the preparation of solid dispersions of α-zirconium phosphate on amorphous zirconia. The support materials used were two different zirconia SOIS, whose mean particle sizes were 13 and 40Å. The ZrP:ZrO_2 w/w ratio ranged from 0.3 to 3.0 and materials possessing a good degree of dispersion were produced. The surface area for these materials was around 185 m^2g^{-1}, and they were thermally stable up to 650°C. Compositional analysis indicated that 50% ZrP, by weight, was present.

The zirconium phosphates/diphosphonates described above possess a certain amount of surface acidity due to their surface P-OH groups, and consequently they are potential catalysts for processes requiring a moderate strength acid. However, some reactions require more acidic catalytic sites. Potential materials were synthesised by using topotactic exchange, contacting the solid with a solution containing a stronger acid. Four phosphoric sulphonic were prepared for this phase of the work:

- phenyl-1-phosphoric 3-sulphonic acid
- 1,3-dimethylphenyl 2-phosphoric 4- sulphonic acid
- phenyl 1,3-bis-phosphonomethyl sulphonic acid
- benzylphosphonic sulphonic acid

These strong acids can be used to functionalise/modify zirconium phosphates, diphosphonates directly or by using a derivative. Mesoporous ZPDP was functionalised using either phenyl-1-phosphonic 3-sulphonic acid (SP) or with phenyl-1-phosphoric 3-chlorosulphonic acid (CSP) to compare the ease of use, and products formed. It was concluded that CSP was more convenient to use and led to a product with a higher concentration of acid groups relative to SP. It was also found that the solvent used affected the product formed, with DMSO presenting a particular challenge because of its reactivity towards zirconium phosphates. Propanol and dioxane/water were the preferred reaction media. The functionalised material, abbreviated to ZPDP.CSP, showed a surface area of 230 m^2g^{-1}, and a pore volume of 0.44 cm^3g^{-1}.The pore size distribution curves were shown to be similar to that of the original ZPDP.

Similarly, the addition of SP or CSP to zirconium phosphate dispersed on porous silica led to compounds derived from class b) functionalised with highly acidic groups. Materials produced by this route had a surface area of 220 m^2g^{-1}, a mesopore volume of 0.115 cm^3g^{-1}, and an ion exchange capacity of 0.94 for SiO_2-ZP.CSP and 0.73 for SiO_2-ZP. SP.

3.3 LAYERED DOUBLE HYDROXIDES

The LDH's studied were selected by choosing di- and tri- valent metal ions that were expected to be active for the target chemical reactions using previous catalyst research and development for guidance. The preparation of new LDH phases, under well controlled conditions, with original chemical compositions was an important aspect of this work.

For the synthesis of glycol ethers LDHs based on the [Cu-Cr] and [Cu-Al] systems were studied. The lamellar compounds were then pillared by oxoanions to improve their chemical and thermal stability, and to create internal microporosity.

The dehydrogenation of ethylbenzene to styrene is principally carried out in thevapour phase. Catalytic systems, where oxygen acts as a hydrogen acceptor yielding water as a by-product and providing the thermodynamic driving force, can occur at lower temperatures leading to a more energy effective conversion and an improved yield of product. Existing catalysts for oxidative dehydrogenation are based on Al-O, Mg-P-O or V-Mg-O chemical systems. From these data and from earlier work, the following precursor materials were selected for investigation for the oxidative dehydrogenation of ethyl benzene:

- [Mg-Al] : Cl, V_2O_7, P_2O_7, Cr_2O_7, $V_{10}O_{28}$, $Fe^{III}(CN)_6$,
- [Ni-Al]: Cl, V_2O_7, P_2O_7,
- [Zn-Al] : Cl, V_2O_7. P_2O_7,
- [Mg-Fe] : C03,
- [Co-Fe] : C03.

The coprecipitation of the mixed metallic hydroxides is a one step direct preparation method which allows the accurate control the various parameters of the synthesis. Therefore it is a suitable method for the preparation of pure LDH's phases. A list of the various compounds prepared using optimised conditions is given in Table 2.

Coprecipitation is frequently not a suitable preparative method for the synthesis of LDH's intercalated with oxometallic anions. This is particularly true when competing metallic salts precipitate preferentially to the hydroxides in the mother solution, as is the case with a large variety of oxometallates. The anionic exchange route appears to be the only alternative method to synthesise such compounds. A series of oxometallate containing LDH's were prepared by this procedure, the list is given in Table 3. The exchange reaction is easily monitored by the measurement of the variation in basal spacing, which, in turn, is related to the charge and geometry of the intercalated anions. Chemical analyses have confirmed a complete exchange occurred in nearly all cases.

