

SYNTHESIS REPORT

FOR PUBLICATION

CONTRACT N° : BRE2-CT91-0462

PROJECT N° : BE-4275

TITLE : COORDINATED EUROPEAN ACTIVITY on
PILLARED LAYERED STRUCTURES (CEA-PLS)

PROJECT
COORDINATOR : Henri VAN DAMME

PARTNERS : A.A. G. TOMLINSON
P. PALVADEAU
J.H. PURNELL
N. GANGAS

STARTING DATE : 01/07/91 DURATION : 48 MONTHS



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

DATE : October 1995

CEA - PLS: Co-ordinated European Activity on Pillared Layered Structures and related porous materials

RESEARCH AND INDUSTRIAL OPPORTUNITIES IN THE EUROPEAN UNION

H. Van Damme¹, A.A.G. Tomlinson², P. Palvadeau³, H.J. Purnell⁴ and N. H. J. Gangas⁵

(¹) Centre de Recherche sur la Matière Divisée, CNRS-Université d'Orléans, F-45071 Orléans cedex 2; (²) ICMAT-CNR, Area delle ricerca di Roma, via Salaria km 29,5, CP 10,1-00016 Monterotondo; (³) IPCM-University de Nantes, 2 rue de la Houssinière, F-44072 Nantes cedex; (⁴) University of Wales, Chemistry Department, SA2 8PP Swansea, UK; (⁵) Stratton Hi-Tee Ltd, Kifissias Av. 108, GR-1 1526 Athens.

Abstract.

Pillared Layered Structures are obtained by propping apart a layered host material such as a **clay**, a phosphate, or a layered double hydroxide, with organic molecules, inorganic **polyions** or **colloids**. They are extremely versatile **nanoengineered** and multifunctional porous solids. A Concerted European Action of 51 active member groups including 8 industrial partners was setup with the aim of focusing their activity on application-oriented activities, sharing **information** and know-how by meetings and exchange of **personel** and **finally** producing reference- or standart **materials** in the most important **families** of PLS materials. During the four years of the **project**, 13 industry-academia meetings were organized on various topics **such** as « PLS in catalysis »; a PLS in organic synthesis »; « PLS in separation »; « PLS in environmental engineering processes »; « PLS in electrochemical applications » or « **PLS-based** sensors ». Short- to medium-term **staff-exchanges** were encouraged and led to a **total** of more than 60 man-week exchanges between groups. In **collaboration** with academic groups, two SMES produced several reference pillared materials which are now openly available in kilogram quantities. New materials and/or demonstration prototypes have been obtained for catalytic applications, such as **glycol** ether production, syngas conversion, **alkylation** reactions or hydroisomerisation of normal paraffins; for environmental applications and clean processes, such as phenol removal or heavy metal scavenging from waste water or the clean production of **γ-butyrolactone**; for separation applications such as **oxygen/nitrogen** separation, smoke filtration or edible oil cleaning; for glucose **oxidase** or humidity sensors; for **protonic** conductors in batteries; for plastic stabilizers.

1. Introduction

Over the past ten years an important class of materials has emerged which are prepared by propping apart layered materials with molecular or **colloidal nanostructures** acting as **pillars**. This new family of advanced materials is generally referred to as Pillared Layered Structures (PLS) [1]. Whilst interest was initially **centred on smectite** clays [2, 3], whose molecular sieving and catalytic properties suggested their use as catalysts in oil cracking and organic synthesis, the field has later expanded to include additional novel materials touching on other **industrially** and economically important areas.

The primary reason for this interest lies in the fact that PLS are an example "par excellence" of *materials by design*. They provide **supermesh** host structures in which chemical reactions or physical processes can proceed under gas-phase conditions, but at liquid/solid state densities. It is possible to engineer or tailor these porous structures. A capability of material manipulation such as this is able to provide new composites of high industrial interest in the **future**. They are apt for a wide range of fields of application from catalysts to molecular sensors.

Probably the best known example of a layered chemical structure is graphite, in which the carbon atoms form an hexagonal array in sheets which are infinite in two dimensions. The individual sheets interact to provide a moderately stable structure. The sheets may slide over each other under pressure and also separate vertically by intrusion (intercalation) of other substances. Comparable structures exist widely in Nature, **mainly** as the family of clays, but here the sheets are electrically charged so that balancing ions exist between the sheets and the overall energetic are such as to prevent sliding but **still** to allow vertical sheet separation (swelling). In **fact**, such layered structures are very common in inorganic chemistry and in recent years a whole new area of the subject **has** emerged.

Whilst the ability to swell is advantageous in many situations, there are many more areas of potential application where it is disadvantageous since it introduces instability. Techniques have been, **and** continue to be, developed wherein chemical moieties can be inserted between the sheets to fix their separation and this, in turn, **allows** the attainment of both controllable microporosity with fixed but adjustable, structured dimensions and also offers considerably improved thermal and hydrothermal stability. This ability to **generate** such "tailored" **nano-** or **mesoporous** structures, as illustrated in Fig. 1, is an aspect of *nanometre engineering*.

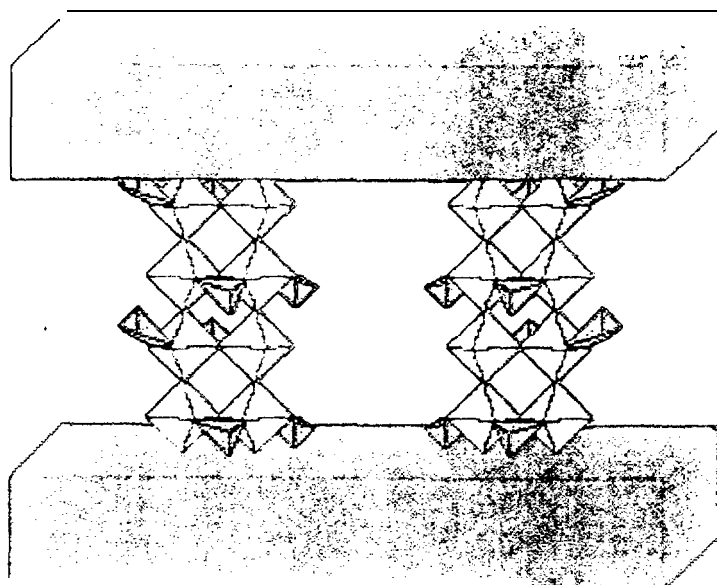
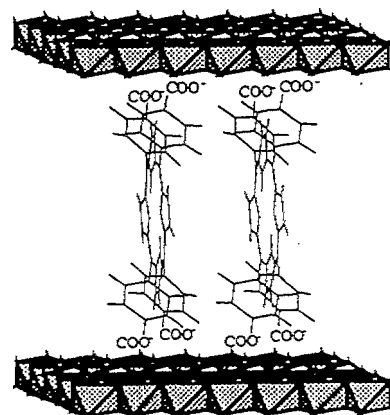


Fig. 1 Molecular model of inorganic **polymeric** pillars propping apart two phosphate layers.

The current description of PLS extends far beyond its meaning of only a few years ago when **alumina-pillared clays** were the only examples of such materials. Among the numerous examples that could be cited, there are *pillared phosphates*, *phosphonates*, *layered oxides*, *hydroxides* and *oxyhalides*. They show a remarkable variety of composition, structure, **microtexture** and properties. Four broad sub- groups may be identified in the PLS **family**:

- ◇ *Expanded Layered Structures (ELS)*, in which organic molecules or coordination compounds are simply intercalated into a layered host. ELS are characterised on the one hand by the strong (but not covalent) interaction of the intercalated moieties with the host lattice, which makes the intercalation process quasi-irreversible and gives the material a satisfying stability, and on the other hand, by their sharply-defined microporous structure. Examples include surfactant-modified clays developed by P. Labbé and his coworkers at the University of Grenoble for electrochemical applications, or the porphyrin - layered double hydroxides (LDH) expanded structures synthesized by J.P. Besse and his co-workers in the University of Clermont-Ferrand, as illustrated in Fig.2.

