

## Porous solids:

I

Genesis, mechanisms of formation, structures and their applications in the **domains** of energy, sustainable development and health.



Achievements of Pr. Gérard FEREY

### Note to the reader

#### Achievements ?...

I like the originality of Georges Seurat, the French painter of the XIX<sup>th</sup> century. He was the inventor of pointillism, a new style of painting which, starting from a random cloud of dots of pure colours, *a priori* without any relation to each other, arrived to a coherent representation of, for instance, an elegant body, a nice landscape, or a famous monument, according to the inspiration.



In the same way, a young chemist is also a cloud of dots during his first research experiences. Later, if he is creative, he will find his orientation from his inspirations, assemble the different clouds in a personal way and will realise one or several paintings over the years : his achievements.

It is time for me to expose my paintings. Only my last 20 years of **research**, **exclusively dedicated to porous solids** first inorganic and then hybrid, will be detailed in this pages. After a CV, some quantitative informations and a preface presenting my philosophy of research in this domain, the corpus of my scientific activity will follow.

This corpus will be divided in three parts, respecting the temporal evolution of my works.

The first is dedicated to templated inorganic porous solids. The two others concern organic-inorganic hybrid porous solids, often called Metal-Organic Frameworks (MOFs) or Porous Coordination Polymers (PCPs). In Part 2, the presentation is exclusively reserved to a new and strange phenomenon in the crystallized solid state : the **« breathing effect »** that I discovered in 2002, simultaneously with a Japanese colleague (Pr. Kitagawa). It exhibits very large reversible variations of the cell volumes of the flexible solids (> 300%) without any loss of crystallinity. I was alone, however, to explain at the molecular level its origin and its properties. The last part, oriented by an integrated strategy, is a general description of my contribution to the knowledge of this fascinating new class of solids, either rigid or flexible, from the chemistry to the properties and applications, through the mechanisms of formation and structural prediction.

The list of my publications and invited lectures will appear at the end of this booklet.

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□ AND NOW...



### PREFACE

### A brief overview of the origin, the used strategy, The results and applications of porous solids

This document represents the works I performed with my young group since 1992 on new porous solids. With the years, these compounds are now considered as strategic materials.

This topic began in 1756 with the discovery by A.F. Crönstedt of the strange behaviour of mineral stilbite, a sodium calcium aluminosilicate, the first zeolite. This new class of solids, natural or synthetic, attracted continuous academic and industrial interest for the search of new solids and their applications which mainly concerned, even recently, petroleum industry, catalysis, gas separation and fine chemicals. Some authors consider that, directly or indirectly, these materials generate 15-20% of the Gross Domestic Product of the industrial countries.

The outstanding properties of zeolites and related compounds were due to a unique triple structural characteristic of these solids, first evidenced in 1930 simultaneously by L. Pauling and J. Moore: (i) an inorganic skeleton of atoms (metal aluminates, silicates, phosphates, arsenates...) bound exclusively by strong bonds, within which periodically appear (ii) pores generated by the templates (mostly organic amines) used for the reaction at the surface of which the atoms with unsatisfied bonds create a reactive internal surface which will play a role for catalytic reactions and gas adsorption.



Until recently, these porous solids had only an inorganic framework, even the amorphous mesoporous materials discovered by Kresge (1992), and the literature reports thousands of new solids, with often their structures and some properties (see *Handbook of porous solids*, by F. Schüth, K.S.W. Sing and J Weitkamp, Wiley-VCh (2002)).

After having devoted many years to the structural chemistry and physics of inorganic fluorides of 3d transition metals, our entrance in the theme in 1992 was motivated both by an aesthetical attraction toward these fascinating structures and by the hope to bring some originality in the community, by introducing more physical chemistry than before.

This implied first to become familiar with the chemistry of theses solids, adopting the well known trials-and-errors method for the syntheses, usually performed in hydrothermal medium, a technique with whom we were already familiar. By varying the classical physical parameters (temperature, pressure, pH, concentrations) and the nature of the templates, many new compounds, – corresponding to purely inorganic skeletons - were isolated and their structures solved, as all chemists usually do.

At that time, my past of crystal chemist was of great help. I indeed noticed that, among the various observed structures, some invariants appeared. This remark influenced the rest of my trajectory over the years. Instead of regenerating the structures from the 3D translation of the independent crystallographic sites deduced from crystallography, it appeared that this regeneration could be done from the juxtaposition of polynuclear species, called secondary building units. That was true for inorganic porous solids, but I showed that it was general for all the known inorganic structures (see my article: "Building units, design and scale chemistry", *J. Solid State Chem.* **2000**, *152*, 37-48). It provided first a new way for regarding structures.

#### The onset of an original strategy

A question then arose. Was it just a new way of description of structures or, beyond, was it the indication of an approach for elucidating the mechanisms of formation of these porous solids?

Indeed, if the community *observed* the formation of new solids, was able to solve their structures, nobody had explained experimentally how these solids form, despite theoretical hypotheses for doing so...

In other terms, the evidence of these secondary building units (hereafter labeled SBU) could signify that the latter could be the reactive species *during* the reaction, before their assembly at the end of the reaction. For being credible, this heterodox idea had to be tested experimentally by developing methods able to identify in real time, during the hydrothermal reaction at 200°C and 30 bars, the reactive species leading to the final product. It was a challenge that we are always alone to have realized by using various complementary *in situ* techniques (NMR. IR, EXAFS, diffraction) which converge toward the same conclusions.