Table 2 LDH precursors prepared by **coprecipitation**.

Systems	M^{II}/M^{III}	pH of coprecipitation	Use
[Cu-Cr-Cl]	1.97	4.5	Precursor for bionic exchange reactions
[Mg-Al-Cl]	2.86	10.0	Precursor for Anionic exchange reactions and for improved surface area
[Zn-Al-Cl]	2.74	8,0	Precursor for Anionic exchange reactions
[Ni-Al-Cl]	2.74	11.0	Precursor for Anionic exchange reactions
{Mg-Al-CO_3]			for improved surface area
[Mg,Cu-Al-CO_3]			LDH with variable composition
[Mg,Ni-Al-CO_3]			LDH with variable composition
[Mg,Co-Al-CO_3]			LDH with variable composition
[Mg,Zn-Al-CO_3]			LDH with variable composition
[Mg-Fe-CO_3]	2.00	10,0	Oxidative dehydrogenation of ethyl benzene
[Mg-Fe-CO_3]	3.00	8,5	Oxidative dehydrogenation of ethyl benzene
[Co-Fe-CO_3]	3,00	12,0	Oxidative dehydrogenation of ethyl benzene

Table 3 Lists of **Oxometallate** containing **LDH**

$[M^{II}-M^{III}]$	M^{II}/M^{III}	cro4	Cr_2O_7	P207	V207	V_4O_{12}	$V_{10}O_{28}$	Mo_7O_{24}
[Cu-Cr]	1.97	X	x		x	x	x	x
[Mg-Al]	2.86	x	x	x	x		x	
[Zn-Al]	2.74		x	x	x			
[Ni-Al]	2.74		x	x	x			

The use of the reconstruction method was envisaged as a preparative route for materials having modified textural properties, namely specific surface area and porosity. This method involves the calcination of a carbonate LDH precursor to form an amorphous mixed oxide with a higher surface area, and then the dehydration back to an LDH structure. An investigation was undertaken to see if the so called “structural memory effect” was also affecting the powder morphology. The reconstruction was then assessed for the [Mg-Al-CO_3] system in a series of water/alcohol mixtures.

Powder X-Ray diffraction (PXRD) was systematically used to identify the resulting phases of the various preparation methods in order to optimise the synthesis conditions. Moreover, the modification of the interlayer spacing under anionic exchange is direct proof that exchange has occurred, and is a means of identifying the anionic species and their orientation in the interlayer domain, see Table 4.

Table 4 Interlayer distance of exchanged LDH compounds

d (Å)	c1	P_2O_7	$Cr0_4$	Cr_2O_7	V_2O_7	V_4O_{12}	$V_{10}O_{28}$	Mo_7O_{24}
[Cu-Cr]	7.70		8.42	8.95	7.62	9.4-9.6	11.6	12,6
[Mg-Al]	7.88	8.50	8.63	9.26	8.87		10.21	
[Zn-Al]	7.73	8.80			8.31			
[Ni-Al]	7.80	8.05			7.80			

The structural modification observed after the exchanges show that the expansion properties of LDH intercalated by oxometallates are limited to basal spacing not higher than 13 Å, which means an interlayer space not greater than 8.5 Å.

For the coprecipitation of multi-metallic element systems, the linear evolution of the a cell parameters (Vegard law) confirms the formation of solid solutions. For the case of [Mg,Cu-Al-CO_3] with a Cu/Mg ratio between O and 100 %, PXRD has proved that it is possible to continuously vary the Cu/Mg composition in the LDH.

LDH's are known to display variable thermal stability dependant on their chemical composition. The evolution of the d-spacing under calcination and the optimal temperature where the material retain a lamellar structure have been directly analysed by PXRD techniques in a complementary way to the recording of TGA and DTA profiles. The exchange of anions in LDH's was easily monitored by FTIR spectroscopy,

The specific surface area and porosity measurements were made for:

- chloride and carbonate LDH precursors,
- oxometallates containing [Cu-Cr], [Mg-Al], [Zn-Al] and [Ni-Al] LDH compounds,
- various [Mg-Al-CO_3] LDH phases prepared under difFerent coprecipitation or reconstruction conditions,
- various calcined LDH phases,

The general conclusion which emerged from these measurements was that, except for [Mg-Al-$Fe^{III}(CN)_6$] (260 m^2g^{-1}), the compounds had surface areas less than 50 m^2g^{-1}. This was true whatever the nature of the host matrix and the guest anionic species and whatever the preparative technique. This arises undoubtedly from the high charge density of the LDH materials, the crystallite of which have a marked tendency to agglomerate, However, some of the calcined phases can display much higher surface areas, 110-195 m^2g^{-1}.