Fig.2 Expanded Layered Structure obtained by intercalating an anionic porphyrin derivative into a Zn-Al Layered Double Hydroxide.



- ◇ *Molecularly Crosslinked Layered Structures (MCLS)*, in which organic groups are covalently bonded (‘grafted’) onto the host surfaces. The bond may be single, which leads to pendant organic groups, or double, yielding crosslinked structures. MCLS are tunable organic-inorganic materials, which have a high potential on account of their solid-state properties. Tetravalent Zr-, Ti- and Sn-derivatives are the most extensively developed members of this family of materials (Fig. 3) (University of Perugia, University of Malaga), but new derivatives of Pb, Bi, Al and U have been prepared, which retain their microporous structure at temperatures as high as 500°C.

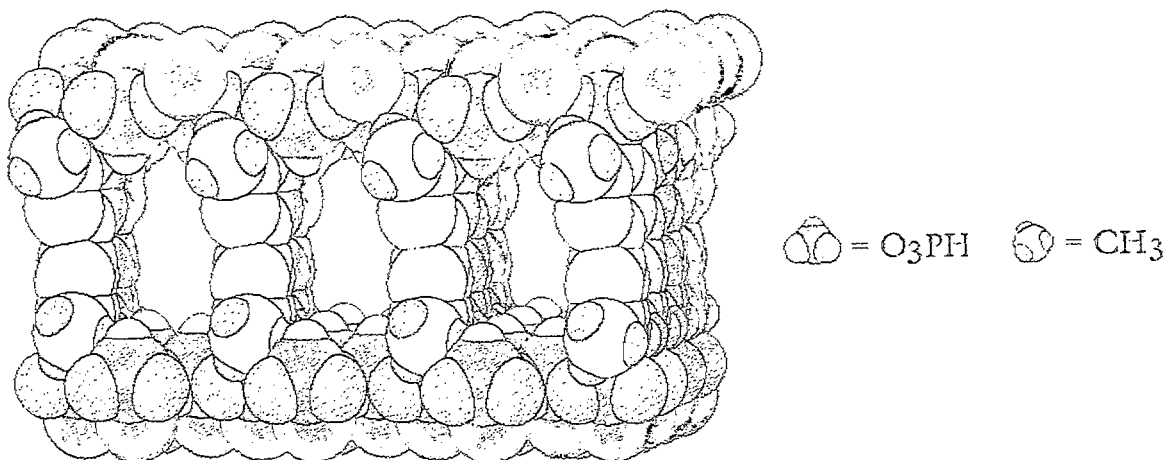


Fig. 3 A covalently pillared y-type zirconium phosphate diphosphonate (University of Perugia)

- 0 *Pillared Structures (PILS)*, in which inorganic polymeric species iono-covalently crosslink the layered host. PILS are, in the ideal case, thermally stable structures with at least a periodic one-dimensional order perpendicular to the layers. Pillared Layered Clays (PILCs), historically the first example of PILS, fall today within the wide sub-group of PILS, which corresponds to the

original definition of a PLS.

Fig. 1 illustrates such a material (ICMAT-CNR, Roma). Pillaring may be performed by intercalating directly a bulky inorganic polyion or by hydrolyzing and polymerising in situ an organometallic precursor. In order to obtain the cross-linked thermally stable material, a final calcination step is required in both cases, as summarized in Fig. 4.

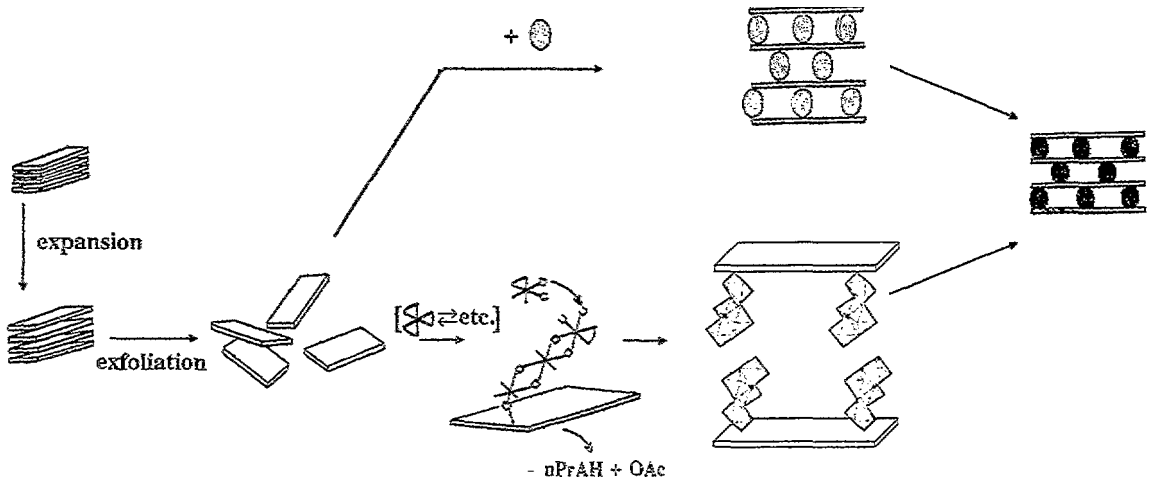


Fig.4 Some current methods for producing oxide-pillared layered solids

Alumina clusters still remain the most popular pillars, but an increasing variety of mixed alumina-based pillars are developed, such as Al-Fe , Al-Cu or Al-lanthanide oxides [] or even small perovskite-type La-Ni, La-Co or La-Mn clusters .

- ◇ *Colloidal nanocomposites (CNC)* which are, to some extent, the amorphous version of the previous subgroup. CNCs are poorly ordered materials, which can be prepared by simply mixing, concentrating and drying two colloidal suspensions (Fig.5). They may also be prepared by sol-gel methods or from ELS precursors . As far as porosity is concerned, CNCs are ill-defined materials but they may be very interesting for other purposes.