The foreseeable consequences of such a hypothesis were numerous. Indeed, if it was true:

• the mechanism of the reaction would be solved and the reactive SBU identified;

• an examination of the possibilities of connection between these SBUs would become possible with a recourse to computer simulation. Among them, the experimental one exists, The structural solution is obtained just from a comparison between the theoretical and observed X-ray powder patterns. This opens the way to the prediction of structures;

• it opens the possibility of rationally obtaining 'tailor-made' solids from a given SBU ;

• this would have important consequences for the companies, always asking for precise or tunable dimensions of the pores for dedicated applications (energy, health...)

This strategy, despite unusual in the community of porous solids, was proved to be successful. It is at the origin of the now worldwide recognition of our works.

#### Solids concerned by this strategy

They were successively of two types:

#### 1. Inorganic porous solids templated with amines (1992-1997).

Our strategy aiming at a clarification of the mechanisms of formation of these solids implied a careful choice of the chemical elements present in the structures. Indeed, as we privileged *in situ* NMR for solving the problem, most of them had to correspond to resonating nuclei in order to collect a maximum of independent informations for establishing the mechanisms. We chose initially the synthesis of aluminum and gallium oxyfluorophosphates templated with various amines for this purpose.

In a first step, many solids (*labeled ULM-n* - *for University le Mans* - because the work was done in Le Mans) were obtained by trials and errors and structurally characterized, including a porous gallium phosphate which evidenced the largest pores ever discovered at that time (ULM-5). A strong correlation appeared between the experimental parameters (P, T, pH...) and the nuclearity of the SBU, inciting us to go further in the knowledge of the formation of ULMs. Two new solids were selected for their simple structures based respectively on tetrameric and hexameric SBUs for trying to elucidate how they form.

*In-* and *ex-situ* NMR methods were privileged both for using its local probe properties to complement X–ray diffraction but mainly to follow the evolution of the spectra of each nucleus during the reaction (200°C, 30 bars) for proposing a mechanism with a maximum of independent informations. It was done, showing the progressive condensation of monophosphate complexes leading the observed SBUs, and also the key role that the charge density of the amines play during the reaction. This will be explained in detail in part 1 of the present notice.

Once demonstrated, <u>during</u> the reaction, the reality of the existence of the SBUs which are found in the final structure, the extension was to replace Al and Ga in the framework by transition metals for inducing physical properties which were never evidenced before. This lead to new series based first on Fe<sup>3+</sup> which provided the first examples of magnetic porous solids. They were followed by other series of already unknown (i) porous vanadium fluorophosphates for which EPR was a good tool of characterization and of (ii) titanium III and IV fluorophosphates (now used as precursors for white paintings) whose mechanisms of formation were also elucidated, evidencing other types of SBUs.

The reality of reactive SBUs during the syntheses induced a new step in our approach. Their geometry being known, it became possible to look at all the possibilities (real or virtual) of connection of these SBUs to ensure a threedimensional porous framework. Experimentally, it would have taken tens of years. Computer simulations take some days, as soon as a program exists. We wrote it successfully and reached the prediction of structures. At that time, it was not usual in the community but brought a new dimension to my career, and provided another tool that I systematically use now in several domains.

Despite exciting on the front of intellectual knowledge, this topic was rather disappointing regarding possible applications. First, the solids we created do not present spontaneously any porosity, due to the presence of templating amines in the pores. Even necessary for the synthesis, they are strongly fixed to the inorganic skeleton and very difficult to extract for rendering the solid porous. Very often, and unfortunately, the structure collapses during the extraction. It is the first default. Independently of the real accessibility to the pores, the second one relates to their size. Even for the largest, they are microporous (diameter < 2 nm) and their dimensions remain small for numerous applications. This is due to the use of tetrahedrally coordinated anions (silicates, phosphates) and the small nuclearity of the SBUs. The exciting discovery of mesoporous solids circumvented this limitation but, in particular, their amorphous character drastically restricted their potential.

These various constraints: difficulty of extraction of the template, limited accessibility, need of large pores... explained our orientation toward the field of hybrid porous solids, pioneered by R. Robson in 1989.

#### 2. Hybrid organic-Inorganic porous solids (1997-...).

Robson was a coordination chemist. Initially, he wondered about the possibility of designing and constructing ligands intended to bind two metal centres in close proximity for creating first binuclear and then tetranuclear compounds. From this idea, a progressive incrementation lead him to discover the first coordination polymers, with a hybrid organic-inorganic three-dimensional framework. [B. F. Hoskins and R. Robson, J. Am. Chem. Soc., 1989, **111**, 5962; J. Am. Chem. Soc., 1990, **112**, 1546].

I am a solid state scientist and my approach, purely structural, was completely different. From my previous experience on crystallized purely inorganic porous frameworks, I had had the regret to observe that the dimensions of the pores were always rather small. My analysis was that the small size of tetrahedral anions (silicates, phosphates) linked to the metallic cluster was responsible of these limited dimensions, which prevented from any modulation of the size of the pores and their windows. Therefore, as soon as it became possible to replace tetrahedral anions by organic ligands linked to these clusters, the above limitation was overcome. The size of the pores could become easily tuned as a function of the characteristics of the ligand (length of the carbon chain, curvature...). This was the first step of my evolution toward hybrid solids chemistry, which first concerned polyphosphonates as a continuum of my previous experience, but I rapidly chose poly-carboxylates, more numerous and which, through the COO functions, have the advantage of only two possible connections with the inorganic part.