In all samples, a broad pore size distribution was observed. The major contribution arose from mesoporosity in the range of 200 to 600 Å, with both the materials and the calcined derivatives having little microposity. The highest microporosity was exhibited by [Cu-Cr-V_2O_7] which had nearly 40 % of its porosity as micropores.

The reconstruction method led to materials with lower surface area and no memory effect of the textural properties of the intermediate oxides. The nature of the solvent used during the direct synthesis, or during the reconstruction method, was found to have a clear effect on the surface and porosity properties of materials.

Other characterisation techniques employed included:

- Scanning Electron Microscopy (SEM) - as a complementary technique to N_2 adsorption-desorption isotherm measurements in order to determine how thermal treatments can affect the morphology of untreated and calcined powders and to relate the results to the surface properties and catalytic activities.
- Extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (xANES). These were used to study the local environment of specific atomic probes in [Cu-Cr] LDH materials. XANES, at the Cu K edge, has shown that copper exists in a similar electronic state in all phases. Simulations of [Cu-Cr-Cl] EXAFS spectra at the Cu and Cr K edges have given information on the local symmetry of both elements in the LDH. These show that Cr^{3+} is surrounded by 4 oxygen atoms a distance of 1.97 Å away, and 2 oxygen atoms at 2.12 Å and that Cu^{2+} is surrounded by 4 oxygen atoms at 1.91 Å and 2 oxygen atoms at 2.03 Å.

For the scale up to semi-commercial quantities the precursor used was [Cu-Cr-Cl]. The principal optimisations achieved were to increase the solids content of the reacting mixture from around 1% to 4.5%, and to virtually eliminate the washing steps, removing the problem of colloidal copper and chromium species being formed during washing. With the optimised synthesis $[Cu_2Cr(OH)_6]Cl$ was prepared on a 5kg/batch scale. The crystallinity and specific surface area of the laboratory and scaled-up products were found to be very similar.

The preparation of sodium metavanadate intercalated [Cu-Cr-Cl] was also scaled-up. Following the synthesis of [Cu-Cr-Cl] from a pressed filter cake, an intermediate intercalation with terephthalic acid was required. The third step involved the exchange of the terephthalic acid by metavanadate to give $[Cu_2Cr(OH)_{6.4}](HV_{10}O_{28})_{0.15}TPA_{0.13}$. Chemical analysis showed that the TPA could not be completely separated, with some remaining within the final product. Using an analogous procedure, intercalation with sodium molybdate was also successfully scaled up.

3.4 SCALE UP OF LABORATORY SYNTHESES

The successful scale up of selective laboratory syntheses was achieved by adopting a systematic approach. This addressed five aspects of the preparation to be scaled up:

1. *Reproducibility of Laboratory Synthesis*
   Prior to any attempt to optimise or scale up a preparative route it was first confirmed that the recipe provided was reproducible in another laboratory.

2. *Modification of laboratory route with regard to production on pilot plant scale.*
   Laboratory synthesis routes are generally not optimised with respect to production. Therefore, before starting to scale up the synthesis it was necessary to optimise the laboratory route first, with particular attention being paid to finding a low cost and **environmentally acceptable** preparative route.

3. *Development of production engineering*
   Before starting the scale-up of the preparation, the process engineering has to be optimised. For the applications envisaged in this project the following single process steps were investigated:
   - Selection and testing of suitable, low priced raw materials
   - Purification of the clays involved
   - Optimisation of the reactor design
   - Optimisation of the filtration and washing processes
   - Optimisation of the drying and calcining processes
   - Development of process engineering to prepare catalytic extrudates and granules
   - Regeneration or disposal of by-products in an environmentally acceptable manner.
4. *Scale-up of preparations*
   After having successfully completed steps 1 to 3 above, the production of the catalysts on a pilot plant scale (1 -10 kg) was undertaken.

5. *Characterisation of products*
   The samples produced by the scaled-up preparative route were characterised to show whether their physical and chemical properties were identical to samples from the laboratory scale preparation. Only if they were, would samples be passed *on for* further testing.