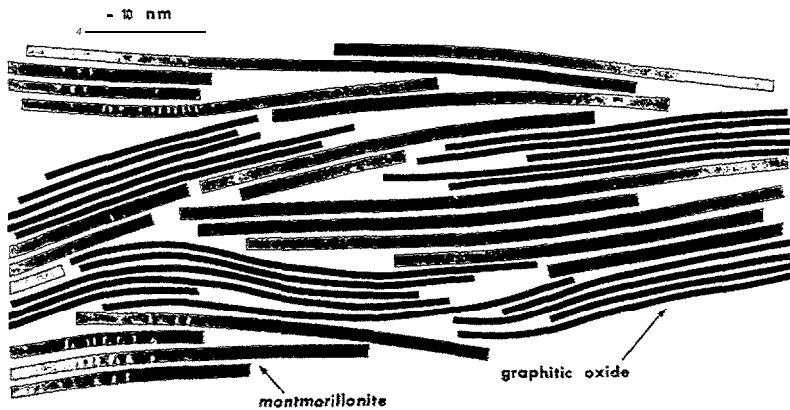
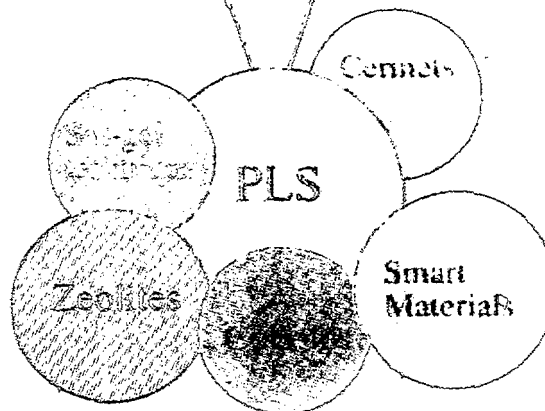
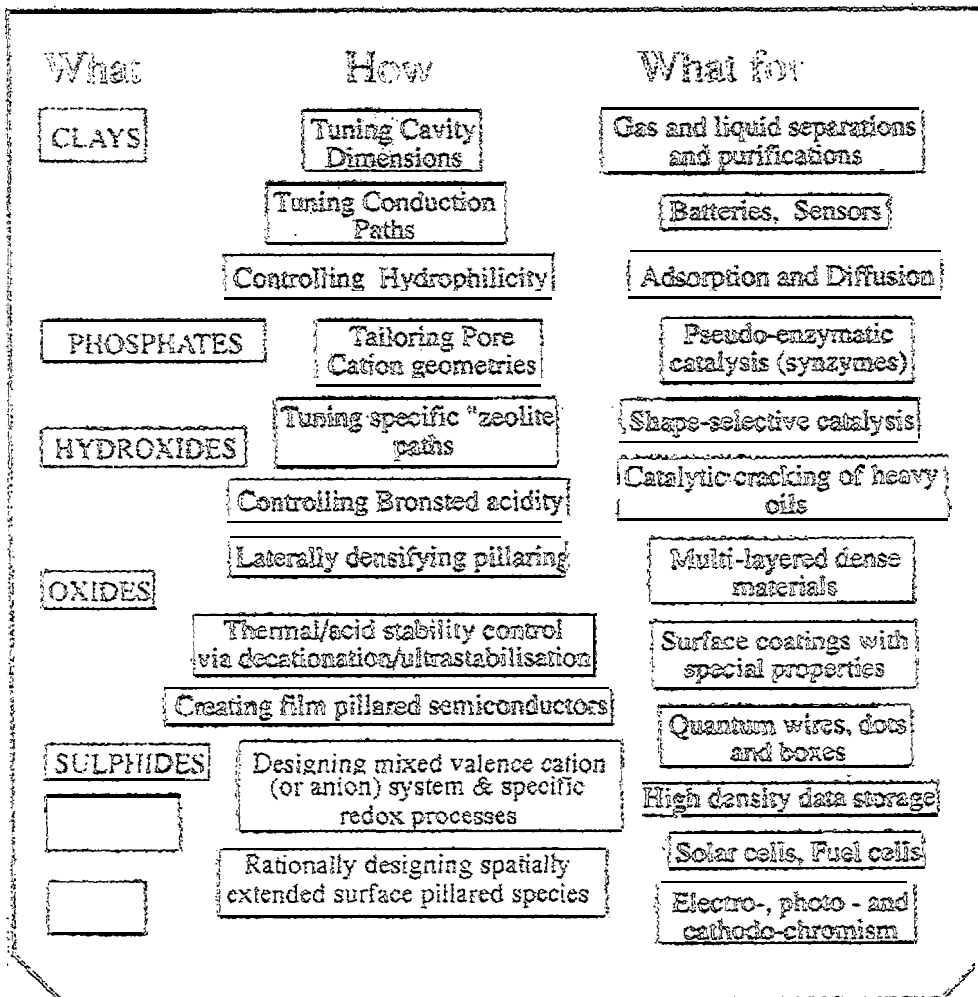


Fig. 5 Structure of a smectite clay - graphitic oxide colloidal nanocomposite .

In summary, the pillaring process opens the way to providing:

- *solids of enormous surface/volume ratio*, with accessible internal surface areas of up to $800 \text{ m}^2 \text{ g}^{-1}$,
- *a controllable internal structure* into which, in addition, reactive sites and reactive species can be readily introduced. These sites and reactants can be chosen to match the application being sought

The Range of Materials and Uses



and, of course, comprise a much higher proportion of the material than is the case in more conventional solids.

• *multifunctionality*, as far as chemical, catalytic, optical, ionic or electronic properties are concerned

As will be shown in section 3, this combination of properties permits to envisage a wealth of applications in the following fields:

- Heterogeneous- and supported homogeneous catalysis
- Separation and membrane technology
- Scavenging and controlled release for environmental, agricultural and pharmaceutical applications
- . Electrodes, electroactive materials and electronic devices
- . Photoactive Systems: pigments, photocatalysts, luminescent materials and optical devices.
- . Sensors
- Coatings

2. The CEA-PLS

The Co-ordinated European Activity on Pillared Layered Structures started officially on first of July 1991 for four years, with 24 academic and 5 industrial groups. In June 1995, it had extended to more than 50 groups, including 8 industrial companies []. The purpose of the CEA-PLS was to synergetically organize the growing activity in this field by:

- * bringing together the active european industrial and *academic* groups;
- * focusing their activity on application-oriented activities
- * sharing information and know-how by meetings and exchange of personnel
- * producing reference- or standart materials in the most important families of PLS materials.

During the four years of the project, 13 meetings with 20 to 55 participating groups were organized on topics such as « PLS in catalysis »; « PLS in organic synthesis »; « PLS in separation »; « PLS in environmental engineering processes »; « PLS in electrochemical applications » or « PLS-based sensors ».

Short- to medium-term staff-exchanges were encouraged and led to a total of more than 60 man-week exchanges between groups.

In collaboration with academic groups, two SMES (STRATTON Hi-Tee in Greece and Reagens Spa in Italy) produced kilogram quantities of three reference pillared clays and one reference layered double hydroxide:

- ◇ AZA: a Al-pillared clay prepared from a Greek bentonite which is a montmorillonite with a beidellitic character. Nitrogen BET surface area: 225 m²/g; d₀₀₁ X-ray diffraction spacing: 1,82 nm.
- ◇ FAZA: a mixed Al-Fe pillared clay prepared from the same parent material, Nitrogen BET surface area: 240 m²/g; d₀₀₁ X-ray diffraction spacing: 1.83 nm.
- ◇ ATOS: a Al-pillared saponite, prepared from a saponite clay from TOLSA S. A., Spain. Nitrogen BET surface area: 230 m²/g; d₀₀₁ X-ray diffraction spacing: 1.82 nm.
- ◇ One non-pillared Al-Mg LDH is proposed by Reagens s.p.a., Italy.

Each of these materials is now available upon request []. To our best knowledge, this is the first time that a set of reproducible pillared clays is available in large quantities to the european and international scientific community. Other *materials*, including Al-Cu pillared clays and pillared acid-activated clays are currently being prepared.

3. Selected results

3.1. Catalysis

In heterogeneous catalysis, PLS materials were shown to be particularly effective and selective for the following reactions:

- ◇ *Alkylation of benzene on pillared saponite.* Saponites are a type of trioctahedral smectites, not very common in Nature, characterized by the presence of tetrahedral substitutions of Si by Al, which gives these clays a high acidity. TOLSA s.a. has deposits of this mineral in Vicalvaro and Yuncillos, with a very high surface area and a high percentage of tetrahedral substitution. The activity of the Al-pillared saponites in the alkylation of benzene with n-dodecene in continuous flow gives very good results for long reaction times, with nearly quantitative conversions and linear alkyl benzene selectivities greater than SOY..
- ◇ *Isopropanol decomposition on AZA and FAZA reference materials.* The decomposition of isopropanol was studied by the Ioannina group as a probe reaction for the sake of comparison with Zeolithe-Y. Although the reaction rate is one order of magnitude higher on the Zeolithe than on the clays, the figures are almost equal when the comparison is made per unit surface area.