The second question was : can the solid be built from SBUs, as it was the case for the purely inorganic porous frameworks ? The reply needed to perform once more *in situ* measurements, this time EXAFS and NMR, which here also proved the reality of the SBU during the reaction

The third question arose from topological considerations. How the structure can be considered ? The final structure is the result of the combination of organic and inorganic connectivities (*connectivity : number of connections that a moiety (for example the ligand) can give with the other type of moiety (the metallic cluster*). Their association provides the hybrid SBU, the global connectivity of which determines the structure, the size and tunability of the pores through their the length of the carbon chain of the ligand.

Fig.1. – Scheme of the formation of an hybrid framework described in terms of connectivities (3 for the ligand trimesate, 4 for the inorganic cluster (here a dimer of copper(II)). Their association generates the framework from the resulting 4-connectivity of the hybrid SBU (red: oxygen; grey: carbon; blue polyhedron: copper).



Fig.1. – Scheme of the formation of an hybrid framework described in terms of connectivities (3 for the ligand trimesate, 4 for the inorganic cluster (here a dimer of copper(II)). Their association generates the framework from the resulting 4-connectivity of the hybrid SBU (red: oxygen; grey: carbon; blue polyhedron: copper).

It became clear that the connectivity of the inorganic SBU (also called 'brick' in the following) played a key role in the construction of the structure of the final solid. However, whereas the organic ligand remains unchanged during the reaction, the problem of the inorganic brick is that its nature and nuclearity are strongly dependent on the <u>real</u> chemical conditions of the synthesis reaction (pH, temperature...). Therefore, if one wants to obtain 'tailor-made' solids, instead of those resulting from the' trials and errors' method, it is necessary to correlate the structure of the inorganic brick with the synthesis parameters during the reaction.

For that, two ways: (i) either choose inorganic precursors containing clusters which remain invariant after reaction with organics, but it is rather rare; (ii) once more, perform dedicated *in situ* measurements for observing the evolution of species during the reaction, up to the formation of the formation of the final brick. This implies a careful choice of the cations (ex.: Al<sup>3+</sup> for NMR studies) for obtaining pertinent local informations on the synthesis pathways. For each way, an example will be presented.

This means that, starting from the initial experience of 'trials and errors' syntheses, we went further by a systematical recourse to physical chemistry for understanding the formation of these hybrids, leading downwards to an approach of 'tailor made' chemistry of these solids in the same way as it was developed by us for purely inorganic porous frameworks. Once elucidated the reactive bricks, computer simulations can enumerate the list of all the possible connections between a reactive inorganic brick and a ligand. We adapted our previous program to the case of hybrid solids. The creation of this virtual library provides many solutions. Once classified the different virtual structures by decreasing lattice energies, a few (3-4) theoretical solutions, reasonable in terms of energy, emerge and contain the experimental structure. The numerous advantages of such an approach which remains unique in the community, will be detailed in Part 2 with the examples of the mesoporous crystallized MOFs MIL-100 and -101 (*MIL standing for Materials of Institut Lavoisier*).

With such an integrated approach, we were able either to come back to chemistry with new ideas, tested experimentally by a rational choice of the initial chemical parameters, or think about properties and their possible applications.

At this stage of the study, we had only envisaged rigid porous solids. In 2002, we however discovered simultaneously with S. Kitagawa in Japan a new property of the crystallized solid state matter: the occurrence of large reversible swelling effects with variations of volumes in the range 40 -300%. It was initially considered as a curiosity, but I very quickly understood that, beyond the spectacular effects, it deserved to be thoroughly studied and explained, not only from a chemical point of view but also from a physical one. Indeed, such a sensitive flexibility could provide quantitative informations on the nature and the strength of the interactions between the framework and the guests inserted within the pores. These guests, at variance to what occurred in purely inorganic porous frameworks, are not the strongly fixed templating amines, but solvent molecules, less bound, which can therefore be easily evacuated. The intensity of swelling is therefore directly related to the strength of the host-guest interactions. The latter govern the physical coditions required for obtaining activated samples in which the pores are empty and therefore usable for potential applications. This topic - hereafter called 'breathing effect' – represents an important and always expanding domain of our research.



Fig.2. – Structures of the chromium(III) terephthalate MIL-53 in its hydrated (left) and anhydrous (right) forms represented at the same scale (colour code: Cr: green; C: grey; O: red;  $H_2O$ : blue). The difference in cell volumes is 40%.

Up to now, mixing 'trials and errors' method and rational design, more than 150 new structure types have been discovered and structurally characterized, with various metals at different oxidation states.

#### Properties of these porous solids, valuable for applications.

#### Preliminary remark:

As synthesized, our different solids are not porous. The pores are indeed occupied either by the templating amines for inorganic frameworks or by the molecules of solvent in the case of hybrid solids. Except for some properties exclusively induced by the framework, in the majority of the situations, the property depends on the pore (and therefore on the internal surface). This means that a careful attention must be paid to the activation of the product for getting the entirely empty pore volume for optimizing the searched property. This point is neglected by the majority of colleagues who think that it is sufficient to systematically heat around 150-200°C to obtain - without physical verification - the empty pores. This explains why, for a given product and a specific property, the literature is full of contradictory and puzzling results. This casts doubts when applications are envisaged. It is the reason why, for all the solids I discovered with my group, the efficiency of the activation was measured in a first step by TGA but after, by the much more sensitive IR spectroscopy, able - being a local probe - to detect traces of remaining species in the pores, what TGA cannot do. The study of the properties always began after being sure of the complete activation. This explains why my results were never questioned.