4 RESULTS

4.1 PILC's

A selection of clays and pillared layered were assessed for four different reactions:

- Etherification of olefins to produce MTBE and TAME
- Catalytic cracking
- Ethylene hydration.

Etherification of C4 and C5 iso-olefins with methanol can lead to the production of methyl-t-butyl ether (MTBE) and t-amyl methyl ether (TAME), respectively. These are important gasoline components, A range of clay based catalysts were tested along side a current commercial catalyst, Bayer SP 118 ion exchange resin. Screening at 80°C gave encouraging results with one clay showing comparable activity to the commercial catalyst. In order to retain this activity at normal operating temperatures, 60°C, some pre-treatment was required to reduce/control the amount of interlamellar water. The exact method of integral water removal is a key variable in the use of these clay catalysts, Under non-optimised pre-treatment conditions the performance of the preferred clay (88% methanol conversion) was comparable to that of the SP 118 resin (800/0). A patent ‘5) has been filed for this.

Similarly, a range of clay based catalysts, were tested for TAME production alongside a current commercial catalyst, Bayer K2631 ion-exchange resin. Several clays performed well, although always poorer than the commercial catalyst. Attempts were made to improve the clay’s catalytic performance by increasing the acid loading and controlling the amount of initial free acid. Whilst these steps were moderately successful, no clay was comparable in performance to the current commercial catalyst, unlike the situation for MTBE production.

Cracking catalysts employed in commercial fluid catalytic crackers (FCCs) have to stand the extremely severe hydrothermal environment that exists within the regenerator section of these units. Consequently, hydrothermal stability is often the key difference between good and poor catalysts. A stability test based on exposure of the catalyst to an atmosphere of 100°/0 steam at 816°C (1500°F) for 5 hours was developed from an existing ASTM procedure. Results are shown in Table 5, and show that none of the three PILCs assessed had suitable hydrothermal stability, The catalyst CN 1 is based on a sample of a Chinese rectorite which, being an interstratified clay, has a surface area roughly half that of the pillared montmorillonites. In contrast to alumina pillared rectorites that have been reported in the literature ’[13, 14)], this sample of pillared Chinese rectorite was not steam-stable, losing more than 90°/0 of its surface area. The reason for this different behaviour is most likely due to the nature of the smectite components of the clays, Those where it has beidellitic character ie the negative charge originates in the tetrahedral layer, appear resistant to hydrothermally induced collapse. In this sample of Chinese rectorite the smectite layer appears to be montmorillonite, in which isomorphous substitution in the octahedral layer results in a “smeared” negative charge which does not interact as strongly with the pillaring species. The collapse of the pore structure of the pillared montmorillonites is to be expected for this reason.

Table 5 Steam Stabilities of Pillared Clay Cracking Catalysts

Code No.	Catalyst Type	Fresh Surface Area (m^2g^{-1})	Steamed Surface Area (m^2g^{-1})
CN 1	Al Pillared Rectorite	120	14
EXM 534	Al Pillared Mont	221	<5
EXM 551	Zr Pillared Mont.	263	<5

The ethylene hydration study was carried out in a catalyst test unit modified to handle ethylene and the corrosive environment generated by phosphoric acid. The run conditions chosen were designed to mimic those currently used in commercial plants, A performance versus temperature profile of a commercial ethanol catalyst was first obtained to confirm the integrity of the analysis procedure and test unit. This was followed by evaluation of a range of layered materials with and without presence of phosphoric acid.

An alumina pillared clay, prepared on a semi-commercial scale (20 kg) proved to be the most active and selective for ethylene hydration. It gave 5°/0 ethene conversion with a selectivity to ethanol of 90°/0, and a comparable ethanol productivity (87 g/Lcat/h) to a PA/silica catalyst. However, repeated attempts to reproduce the initial performance proved unsuccessful.

4.2 PHOSPHATES AND PHOSPHONATES

Some of the most promising Zr Phosphates and Phosphonates were assessed for their catalytic activity. However, time did not allow for materials produced towards the end of the project to be included, despite the fact that several of these materials look even more suitable as potential catalysts. A summary of the results obtained is given in Table 6.