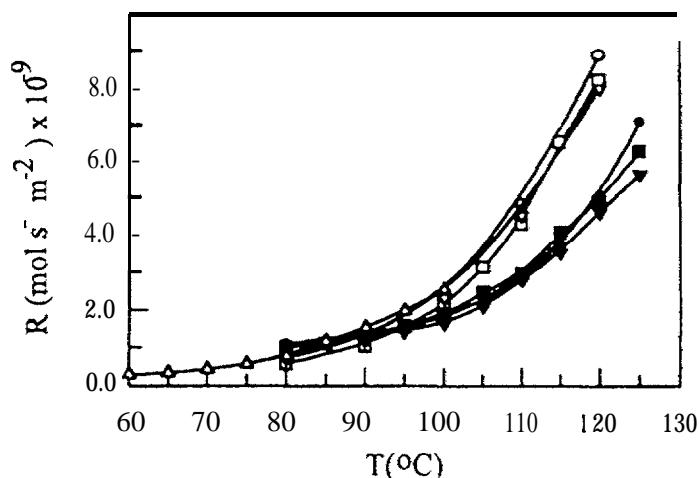


Fig. 6 Reaction rates versus temperature calculated per unit surface area of three granulometric fractions of AZA (open symbols) and FAZA (dark symbols). The data from Zeolithe-Y are also shown for comparison (Δ).

- ◇ *Cracking of n-heptane on Cc-Al and Ga-Al pillared clays.* Cc-Al- and Ga-Al-pillared clays were impregnated with Pt in order to use in the classical catalytic test of the hydroisomerisation-hydrocracking of n-heptane and the results were compared with those obtained with a commercial HY Zeolithe as reference by the Santander group. It was shown that the incorporation of Ce in the pillars increases dramatically the total conversion and yields high selectivity for cracking, approaching the results obtained with the reference Zeolithe.

◇ *Hydroconversion of normal paraffins.* Isomerisation of normal paraffins in branched isomers is of industrial importance because it allows to increase the octane number of gasolines. In this reaction, hydrocracked gaseous fractions (C 1 to C4 hydrocarbons) should be limited as much as possible. Hydroconversion is usually done over Pt/H-Zeolites (mordenites; faujasites).

In early work by the Louvain and Leuven groups, it was shown that Al-pillared beidellites were efficient catalysts for that reaction. Subsequent work showed that the nature of the starting clay had a determining influence on the catalytic performances of the catalyst. Beidellites, with tetrahedral lattice substitutions, were markedly superior to montmorillonites, with octahedral lattice substitutions. This was assigned to the formation of Si-OH.. Al acid sites by proton attack of tetrahedral Si-O-Al bonds in the beidellites.

It was confirmed by the Louvain group that pillared saponites, which also have tetrahedral lattice substitutions, are definitely better activities and produce higher yields of isomers than pillared montmorillonites. For each type of clay, the best results are obtained over the Al-pillared form. Zr-pillared clays are the least active and the mixed Al-Zr catalysts have intermediate performances.

◇ *Ethylbenzene conversion over pillared clays.* An extensive programme of catalytic scoping of oxide-pillared clays and group IV phosphates has been performed in the Monterotondo ICMAT-CNR and IC-CNR groups, with objectives related to conversions of petrochemicals feedstocks, starting from ethylbenzene (EB). Initial work on the EB to DEB conversion included extensive comparisons with mid-pore zeolites. PILCs give higher conversion and as comparable a selectivity for *p*-DEB, as ZSM-5 and other mid-pore zeolites. This might imply that PILCs contain specific pore exit channels of dimensions similar to those found in ZSM-5 zeolites rather than a random supermesh structure. Conversely, the low activity of pillared phosphates is attributed to carbocation formation.

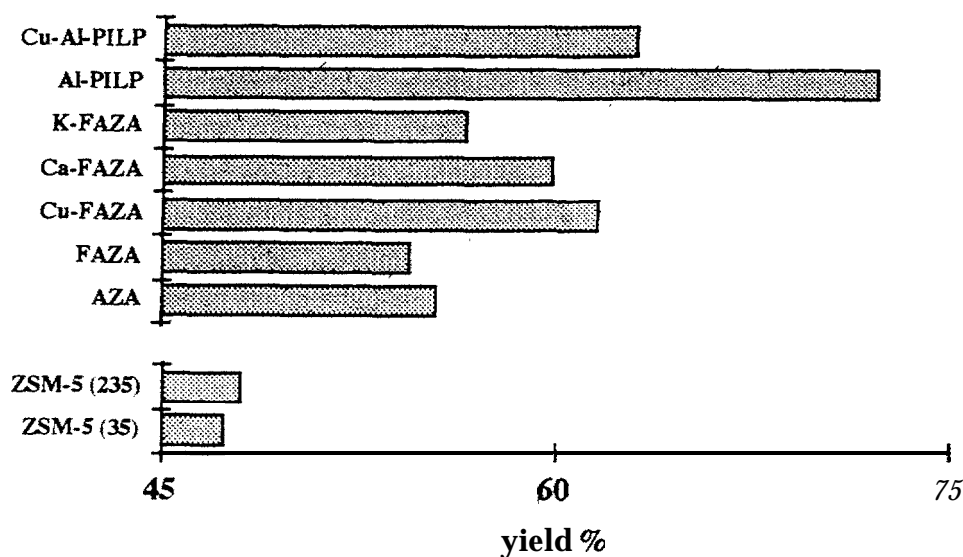


Fig. 7 p-Selectivity for ethylbenzene to diethylbenzene conversion on pillared clays (AZA and FAZA), pillared phosphates (PILP) and ZSM-5 Zeolite.

◇ *Syngas conversion on Al-Fe pillared smectites.* This was investigated by the Orléans and Poitiers groups on one hand and by the Madrid (Universidad Autonoma) on the other hand. Both set of results showed that these mixed-pillared materials are shape selective bifunctional catalysts for this reaction .

◇ *Propene conversion to acetone and deep oxidation of volatile hydrocarbons on bifunctional pillared clays.* The Venezia group demonstrated that a natural (i.e. non purified) bentonite pillared with Al, Al-Fe or Al-Ru polyoxocations were active catalyst for the vapor phase conversion of propene to acetone in the 150-350°C temperature range. On the other hand, bentonites pillared with Al-Cr, Al-Ru or Al-Fe are to varying degree active catalyst for the deep oxidation of volatile chlorinated hydrocarbons in the 300-400°C range. The G--material is by far the most active and stable catalyst, with a conversion larger than 99% at 300°C. The properties of this material appear to stem from the combination of an intermediate acid strength together with a good oxidant.

Expanded or Molecularly Crosslinked Layered Structures (ELS and MCLS) are ideal materials for supported homogeneous catalysis, provided the active site of the intercalated molecular species remains accessible to the substrate. This is the basis for pseudo-enzymatic catalysis with PLS. Several reactions were studied:

◇ *Organic substrates oxidation by hydrogen peroxide on iron-histidine intercalated in α -Zr phosphate.* This was investigated by taking indigocarmine as model substrate by the IMAI-CNR group at La Sapienza in Rome. The intercalated complexes were found to be more active than when they are used directly in solution with, in addition, the advantage of being anchored to insoluble matrices which minimize the losses and facilitate their separation and their recovering.

◇ *Selective hydrocarbon oxidation on manganese porphyrins incorporated or grafted to montmorillonite, phosphoantimonic acid or silica.* In order to reproduce the cyt-P-450 enzymatic selectivity, the Paris V group prepared pseudo-enzymatic catalysts by intercalation of metalloporphyrins into layered inorganic structures. The metalloporphyrin which plays the role of the active site, is the actual oxidation catalyst. The layered structure plays the role of the proteic chain of the enzyme.