#### What were the properties interesting porous solids?

It must be noted first that, curiously, up to 1990, the frameworks contained essentially diamagnetic metals (AI, Ga, Si, Ti<sup>4+</sup>), with sometimes small amounts of paramagnetic ones just acting as dopants... Since many decades, cracking, catalysis, selective separation and gas adsorption were the main applications of zeolites and related solids. These properties are always systematically studied, whatever the inorganic or hybrid frameworks.

#### What new properties can be generated in porous solids?

However, owing to the already mentioned triple characteristic of this family of solids, the solid state chemist that I am thought that so limited properties were studied, whereas it was possible to imagine:

- playing on the skeleton, to introduce in it as it exists in dense phases physical properties like magnetism, conductivity or optical properties by a proper choice of cations favouring such behaviours (3d transition metals for the two first, 4f ones for luminescence). Our attempts were successful;
- (ii) Playing on the pores, and, in the case of hybrids, the tunability of their dimensions, to store a variety of species (gaseous, molecular, organic [including drugs], metallic) which themselves induce new performances in the fields of gas separation and catalysis, on one side, and, on the other side, of the storage and delivery of anti-tumoral and anti-retroviral drugs. Here also, it worked.
- (iii) Playing on the nature of the internal surface, to modify chemically it in order to change the acido-basic properties of the solid (important in catalysis) or to graft new functions on this surface for adding properties which could not exist alone in the initial solid, but which improve the range of possible applications of this family of solids.

One must note that, as it was the case for the synthesis, we tried **not only to measure** the property, but **to explain** it at the molecular level from physical chemistry and physics. Computer simulation was used frequently for seeing the adequation between experience and theory.

We often were the first to introduce most of these new properties in the family of porous solids. Our past of solid state scientist helped a lot: the first to generate magnetism and conductivity, the first to use hybrids for drug storage and delivery, the first to evidence their catalytic properties.

#### From interesting to useful: benefits for mankind.

Whatever the interesting academic character of this family of solids and their possible applications, this remains at the laboratory scale and represents a benefit for fundamental knowledge. If one wants that these products become useful for the society, this requires two conditions: (i) the solids must represent a potential solution for some of the problems which concern our society; (ii) the companies must find an economic interest for developing their production, even if the market does not exist; (iii) the scaling-up of the synthesis and shaping must be easy, reproducible **and cheap** for a production at the scale of several tens of tons, being easily accessible by the public. BASF estimated that the three conditions were fulfilled with our materials and contacted me for an eventual collaboration.

I followed all the steps of the development, thanks to the fruitful cooperation of Ulrich Müller and his group, in BASF Ludwigshäfen. I learnt a lot from them. In particular, I discovered that their criteria for an industrial development are different from ours. We have the envy of discovery new solids, to create new dimensions for solid state matter, to increase the basic knowledge, whatever the price of our syntheses. On the contrary, for an engineer, the cost price of the production is an important parameter. It includes the price of the precursors, and favors synthesis in aqueous medium. I have learnt that at their contact, and, as soon as I have discovered a new structural type interesting for applications, this now influences the choice of my new systems, starting with cheap cations (AI, Fe, Ti...) and ligands, with synthesis in water.

A plant has been built up, and now, at least two of my materials (MIL-53(Al) and MIL-100(Fe)) are produced industrially and developed within a Large European Project in collaboration with BASF and the petroleum company TOTAL.



# **CORPUS. PART I**

## POROUS SOLIDS WITH AN INORGANIC MATRIX

## POROUS SOLIDS WITH AN INORGANIC MATRIX

(ULMs, VSBs, MILs: mechanisms of formation, structural prediction and generalization).

This topic began in 1992, after my come back to Le Mans after four years in Paris as a deputy director of the chemistry department of the headquarters of CNRS. Before this stay, as a solid state chemist, I was involved in Le Mans in the chemistry and physics of *3d* transition metal fluorides. During that very benefitial period, I had developped a strong chemical experience on hydrothermal synthesis and a good knowledge of the physics of the solid state, particularly in crystallography, magnetism (including magnetic structures) and in ionic conductivity. Coming back to my laboratory, I estimated that it was the good moment for changing my domain of research and explore new fields. As I already said in the preface, my choice went to inorganic zeolite-related porous solids to suppress the old frustration I had had to do not have the opportunity to study this fascinating family of solids in my young age. This attraction had an aesthetical origin : the beauty of the zeolite structures, reminiscent of Op'Art and Vasarely paintings.

At that time, two beautiful structures with large pores were published : the mineral Cacoxenite [P. B. Moore and J. Shen, *Nature.*, 1983, **306**, 356] and the synthetic cloverite [B Estermann *et al*, *Nature.*, 1991, **352**, 320]. Both were metallic phosphates (M = Al,Fe for cacoxenite ; Ga for cloverite). This incited me to follow this new orientation.



Fig. 1.1. Structures of natural cacoxenite with large tunnels and synthetic cloverite and its important cages. Note that the latter can be described from octamers of corner-linked tetrahedra (green for Ga and yellow for P). In cacoxenite, the metals (AI, Fe in green) are in octahedral coordination and P always in tetrahedral one.