Table 6 Summary of results from catalytic testing of phosphate and phosphonates

Materials used	Surface area (m^2g^{-1})	Catalytic tests
$Si0_2$-ZP 36%	456	Ethylene Hydration (+) Oxidative dehydration (++) Methyl -t-butyl ether syn (-)
SiO_2-ZP 60%	240	Ethylene Hydration (++)
SiO_2-ZP.SP	220	Ethylene Hydration (-) Butene Alkylation (+) Methyl -t-butyl ether syn (++)
ZPDP*	290	Ethylene Hydration (-) Butene Alkylation (-)
ZPDP. SP*	290	Ethylene Hydration (-)
ZPDP.CSP*	230	Ethylene Hydration (-)

* Mesoporous materials with an average pore diameter of40 Å

The alkylation of isobutane produces alkylates, predominantly C8 alkanes. These, in turn, contain trimethyl pentanes (TMPs), the desired components. Commercial processes produce around 60°/0 TMPs. Zirconium phenyldiphosphonate phosphite was found to be active and selective at 250°C over a 4 hour run with C8S accounting for ca. 66°/0 w/w of the product. However, the C8 fraction was evenly split between alkanes and alkenes, with TMPs making up only 12°/0 of the C8 fraction.

Six zirconium phosphate materials were evaluated for ethanol production from the hydration of ethylene. Activities were found to be on the low side, relative to the 4°/0 ethylene conversion found for a commercial ethanol catalyst. The best material was SiO_2-ZP 60%, which gave 3% ethylene conversion at 300°C and an ethanol productivity of 49 g/ litre catalyst/hour.

The skeletal isomerisation of 1-butene requires high temperatures, around 500°C. This restricts the choice of potential catalysts to the inorganic materials, zirconium phosphate dispersed on silica. Experiments were performed at 480°C, with the catalytic activity being determined after 30 minutes: 7% 1-butene conversion was obtained with a 70% selectivity.

4 . 3 LDH's

The catalytic activity of the LDH's prepared was assessed for 2 reactions:

- the formation of glycol ethers from the desired epoxide and alcohol, and
- the dehydrogenation of ethylbenzene to styrene.

The reactions were carried out in a conventional medium pressure continuous flow unit (30 bars) using a fixed-bed reactor. Screening tests assessed the activity of the six layered double hydroxides ([[Cu-Cr-Cl], [Cu-Cr-CrO_4], [Cu-Cr-Cr_2O_7], [Cu-Cr-V_2O_7], [Cu-Cr-$V_{10}O_{28}$], [Cu-Cr-Mo_7O_{24}]) and two 400°C calcined phases [Cu-Cr-Cl], [Cu-Cr-CrO_4], under three different reactor temperatures 80, 100, 120°C.

Two positive conclusions arise from this study. The first important one is that the LDH catalysts display very high selectivity values, always greater than 95°/0 and nearly 10O”/O for vanadate and molybdate pillared LDH's. The second conclusion is that the materials display a very high efficiency with a rate of epoxide conversion of about 50°A - 60°/0 and even 90°A for [Cu-Cr-Cr_2O_7] under fast contact time.

Following these successful results, further assessment, and some development, was undertaken using 1.5 kg batches of [Cu-Cr-Cl], [Cu-Cr-Mo_7O_{24}] and [Cu-Cr-$V_{10}O_{28}$] from scaled up preparations. All three materials were found to be active and selective. Epoxide conversions of greater than 95°/0 were achieved, although this was accompanied by the loss of selectivity to glycol ethers (<93%). These successful results have led to the recent filing of a joint BP Int/UBP patent(b).

The LDH's listed in section 4.3 were assessed as potential catalysts for ethylbenzene oxidative dehydrogenation. The best results regarding conversion and selectivity were obtained with [Mg-Al-Cr_2O_7] and [Mg-Al-V_2O_7]. Further tests were performed in order to optimise ethylbenzene conversion. The parameters that were changed, and their influence, were:

- Air/ethyl benzene ratio - where the principal change arose from variations in space velocity.
- Chromium loading - which had a large effect, primarily due to differences in acidity.
- The calcination temperature of the LDH precursor - where increasing calcination temperatures led to a reduction in selectivity.
- Acid treatment of [Mg-Al-CO_3] with H_3PO_4 - which inhibited catalytic activity, and
- basic treatment of [Mg-Al-CO_3] with KOH - which also inhibited catalytic activity.

4.4 ADSORPTION OF ORGANIC COMPOUNDS

A second area of commercial application that was considered within the project, albeit very briefly when compared to catalytic studies, was the prospects of using the new materials as adsorbants. Organic molecules were used to probe the size of micropores in pillared clays and some commercially available zeolites. The pillared clays were able to adsorb larger organic molecules from the vapour phase than commonly available zeolites with the largest pore size. Both the Al- and Zr- PILCs could adsorb molecules up to 10.4 Å in diameter. The Zr-PILC prepared from Volclay + zirconyl chloride, showed a higher adsorption of the large organic compounds relative to the Al-PILC, consistent with the higher pore volume described in Table 1. These data indicated that the pillared clays maybe useful as dry absorbents.