Tetra-cationic and tetra-anionic manganese porphyrins have been intercalated within montmorillonite clay, phosphato-antimonic acid and LDHs. The interlayer spacing is small in montmorillonite ($A = 0.43$ nm) and much larger in phosphato-antimonic acid ($A = 1.15$ nm), suggesting a in-plane orientation in the clay and a tilted orientation in the phosphato-compound.

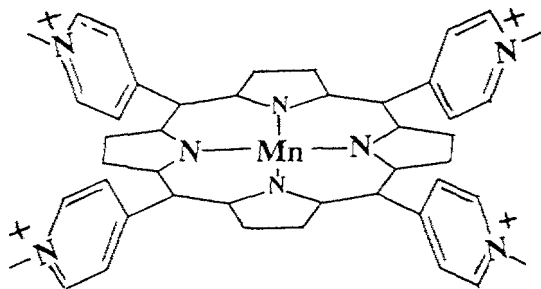
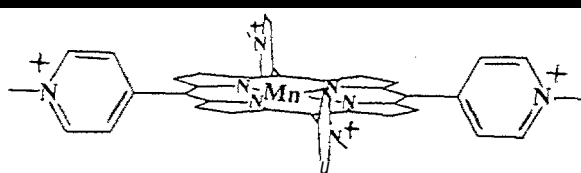


Fig. 8 Orientation of Mn tetracationic porphyrins in montmorillonite clay (left) and in phosphato-antimonic acid (right).

Some of these compounds are very good catalysts for alkene epoxidation and alkane hydroxylation by PMO. Even poorly reactive linear alkanes like ethane, propane, pentane, and heptane give high

oxidation yields, much higher than those obtained with the corresponding soluble manganese porphyrin catalysts. In addition, the porphyrin catalysts supported on montmorillonite exhibit a marked shape selectivity in favor of small linear unreactive alkanes like pentane.

3.3 Adsorption, separation, membrane

This is undoubtedly the application field which requires the finest control of the porosity. An important systematic work was performed by the Laboratory of Inorganic Chemistry of the UIA in Antwerp on the modification of pillared clays for adsorption and separation purposes, including. Three routes were extensively explored and shown to be efficient: *ion-modification* by cations or anions from an alkaline or acidified solution, respectively; *templating*, using amine molecules during synthesis; *carbon deposition* (coking), followed by controlled oxidation.

One example of application which was particularly studied is the removal or the separation of phenols. Heavy metal scavenging is another case.

◇ *Adsorption and separation of chlorophenols on columns of Al-PILCs.* At the University of Ioannina, it was shown that a prototype Al-pillared clay was a very good adsorbant for di(DCP), tri-(TrCP) and pentachlorophenol (PCP). Furthermore, the adsorption of the above chlorophenols on the clay from equimolecular mixtures of them proceeds to different extent in equilibrium. PCP is adsorbed by about 95%; TrCP by about 75%; and DCP by about 26%, in aqueous conditions and batch experiments. Equally interesting is the fact that resorption of the adsorbed species takes place easily using acetone or acetone-water mixtures, depending on the chlorophenol.

Going one step further, it was shown that the adsorption and resorption selectivity pillared clays can be used for *better and easier separation of the chlorophenols by liquid chromatography*. The process starts by adsorption of the chlorophenol mixture on the PILC column. Selective extraction is then performed by passing successively water, a water-acetone mixture and finally pure acetone. This methodology is a promising technique which might also be applied to other organic mixtures which up today are usually separated using traditional liquid-liquid extraction methods.

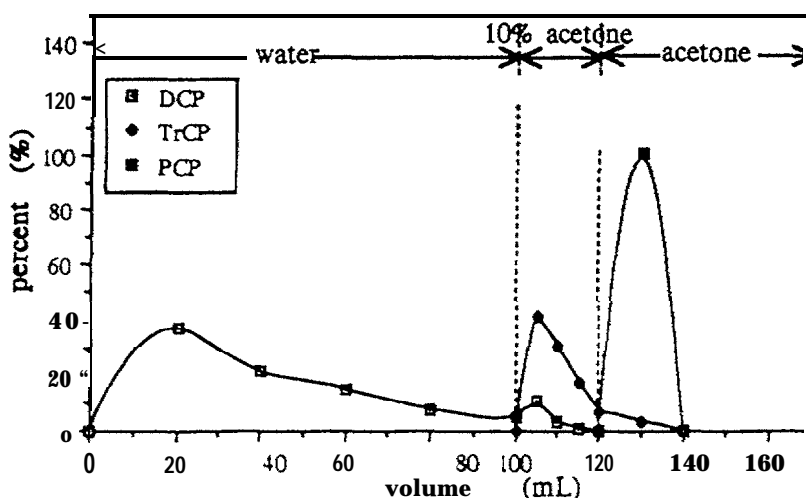


Fig. 9 Separation of DCP, TrCP and PCP by using columns of Al-pillared clay washed by the indicated solvents.

- ◇ *Removal of phenols from water using hydrotalcite-like compounds (LDHs).* The Cordoba group showed that trichlorophenol (TCP) and trinitrophenol (TNP) are both adsorbed by anion exchange in the interlayer space of the adsorbent. It was shown that calcination at 500°C allowed for the complete elimination of the organics with the concomitant decomposition of the hydrotalcite to a mixed magnesium-aluminium oxide, which can be totally recycled by dehydration and regeneration of the original LDH structure. The adsorption capacity of the regenerated product was shown to be identical to that of the initial material.
- ◇ *Heavy metal scavenging for environmental cleansing.* The Greenwich group has investigated the removal of heavy metals (Cd, Cr, Cu, Pb, Mn, Hg, Mo, and Zn) by alumina-, zirconia-, titania- and silica-pillared montmorillonite. Silica pillared clay is the best material. Special attention has been paid to silica-pillared montmorillonite for the adsorption of Pb. The adsorption was studied under both acid (pH4) and base (pH8) conditions. The exchange capacity was compared to washed sand, which is used industrially to remove water metals from waste water. The silica-pillared clay was able to reduce the concentration of Pb in waste water from 10 ppm down to 20 ppb, and was more effective than the acid washed sand. Problems still exist with clay regeneration.

.3.3 Environmental catalytic applications

The term « environmental catalysis » includes not only basic and applied aspects in the field of chemistry and engineering of pollution control through catalytic pollutant removal processes, but also new industrial achievements in the design of less polluting and/or safer catalytic processes.

- ◇ As an example of catalytic removal of pollutants, the Bologna group studied *the selective catalytic reduction (SCR) of NO by ammonia*, reaction of high industrial and environmental interest, on pillared clays and LDHs. Both AZA and FAZA reference materials exhibited good activities, with maximum conversion at 673K for AZA and at higher temperature for FAZA. Both catalysts formed as by-product N_2O (greenhouse gas) and exhibited similar values of maximum conversion of NO, notwithstanding the presence of iron in FAZA.

Taking into account the good CR behaviors of Cu-supported catalysts, AZA and FAZA were also used after cation-exchange with copper ions, with dramatic improvements of the catalytic performance. Cu-FAZA is particularly interesting since, contrary to Cu-AZA, it exhibits full conversion of NO over a wide temperature range with no deactivation. Furthermore, Cu-FAZA may be successfully employed in SCR of flue gases at high temperature, at which typical Cu-containing catalysts give rise to ammonia combustion.