These two structures were very inspiring to me for several reasons :

- (i) cacoxenite is a mineral and was at that time the only porous solid built quasi-exclusively (Al :Fe = 1 :24) from a paramagnetic metal. Nature had done what chemists failed to isolate. Moreover, in front of the always tetrahedral
   (ii) absorbete the metals are all in actabaded acadimetic wheneves they are tetrahedrally acadimetic metals.
- (ii) phosphate, the metals are all in octahedral coordination whereas they are tetrahedrally coordinated in cloverite.
   Such observed changes were just mentionned, not explained. It was a challenge.
- (iii) Cloverite was synthesized under hydrothermal conditions, a technique in which I had a strong expertise. This could help me at the beginning of this new domain of research. Moreover, Estermann *et al.* used for the first time a fluorinated medium to ensure better crystallizations, owing to the well known mineralizing character of this element. Here also, my knowledge of fluorine chemistry could help. In addition, compared to other zeolite related

solids in which the cations are exclusively surrounded by oxygen, the introduction of fluoride ions could create a dissymmetry in the environment and preferential interactions with guests. In the same time, as F is an ion

resonating in NMR, this technique could provide local informations on the influence of this element on the global behaviour of the corresponding solids.

These remarks and my previous experience were at the origin of my choice, in 1992, to focus my research on the synthesis and structures of oxyfluorinated metal phosphates. My aim was not to cumulate a lot of new structures for alimenting the databases, but to find and select new structures whose structural characteristics could aliment a way of thinking for approaching the explanation of the formation of these solids.

Such a challenge, which implies to use local probes and to develop *in situ* techniques for observing in real time the evolution of the systems, required first a careful choice of the metals and anions able to play the role of local probes during the reaction. It is the reason why we developped in a first step the study of the system

#### Al(or Ga)/F/PO4 : template (labelled ULM for University Le Mans).

In which all the elements are NMR nuclei. Obviously, at the beginning, we used the 'trials and errors' method for exploring these systems. We had the chance to isolate very soon four illustrating new compounds.



Fig. 1.2. Structures of (left) ( $NH_4$ ) $AIPO_4F$ ; the three-dimensionality is ensured by the connection of tetramers  $AI_2P_2$  (highlighted in grey) through their vertices; one AI is fivefold coordinated; the other at the center of an octahedron. (midlle) In ULM-3 and ULM-4 the brick is the same : an hexamer  $Ga_3P_3$  with two pentacoordinated AI and the central one being octahedral. (right) for diaminohexane, in addition with the preceeding hexamers an octamer  $Ga_3P_3$  appear. The different organization of the hexamers is related the change of templating amines (Color code : AI, Ga : green, P : yellow ; O : red, F :purple, C :grey, N blue).

Whereas the initial synthesis parameters were almost the same, it could be thought that changing the template would condition the topology of the resulting structure, but this remark could not be sufficient for explaining the change from 4 to 8 through 6 of the nuclearity of the brick. Instead of just noting this fact, I decided to go further for seing what was the relation between the nature of the template and the number and nature of polyhedra in the brick. This implied to follow the reaction by *in situ* methods, and among them, NMR was privileged because, in this type of solids, all the nuclei give a specific response during the reaction.

#### 1. Approach of some mechanisms of formation.

Once determined the <sup>27</sup>Al, <sup>71</sup>Ga, <sup>31</sup>P, <sup>19</sup>F, <sup>15</sup>N, <sup>13</sup>C and <sup>1</sup>H NMR characteristics of the preceeding compounds by solid state NMR which agreed with the structural results<sup>159</sup>, an *in situ* study of these systems was envisaged<sup>203</sup>. However, such an apparatus which could resist to the agressive conditions of the synthesis (HF) did not exist. With the help of my coworker Dr Taulelle, we created it.

The NMR observation in hydrothermal conditions needs special and non commercial tubes. These non-magnetic tubes must satisfy the experimental constraints of the NMR experience, resist to the high internal pressures at high temperature (Fig. I. 3)

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Fig. 1.3. Details of the non commercial NMR tube used for **in situ** studies under agressive conditions. The internal walls of the Vespel tubes are covered with inert tetrafluoroethylene.

#### 1.1. The method :

Two different and complementary approaches were used for this study<sup>203,245</sup>.

*Ex-situ* NMR method : After measuring the initial pH, the mixture is placed in a classical hydrothermal autoclave which is introduced in an oven at the chosen temperature of reaction. Independent syntheses were performed at different reactions times between 1 and 48h. At the end of each experience, the autoclave is cooled at 25°C, the final pH measured. Solid and liquid phases are separated. The solid is characterized by X-ray diffraction and solid state NMR and the liquid by NMR for each nucleus at every step. This allows to know *vs*. time the amounts of each element in the solid and the liquid phases.

*In situ* NMR method : it uses the special tubes described above. The real temperature of the sample is measured by a thermocouple placed within the Vespel tube. With this method it is possible to follow the evolution of the NMR signals in real time at various temperatures and, for a given temperature, as a function of time.

One parameter which is also important to observe is the <u>real</u> pH during the reaction because the solubility of the various species is strongly pH dependent. Owing to the particular conditions of the hydrothermal synthesis, the pH indicator must verify some conditions :

- (i) Its acido-basic chemical sensitivity must be optimal in the experimental range of pH. This implies that the  $pK_a$  of the indicator must be close to the pH of reaction ;
- (ii) It must be soluble in water and stable in the pressure and temperature conditions of the synthesis (<475K)
- (iii) It must be chemically inert toward the species existing in the reaction and must only be implied in acido-basic reactions ;
- (iv) The chemical shift of the chosen nucleus must be exclusively dependent of pH.