Pillared or modified clays did not adsorb MTBE or TCP from aqueous solution as effectively as activated carbons. An experiment designed to examine the competitive adsorption characteristics of PILCs to different organic compounds in aqueous solution did find marked differences in behaviour, indicating the PILCs do show selective adsorption properties. Treating the PILC's with a surfactant, eg cetylpyridinium chloride or Tergitol TMN **10,** did increase their ability to adsorb chlorophenols, in agreement with other reported studies(11, 12, 15).

5. CONCLUSIONS

This collaborative project has successfully developed processes for the reproducible and predictable preparation of pillared layered and multi-layered materials which have regular inter-layer spacing and physical and chemical properties required for use in process chemistry and environmental applications. Three different types of pillared layered materials were studied: pillared layered clays, zirconium phosphates and phosphonates and layered double hydroxides. Representative materials have been successfully scaled up to a semi-commercial scale, and the materials prepared were evaluated in a laboratory pilot scale plant for a range of reactions of commercial importance.

Clay based catalysts performed well for the production of the gasoline additives MTBE and TAME, with the MTBE catalyst exhibiting a performance that was comparable to the current commercial catalyst. An aluminium pillared clay has proved active and selective for ethylene hydration and pillared clays have been shown to be highly suitable as catalysts for the synthesis of linear alkyl benzene.

The zirconium phosphate dispersions in silica, functionalised with sulphonic acid groups, gave good results for the synthesis of MTBE. Also these inorganic materials have shown useful activity towards ethylene hydration and the oxidative dehydrogenation of ethyl benzene.

Chromium-copper based LDH's pillared with vanadate or molybdate polyoxomettalate anions have been found to be very selective catalysts for the synthesis of glycol ethers.

6. ACKNOWLEDGEMENTS

The project's partners gratefully acknowledge the EC for their financial support, and Dr Peters, who in his role as Technical Advisor for the EC has enthusiastically supported us, offering us advice and assistance.

7. REFERENCES

1 *G* Alberti, M Casciola, U Costantino, J. Colloid Interface Sci., 107,286 (1985)

2 G Alberti, U Costantino, R Vivani and P Zappelli, *Soft Chemistry Routes to New Materials* International Symposium Nantes (France) (1993)

3 G Alberti, U Costantino, R Vivani and P Zappelli, MRS Symposium Proceedings Vol 233, pp 101-106 (1991)

4 MS Baksh, ES Kikkinides and RT Yang, Ind. Eng. Chem. Res., 31,2181 (1992)

5 BP International, British Patent Office Application 95/01 143.3

6 BP International and University Blaise Pascal, British Patent Office - Application number 9512727.0

7 R Burch and CI Warburton, J. Catal., 97,503 (1986)

8 A Clearfield (cd.), *Inorganic Ion Exchange Materials*, CRS, Boca Raton, FL (1981)

9 Eniricerche and University di Perugia US Patent 5,166,380 (1992)

10 Eniricerche and University di Perugia Italian Patent N MI 95/A 000710 (1995)

11 HS Fogler and KR Srinivasan, US Patent No 4,916,095 (1990)

12 LJ Michot and TJ Pinnavaia, Clays and Clay Minerals, 39(6), 634 (1991)

13 ML Ocelli et al, J Catal., 141,510 (1993)

14 SINOPEC, European Patent O 197012 (1989)

15 KR Srinivasan and HS Fogler, Organohalogen Compd., 3,417 (1990)

16 S Yamanaka and GW Brindley, Clays and Clay Minerals, 27(2), 119 (1979)

DISTRIBUTION:

Dr MP Atkins	BP International Ltd, UK	2 copies
Dr P Zappelli	Eniricerche, Italy	2 copies
Dr T Engelhardt	Süd-Chemie	2 copies
Dr C Forano	Université Blaise Pascal	2 copies
Professor G Alberti	University di Perugia	2 copies
Dr von den Dreisch	Commission of European Communities	3 copies
Dr J Peters	VDI	1 copy
Dr JOW Norns	551, Harwell	1 copy
Dr R Jones	429, Harwell	2 copies
Library	465, Harwell	2 copies