On the other hand, the « anionic clays » (LDHs) were used for exploring the behaviour of iron, chromium and copper ions (well-known active elements in the SCR of NO), either as supported oxides, or as cations stabilized inside an inert matrix. The catalytic performance of the oxides supported on thermally decomposed LDHs was compared with that of the same oxides supported on active carbon, with the aim of obtaining catalysts stable in a wide range of conditions. The best results were obtained with supported CUO catalysts, whereas Cr_2O_3 was active at high temperatures only and Fe_2O_3 exhibited a low activity at all temperatures. On the other hand, with « stabilized ions » (catalysts prepared by thermal decomposition of M/Mg/Al precursors, where M=Cu, Fe or Cr), significant of the catalyst behaviour was observed but the best results were again obtained with the Cu-catalyst.

- ◇ *Catalytic oxidation of phenol by hydrogen peroxide with pillared clays* is another ease of removal of pollutant which was investigated by the **Orléans** and **Poitiers** groups. The catalytic oxidation of organic compounds in diluted aqueous medium, when the pollutant content or the Chemical Oxygen Demand (COD) is low (10 to 50 ppm), appears to be one of the most promising applications of PLS. Indeed, in such conditions, it seems important to increase the concentration of reagents in the vicinity of the catalytically active sites by adsorption in the microporous space where these active sites are located. At present, **Cu-exchanged Al-pillared clays** or **clays pillared with mixed Al-Cu pillars** appear to be the best catalysts, leading to removal of up to **80%** of the phenol in diluted conditions.
- ◇ As an example of clean catalytic process, the **Bologna** group studied the **vapour** phase hydrogenation of **maleic anhydride (MA)** using **Cu/Zn/Al** catalysts. This reaction is the most direct and economic way to produce **γ -butyrolactone (GBL)**, an important intermediate, without using hazardous feedstocks and avoiding problems related to the disposal of the catalyst (unlike that currently occurring with **chromite** catalysts). Furthermore, GBL is without doubt a **useful** intermediate in the production of new solvents on industrial scale, which are more environmentally acceptable than the present chlorine-based solvents.

The replacement of **chromite** catalysts was investigated by comparing the behaviour of **Cu/Zn/M** (**M=Cr, Al or Ga**) catalysts obtained by thermal decomposition of **LDH precursors**. The **Al-containing** catalysts exhibited better performances than the **Cr-catalysts**, while no significant difference was observed between **Ga-** and **Al-catalysts**. **Cu/Zn/Al** catalysts led to complete MA conversion and high yields in GBL, with maximum values obtained with an **Al-content** of about **17%** (atomic ratio) and a **Cu/Zn** ratio between 0.5 and 1. Furthermore, better carbon balances were observed for these catalysts, which may be attributed to lower light hydrocarbon synthesis and tar formation.

3.4 *Electrochemical and solid-state properties. Application to sensors.*

- ◇ *Laponite clay modified electrodes (LCME) for analytical applications.* Laponite is a synthetic hectorite which can be completely delaminated when suspended in deionized water at concentrations less than 10g/L. The drying of this sol onto an electrode surface leads to the formation of an adherent clay film. When transferred into an electrolytic medium, this film can incorporate water to a limited extent allowing the formation of a laponite gel electrode coating. The cation exchange capacity of this laponite gel can be exploited to incorporate into the coating various species such as cationic and anionic surfactants, redox dyes, electroactive mediators, pillar precursors. These properties have been exploited by the **Chambéry** and **Grenoble** groups to control the hydrophobicity and the ion exchange properties of the resulting modified electrode.

LCMEs allow the sensitive detection of cationic or procationic electroactive species using the preconcentration/voltammetry method. The analytical potential of LCMES for assaying hydrophobic organic cations such as model drugs covalently attached to cobalticinium or ferrocene redox labels has been demonstrated, in collaboration with the electrochemistry group in Clermont-Ferrand.

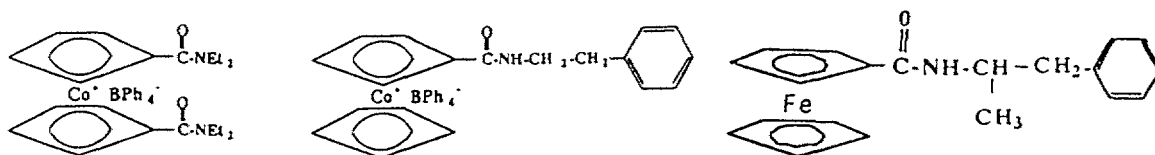


Fig. 10 Model drugs covalently attached to cobalticinium (left) and ferrocene (right) redox labels, intercalated into Laponite.

On the other hand, a new promising method has been developed for enzyme immobilization onto an electrode surface and its application to the elaboration of **amperometric biosensors**. This method is based on the enzyme entrapment within a **laponite clay gel** which occurs upon drying an enzyme **laponite clay sol** onto the electrode surface. The characteristics of the resulting bioelectrode (composition, analytical performance) are determined with **glucose oxidase** as an enzyme model. The method is simple, effective and non **denaturing**. In addition, the **cationic exchange capacity** of the **laponite matrix** can be exploited to **incorporate** in the biofilm **cationic compounds** such as enzyme stabilizers, redox mediators or polymeric precursors. **Methylene blue**, a **cationic redox dye** has been **incorporated** and polymerized within a **L-lactate dehydrogenase-laponite clay modified electrode** to **perform** the biodetection of L-lactate. The permeability of the enzyme **laponite clay gel** can be exploited to incorporate stabilizing additives. For example, exposition of the electrode biomaterial to **glutaraldehyde vapor** greatly improves the performances of the biosensor. By this method **glucose biosensors** have been prepared, without loss of sensitivity over three months of storage at 4°C and more than 450 assays.

- ◇ *PLS as protonic conductors and as electrolytes for fuel cells.* Crown ethers and polyethylene oxide) derivatives of **pillared clays** have been prepared by the **CSIC-ICM group** in Madrid [1]. The protonic conductivity is high and depends on the strength of the **oxyethylene-H⁺** interactions. On the other hand, solid electrolytes for direct methanol and hydrogen/air fuel cells have been prepared by the **Montpelleir (LAMMI) group** with Expanded Layered Structures, Molecularly Crosslinked Layered Structures and Pillared Layered Structures, using zirconium and tin phosphate. One of the best material identified to date is that formed by contacting **butylammonium tin phosphate** with a Keggin ion solution. The ELS produced by ion exchange **BuNH₄⁺/Keggin ion** has a conductivity of $3.10^{-2} \text{ Scm}^{-1}$ at 80°C and 100% RH and protons are the only charge carriers in the system. This represents an increase in the conductivity of tin phosphate by a **factor greater than 100**, the explanation of which lies in the formation of a **highly hydrated gel-like network** in the interlayer region, highly appropriate for **fast proton transfer**.

The above is an all-organic system. Some organic **Zr(Sn)P** intercalates are also protonic conductors. Amine and aminoacid intercalates have conductivities too low for fuel cell purposes, but **nylon-6-ZrP** (nylon produced *in situ* by thermally activated condensation of intercalated **aminocaproic acid**) can be reacted with phosphoric acid. The **resulting material** has a conductivity higher than 10^{-3} Scm^{-1} . This system may be considered as an organised **analogue** of the known « polymer blends » of phosphoric acid and polyamides used as **protonic electrolyte** in smart windows.

For any **practical use**, the electrolyte must be shaped into a form suitable for **incorporation** into a device. For **fuel cells**, and for transport purposes in particular, the electrolyte membranes should be flexible and should retain the properties of the bulk conductor as much as possible. In this line, the organic-inorganic and all-inorganic **ELS** have been included in **organic polymers**, either from soluble **polymer/solvent systems** or by **UV-induced polymerisation**.