Two indicators fulfilling the above conditions were found : Imidazole ( $pK_a = 7$ ) and 1,4 Diazabicyclo(2,2,2) octane (DABCO) ( $pK_a = 3$  and 8.9). The chemical shift of their amine functions made that <sup>14</sup>N NMR could serve as a good pH indicator. This allowed to cover a pH range between 1.5 an 10.5 at room temperature. We established the relation existing between the <sup>14</sup>N chemical shift and the pH of the reaction mixture. It is obvious that, for getting quantitative results a lot of time-consuming calibrations were necessary ( $pK_a v T$ ...).

Before looking at the quaternary system, it was necessary, despite multiple NMR experiments that will not be detailed here, to carefully identify the species occurring in the systems AI/F,  $AI/PO_4$  and  $AI/PO_4/F$  in the same conditions.

#### **1.2** Elucidation of the steps of the formation of $NH_4AIPO_4F$ :<sup>203,245,252</sup>

The evolution of the real pH of the solution during the reaction was followed via the <sup>14</sup>N chemical shifts of the DABCO indicator. Starting from pH3 it rapidly increases during the first hour indicating that , in the induction period of the synthesis, the system undergoes important chemical evolutions. It is probably during this period that the molecular precursors responsible of the nucleation, are generated. pH stabilizes after 2 hours at ca. pH 6. This corresponds to the growth period.

The comparison of the results of *ex-* and *in situ*<sup>27</sup>Al NMR, combined with that of <sup>19</sup>F was particularly informative. Indeed, at the very beginning of the reaction, the primary building units are monophosphate complexes in which aluminum, in sixfold coordination, is linked to two fluorine atoms. Increasing the temperature and subsequent loss of one fluorine leads to fivefold coordinated Al in the monophosphate complexes. The latter dimerize by olation and provide PreNucleation Building Units (PNBU) in which a reorganization creates Al-F-Al bonds. This PNBU which is formed in the solution during the reaction, is identical to the tetramer observed in the experimental solid. For obtaining its precipitation (which is well-known to occur only from neutral species in the solution), the PNBU – with a charge 2- - interacts with two ammonium cations to form the neutral Molecular Building Unit (MBU), leading to the precipitation of the final solid. During this step, ammonium ions seem to play just a role of charge compensator. We shall see in the following that its role is much more important.



Fig. 1.4. The different steps of the formation of the secondary building unit of  $NH_4PO_4F$  deduced from ex- and in-situ NMR. (a) initial fluorinated Aluminophosphate with Al in sixfold coordination, which transforms by increasing temperature and loss of a  $F^-$  into (b) the monophosphate complex with Al in fivefold coordination (c,d); by elimination of water between two monophosphate complexes, dimerization occurs in the form of prenucleation building units (PNBU), initially with no AI-F-AI bonds which are created by a rotation of one AI pentahedron. These bricks, twice negatively charged, interact with two  $NH_4^+$  cations and form a neutral molecular building unit (MBU), necessary – as it is well known - for observing the precipitation of solid  $NH_4PO_4F$  by cooperative elimination of water between these MBU.

Conceptually, this study was very important for the development of the topic. It convinced us that chemistry is not only a pleasant succession of discoveries of new solids by trials and errors (even if I do not criticize this powerful and respectable method that I use also). If one takes time, on selected examples – it was the case here -, to introduce physical chemistry and try to understand at the molecular level the structural characteristics of the final sample, the corresponding knowledge can help to build a more rational approach of the synthesis, in relation with the final structure, and therefore, a step toward the obtention of 'tailor-made' solids. The *in situ* study of the formation of NH<sub>4</sub>PO<sub>4</sub>F had the merit to show that the tetrameric SBU observed in the final solid already existed in the form of a molecular building unit after several condensation processes within the solution before precipitation. However, the observation of the new phases ULM-3 and ULM-4 occurring with the small change of templating diamine, asked for the question of the real role of the cation, beside serving as a charge compensator during the formation of the MBU.

Indeed, ULM-4<sup>168,193</sup> crystallizes when ethylenediamine or diaminopropane are used as templates; for ULM-3<sup>164</sup>, it is diaminobutane. This has two effects: (i) the metallic part of the SBU becomes hexameric in both cases with two external pentahedra and one central octahedron, linked together by fluorine atoms and (ii) the different steric hindrances of the amines led to two different organizations of the hexamers. In the same way as before an in situ study of these systems was undertaken.

**1.3** Elucidation of the steps of the formation of ULM-3 and ULM-4: the complexity of a reaction<sup>189,221,238,246,255,258,274,277,288,290,317,341,392</sup>

a) Influence of the phosphorus source; nature of the metal and time of reaction.

Our first experiences were arbitrary fixed at 48h because, at the beginning, we did not know the time after which

the reaction was complete. This information could be obtained quickly from *in situ* diffraction in real time, a technique developped in the same period in Daresbury by P. Barnes and D. O'Hare. Working in dispersive energy mode, this technique allows to estimate the duration of the reaction from the evolution of the intensity of Bragg peaks *vs.* time.

Our cooperation with D. O'Hare provided us sufficient beam time to study the crystallization of ULM-3 (Al or Ga) and ULM-4 (Al or Ga)  $^{228,246}$ , starting from various precursors. The important information for the chemist was that the reaction pathways depend on the phosphorus source, but lead to the same final product (Fig. 1.5). With  $H_3PO_4$  the solids are formed directly from the solution ; with  $P_2O_5$ , an intermediate phase, further identified as a new gallium fluoro-pyrophosphate appears during 20 mn before leading to ULM-3. For gallium solids, the reaction is achieved in ca. 2 hours but needs 15h for the aluminum compounds instead of the arbitrarily fixed 48h at the beginning of the study .



Fig. 1.5. The influence of the nature of the phosphorus precursor on the reaction pathway : upper row : with  $H3PO_4$ , ULM-3(Ga) is directly formed with an induction period of a few minutes and the reaction is achieved after ca. 2 hours. On the contrary (lower row), with  $P_2O_5$ , an intermediate phase appears during 20 mn before leading o ULM-3, after a dissolution recrystallization process. This phase, that we isolated at lower temperatures, is a new gallium fluoro-pyrophosphate, built up from isolated tancoïte-like chains.

#### b) Preliminary ex- and in situ NMR studies. 245,246,252

We applied the strategy already developped for  $NH_4AIPO_4F$ . The combination of *ex*- and *in situ* NMR results obtained from <sup>27</sup>AI, <sup>31</sup>P, <sup>19</sup>F, <sup>15</sup>N, <sup>13</sup>C and <sup>1</sup>H nuclei are coherent with the proposal of the existence within the solution of

hexameric prenucleation units (Fig. I.6 left) in which aluminum is exclusively in five-fold coordination. The association of these PNBUs occurs first by the formation of P-O-Al bridges with always Al<sup>V</sup>, followed by the onset of Al-F-Al bonds within each hexamer at the end of the reaction.



**Fig. 1.6** . Approach of the formation of ULM-3 from NMR results. The original hexamers, resulting from the trimerization of the monophosphate complexes, form in a first step intra- and inter P-O-AI bonds in the clusters and between them. It is only at the end of the condensation that AI-F-AI bonds are formed.

This procedure applies to both ULM-3 and ULM-4 with however some differences.

- (i) For ULM-4, and at variance to ULM-3, the appearance at the beginning of the condensation of a badly crystallized lamellar phase just before the crystallization of ULM-4. This seems to evidence two different crystallization processes : a direct nucleation-growth procedure for ULM-3 and a crystallization by structural solid-solid rearrangement for ULM-4.
- (ii) The evolutions of the pH of the reactions are rather different. Measured at 25°C after several interruptions of the reaction vs. time, the pH for ULM-3 (6.5 before treatment) stabilizes at 9.5 after 15h. The values are 5 and 7 for ULM-4. When measured during the reaction using the <sup>14</sup>N NMR signal of DABCO, they are respectively 4.75 and 6.25 for ULM-3 and 4.25 to 4.75 for ULM-4.
- (iii) Despite being built up from the same SBU, the final topologies of ULM-3 and -4 are different.

These differences shed some light on the multiple roles that the templating amine could play beside the charge compensator role, initially attributed in the case of NH<sub>4</sub>AIPO<sub>4</sub>F. This point had to be clarified experimentally.

#### c) Back to the role of templating amines.

Changing the length of the amine, keeping the other conditions constant (including Al :P ratio), leads to some



Fig. 1.7. Evolution of the nuclearity of the SBU as a fonction of the length of the amine.

modifications in the inorganic framework. If the ULM-3 topology exists with diaminobutane and –pentane, it is replaced by the ULM-5 type<sup>158,189,221,238</sup> with diaminohexane, –heptane and –octane. In this new structure, always

appear the hexameric units linked by corners, thus forming chains of hexamers, but these chains are connected by a new type of SBU (labelled SBU-4,4), an ordered octamer  $Al_4P_4$  with aluminum exclusively in tetrahedral coordination.

This evolution was highly informative on several aspects. This SBU, usually encountered in aluminosilicate zeolites, was already discovered also as existing as the only type of SBU in the gallofluorophosphate cloverite [B Estermann *et al*, *Nature.*, 1991, **352**, 320]. This solid was synthesized using quinuclidine, a <u>spherical</u> templating amine whereas we

used only linear amines. Moreover, it was well known that the coordination of aluminum is strongly pH dependent (tetrahedral in basic medium, then pentahedral and octahedral as son as pH decreases from basic to acidic). The evolution of the structures in the ULM-n series indicated that the basicity of the reactive medium increased with the length of the amine, in agreement with the *in situ* measurement of the pH observed previously by NMR<sup>230</sup>. These remarks completed our vision of the multiple – and essential - roles of the templating amine during the synthesis. Not only it plays the role of a charge compensator (note that in all the solids, the diamines are always diprotonated and act as dications), but its steric hindrance can influence the choice of the topology (for minimizing the lattice energy during crystallization) and, more importantly, its acido-basic properties govern at different stages the reaction.

Indeed, the sphericity or the linearity of an amine has a direct relation with its acido-basic properties through the values of its  $pK_a$ . Most of the usual spherical amines have low  $pK_a$  (in the range 4-6) whereas they are higher for linear ones (7 for ethylene diamine, ca.11 for diaminohexane). Their values increase with the number of carbons in the chain. When looking in regard the nuclearity of the SBU, it clearly appeared that weak  $pK_a$ . were associated with small SBU and larger ones with increased nuclearity. This led us to reexamine the formation of the solids in terms of charge densities of the species.