- ◇ *Humidity sensors based on a screen-printed anionic clay (LDH)* have been developed by the Clermont-Ferrand (Physico-chimie des Matériaux) group []. The ionic conductivity of LDHs intercalated with a variety of anionic species may be rather high. It is mainly **protonic** (like in the above-mentioned polyethylene oxide) derivatives of **pillared clays**) and closely related to the hydration state of the compound. These materials can therefore be used as humidity sensors provided a reliable device could be formed. Such a device has been constructed with $Zn_{0.67}Al_{0.33}(OH)_2Cl_{0.33} \cdot nH_2O$. The forming of the material by *screen printing* has been optimized in order to obtain adherent thick layers with regular levelling and a good resolution on alumina substrates. Two devices have been studied, one working on A.C. with a two-electrode geometry, and the other on D.C; with a four electrode geometry (Fig. 11). Compared to other humidity sensors based on conductivity or capacity effects, these sensors give a **fast response** and can be produced at low cost in mass production. They could be integrated in micro-ionic devices or in hybrid electronic circuits

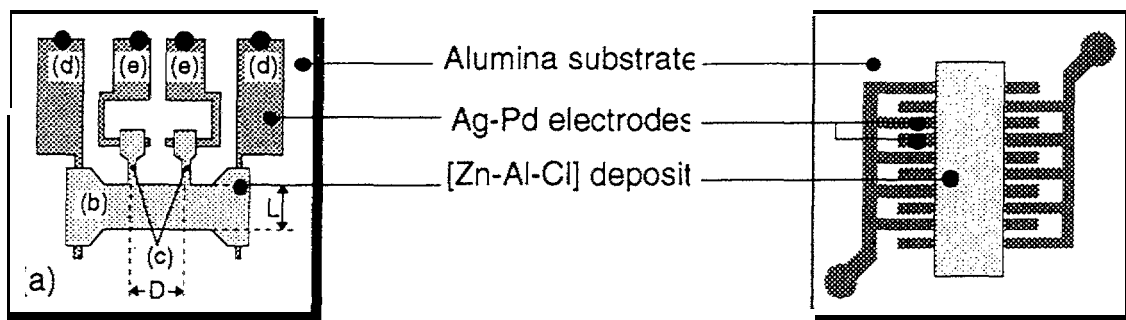


Fig. 11 D.C. (left) and A.C. (right) humidity sensors.

3.5. Optical properties and devices,

In information technology, a **photonic** or optical material is any material with which light interacts for the purpose of information generation, transmission, detection, conversion, display, storage or processing. Advancement in the field requires the synthesis of new materials or, at least, a suitable modification of known materials.

- ◇ *Non-linear optical properties of mineral-dye nanocomposites.* Dye molecules have found broad applications in the generation of laser light. They also have all properties needed for different types of non-linear processes, if they are (i) organised in a host matrix in such a way that they can act collectively; (ii) distorted or in a bistable state for optical switching and information storage. Minerals as hosts for dye offer various advantages such as thermal, mechanical and chemical stability. Their regular crystal structure offers the right conditions for orientation and polarisation. Layered materials such as clays are ideally suited to organize dye molecules in such a way as to generate non-linear optical properties.

The Laboratory of Surface Chemistry of the Leuven University [] has prepared stable crystal violet - laponite suspensions with a loading between 0 and 10% of the cation exchange capacity, and measured the hyperpolarisabilities by Hyper Raleigh Scattering (HRS). Typical parabolic curves are obtained when the intensity is plotted against the intensity of the harmonic (Fig. 12). Furthermore, a quasi-linear relation is found between the second harmonic signal intensity and the

concentration of dye in the suspension. This opens the way to SHG using clay-dyes nanocomposite films.

- ◇ *Size quantization of semiconductors particles in PLS.* Silica-pillared metal (N) hydrogen phosphates have been used by the Montpellier LAMMI group as templates for size-quantization of metal sulfide particles *via the* sorption of Zn^{2+} and Cd^{2+} ions from aqueous solution of their acetates, followed by reaction with H_2S in acetone. Band gaps obtained from optical absorption spectra for occluded ZnS and CdS are significantly increased from those of the corresponding bulk metal sulfides e.g. for bulk ZnS: 3.4 eV; confined ZnS: 4.3 eV. X-ray absorption spectra carried out at the Zn and Cd edges suggest that the discrete « molecule-like » Zn(Cd)S semiconductors confined in the micropores interconnect through windows in the pillar network to form more extended « supercluster » structures.

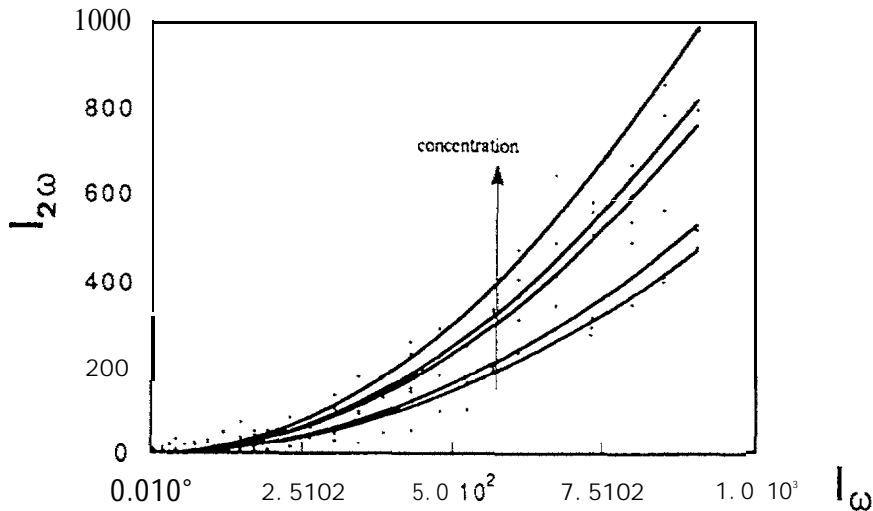


Fig. 12 Second harmonic generation with clay-crystalviolet

3.6. PLS as precursor or additive for other materials: Hydrotalcite as heat stabilizer (in production,.

Traditional heat stabilizer for PVC such as Pb salts show an increase of their stabilizing effect proportional to dosage. Unfortunately, the metal-free stabilizers do not show the same behaviour and only at low dosage is their stabilizing effect proportional to the amount added. The most interesting characteristic of hydrotalcite as heat stabilizer is that, whether the dosage is normal or high, the stabilizing effect increases linearly, like for the heavy metal based (toxic) stabilizers. Hydrotalcites show good synergetic behaviour when used together with other non toxic stabilizers, co-stabilizers, antioxidant in several fields (e.g. pipes, profiles, wires and cables, extruded and calendred sheets, etc). Dehydrated hydrotalcites show interesting in rigid PVC. They are produced by Reagens S.p.A., member of the CEA-PLS .

4. Conclusions

More than ever, Pillared Layered Structures and related materials appear as an extremely rich family of . Several convincing prototype uses were demonstrated at laboratory level. This includes processes or devices which are important for the petrochemical industry (gasoline; key intermediate for the chemical industry), clean industrial processes, environmental applications in cleansing, gas separation and chromatography, energy storage (batteries, fuel cells) and sensors. The examples include:

- * catalytic alkylation reactions (TOLSA S. A., Madrid);
- * hydroisomerisation of normal paraffins (Université Catholique de Louvain, Physico-chimie de la Matière Divisée);
- * catalytic styrene production (ICMAT-CNR and IC-CNR, Monterotondo);
- * ethene epoxidation catalysis for glycol ethers production (BP Chemicals, Sunbury, UK);
- * clean production of γ -butyrolactone (University degli Studi di Bologna, Dipartimento di Chimica Industrial);
- * cleaning edible oils from chlorophyllin residues (Department of Chemistry, University of Cambridge);
- * phenols removal from polluted water by adsorption (The University of Ioannina, Department of Chemistry) and by catalysis (Centre de Recherche sur la Matière Divisée, Orléans and Laboratoire de Catalyse en Chimie Organique, Poitiers);
- * nitrogen/oxygen separation (Universitaire Instellingen Antwerpen, Laboratory of Inorganic Chemistry);
- * heavy metal scavenging in waste water (School of Biological and Chemical Sciences, University of Greenwich);
- * smoke filtration (Universitaire Instellingen Antwerpen, Laboratory of Inorganic Chemistry);
- * biosensors (ESIGEC-University de Savoie, Laboratoire de Chimie Moléculaire);
- * humidity sensors (Université Blaise Pascal, Laboratoire de Physico-chimie des Matériaux);
- * protonic conductors for fuel cells (ICM-CSIC, Madrid and LAMMI, Université de Montpellier);
- * non-linear optical devices (Laboratory of Surface Chemistry, Katholieke Universiteit Leuven and LAMMI, Montpellier);
- * heat stabilizers for plastics (Reagenspa, Bologna);
- * and many others . . .

Whilst catalysis undoubtedly remains the most important application field, this impressive list confirms the broadening of the application fields, as compared to what they were a few years ago.

5. Acknowledgments

This paper is the **collective** work of all the group members who participated in the CEA-PLS:

G. Poncelet, University Catholique de Louvain, Groupe de Physico-chimie de la Matière Divisée (B); J. Luyten and Z. Vercauteren, Vlaamse Instellingen voor Technologisch Onderzoek (VITO), Mol (B); E. Vansant, A. Molinard and N. Maes, Universitaire Instellingen Antwerpen, Laboratory of Inorganic Chemistry (B); R. Schoonheidt, Katholieke Universiteit Leuven, Laboratorium voor Oppervlaktechemie (B); H.C. Bruun Hansen, Royal Veterinary and Agricultural University, Chemistry Department, Copenhagen (DK); C. Bender Koch, Department of Applied Physics, Technical University of Denmark, Lyngby (DK); J. Barrault, Université de Poitiers - Laboratoire de Catalyse (F); P. Battioni, University René Descartes, Laboratoire de Chimie et de Biochimie Pharmacologiques et Toxicologiques, Paris (F); J.P. Besse, C. Forano, A. De Roy and M.E. De Roy, University Blaise Pascal, Laboratoire de Physico-Chimie des Matériaux, Clermont-Ferrand (F); C. Mousty and C. Degrand, Université Blaise Pascal, Laboratoire d'Electrochimie Organique, Clermont-Ferrand (F); G. Bissery, SOLETANCHE, Nanterre (F); D. Jones and J. Rozières, University de Montpellier H, Laboratoire des Agrégats Moléculaires et Matériaux Inorganiques (F); P. Labbe, S. Cosnier and T. Besombes, Laboratoire d'Electrochimie Organique et de Photochimie Redox, Université de Grenoble (F); L. Michot, Laboratoire Environnement et Minéralurgie, INPL, Nancy (F); P. Palvadeau, Y. Piffard, J. Rouxel, B. Bujoli, Institut des Matériaux de Nantes, University de Nantes (F); ESIGEC-University de Savoie, Chambéry (F); H. Suquet and J.F. Lambert, Laboratoire de Réactivité de Surface et Structures, University Paris VI (F); H. Van Damme, F. Bergaya, M. Crespin, J. Choisnet and F. Beguin, Centre de Recherche sur la Matière Divisée, CNRS and Université

d'Orléans (F); N. Gangas, **STRATON Hi-Tee Ltd**, Athens (GR); T. Bakas, The University of Ioannina, Department of Physics (GR); P. Pomponis, The University of Ioannina, Department of Chemistry (GR); D. Petridis, Democritus National Center for Scientific Research, Institute of Materials Science, Athens (GR); N. Papayannakos, National Technical University of Athens, Department of Chemical Engineering (GR); R. Barklie, Trinity College - Physics Department, Dublin (IR); D. Doff, Trinity College - Geology Department, Dublin (GR); G. Alberti and U. Costantino, University di Perugia, Chemistry Department (I); M. Lenarda and L. Storaro, University degli Studi di Venezia, Dipartimento di Chimica (I); M. Berna, REAGENS SpA, Bologna (I); P.G. Zappelli, ENIRICERCHE SpA, Monterotondo (I); A. Tomlinson, ICMAT - CNR, Monterotondo (I); C. Ferragina and P. Patrono, LM.A.I.-C.N.R., Monterotondo (I); M.A. Massucci, Istituto di Chimica Inorganica, University di Roma "La Sapienza" (I); A. Vaccari, Università degli Studi di Bologna, Dipartimento di Chimica Industriale e dei Materiali (I); R. van Santen, Eindhoven University of Technology, Laboratory of Inorganic Chemistry and Catalysis (NL); C. Sequeira, Laboratório Electroquímica, Instituto Superior Técnico, Lisboa (P); A. Jimenez-Lopez, E. Rodriguez Castellon, P. Olivera Pastor, S. Bruque Gamez, Universidad de Malaga, Departamento de Química Inorganica (SP); S. Mendioroz Echeverria, M.A. Martinluengo, Insitituto de Catalisis, Campus Universidad Autonoma, Madrid (SP); C. Pesquera, Departamento Química. Facultad Ciencias, Universidad de Cantabria (SP); V. Rives, Departamento Química Inorganica, Universidad de Salamanca (SP); M.A. Ulibarri, Departamento Química Inorganica, Facultad de Ciencias, Universidad de Cordoba (SP); J. Rodriguez, E. Jaimez, Facultad de Química, Universidad de Oviedo (SP); E. Ruiz-Hitzky, B. Casal, P. Randa and J.C. Galvan, CSIC Madrid - Instituto de Ciencia de Materiales (SP); A. Alvarez and E. Gutierrez, TOLSA S. A., Madrid (SP); G. Bratton, School of Biological and Chemical Sciences, University of Greenwich (UK); C. Breen, University of HALLAM, Sheffield (UK); M. Hudson, University of Reading, Department of Chemistry (UK); W. Jones and R. Mokaya, University of Cambridge, Department of Chemistry (UK); H.J. Purnell, University of Swansea, Chemistry Department (UK); M. Atkins, BP Chemicals, Sunbury (UK); E. Odom, VOLCLAY Limited, Wallasey (UK); E. Fowles, LAPORTE Research& Development, Widness (UK),

A brochure with full addresses of participants is available upon request to H. Van Damme, CRMD, CNRS and University d'Orléans, F-4507 1 Orléans cedex 02, hvd@admin.cnrs-orleans.fr

It is also obvious that this Concerted Action was made possible thanks to the support of the European Community (Brite Euram, contract BRE2-CT9 1-0462, project BE-47) who not only provided financial support but also the right framework for such large collective information exchange and cross-fertilization actions. I.V. Mitchell is particularly acknowledged for his impulsing action and his continuous interest in this project.

6. References

For a general review of the state at the art a few years ago: Pillared Layered Solids: Current Trends and Applications, I.V. Mitchell Ed., Elsevier Applied Sciences (1990).

On the other hand, the work reported in the present synthesis report gave rise to more than 300 papers and patents. A comprehensive list is available upon request to H. Van Damme, CRMD, CNRS and Université d'Orléans, F-4507 1 Orleans cedex 02; E-mail: hvd@admin.cnrs-orleans.fr