#### d) Oligomeric condensations and charge density of the amines.

One must recall that, starting from the precursors existing in the solution, the formation of a solid (i.e. the infinite – and most of the time periodic – condensation of these precursors) only occurs when the species which condense correspond to zero-charged species. As <sup>14</sup>N and <sup>1</sup>H NMR characterizations proved that the amines are dications, the PNBU are dianions. Therefore, in agreement with the theory of Henry, the mechanism of anionic condensation is driven by a decrease of the charge density of the condensed species. As the negative charge of the PNBU remains constant (formal charge :-2) whatever the size of the building unit, we assumed first that the charge density of the species controls the structure. At the anionic level, this charge density will become smaller when the size of the PNBU, when the coordination of Al decreases.

Looking at the amines, the spherical ones - with low  $pK_a$  – are much more acidic than the linear ones. Their charge density will therefore be high, compared to that of linear amines which will decrease when the length of the carbon chain increases.

From that, our second assumption was the following :

Owing to the amine-SBU interactions, the charge density of the amine – fixed by the conditions of synthesis - controls the extent of the oligomeric interaction and therefore the size of the SBU. The solid is then formed by the condensation of molecular mixed ammoniums-SBU with zero-charge.

This justifies that the increase of the size of the linear amines with a weak charge density leads to the passage from tetramers ( $NH_4AIPO_4F$ ) to hexamers (ULM-3 and -4 types) and then (at least partially) to octamers SBU4-4 in ULM-5 in order to lower the charge density of the SBU.

#### e) Infinite condensation forming the solid.

The strong ammonium-SBU association, obtained by the equalization of the electronegativities of each group, can be assimilated to a cation-anion pair, that we called it Molecular Building Unit (MBU), with a zero charge. This condition is necessary for allowing the precipitation of the final solid.

This MBU has a topology and a steric hindrance which will determine both the nature and the characteristics of the various observed structure types (size and shape of the cavities, mode of connection of the SBU...).

Our approach of the mechanism of formation is rather different from what was commonly admitted (without experimental proofs) which considered that the SBU (considered as isolated) arrange themselves around the template which plays the role of structuring agent. In our approach, it is not the template which is the decisive

factor, but the MBUs. Their arrangement corresponds to the creation of a structure with a minimum lattice energy compatible with the various constraints imposed by the effective volume of the MBU (shape, size and movement).



**Fig. 1.8.** Scheme of the formation of porous aluminum fluorophosphates depending on the charge density  $\mathbf{D}^{+}$  (related to the value of  $pK_a$ ) of the protonated amine. A large  $\mathbf{D}^{+}$  implies a small extension of the oligomeric condensation (SBU-4), while a weak  $\mathbf{D}^{+}$  corresponds to an increase of the nuclearity of the SBU (SBU-6). Once equilibrated the electronegativities of each cationic and anionic group, an ammonium-SBU ion pair (MBU) with zero charge is formedwhich allows the infinite condensation and therefore the precipitation of the solid.

From our interpretation of the various *in situ* results, we reconsidered the effect of our initial chemical parameters on the synthesis.

- (a) the pH : If it remains an experimental parameter at the beginning of the reaction, its role at the molecular level is a complex function acting at several levels : (i) it intervenes on the nature of the monomeric species within the solution, the forms of which bearing different charges ; (ii) it determines the protonation or not of the amines and therefore, fixes their charge density ; (iii) it has an influence on the coordination of the metallic cations of the framework ; (iv) it drives the mechanism of the condensation of species. This explains why, for instance, the ULM-3 phase exists in a large range of pH. All the above functions act successively at different values of pH. Therefore, the domain of existence observed macroscopically, just represents the enveloppe of the different functions of this parameter.
- (b) The amine : Its role is essential and multiple. It is the main parameter governing the formation of our phases : (i) it fixes experimentally a known charge density within a system submitted to several variables ; (ii) with its charge density, it determines the evolution of the size and the charge of the inorganic SBUs up to the moment when their electronegativity of the group and their charge density becomes equal to that of the amines ; (iii) as it controls the equality of the charge densities, it is at the origin of the creation of the neutral ion pair (MBU) ammonium-SBU which allows the infinite condensation ; (iv) once the MBU formed, it is the steric hindrance of the amine and its flexibility which will determine the adopted structural type.

The last point was so true that we tested it by using an amine [tris(2-aminoethyl)amine], the pK<sub>a</sub>s of which being the range (8.5-10), therefore *a priori* suitable with the obtention of pure SBU-6, but too large for leading to a three-dimensional arrangement of these SBUs. If our approach was true, a 2D arrangement of the SBU-6 was expected. It was verified (Fig. I.9).



**FIg. 1.9.** – Structure of ULM-8, in which the chemical conditions are consistent with the existence of SBU-6, but with a size of the amine [tris(2-aminoethyl)amine] being too large for obtaining a 3D network.

#### c) The fluorine :

When inserted in the matrix, its strong electronegativity favours stronger and localized hydrogen bonds and an increased SBU-ammonium interaction. Indeed, looking at the different structures, the amines point preferentially toward fluorine rather toward the oxygens. This implies a better stability for the MBU, and probably a better crystallization. Moreover, its presence instead of oxygen within the SBU is a supplementary element for lowering the charge density of the latter.

The role of fluorine when it is at the center of the SBU-4,4 octamer remains rather mysterious. Its chemical shift ( $\delta$  = -65 ppm) strongly differs from that of a bridging fluorine ( $\delta$  = -100 ppm).

As a conclusion of this part, we can only say that, if we were able to go deeply in this aspect of mechanisms, it is because of the high crystallinity of the phases and the high quality of our structural determinations and the accuracy of the NMR determinations. This just arrived when S. Mann [Nature 365, 499 (1993), proposed the name **'Molecular techtonics'** for grouping some emerging ideas trying to explain the formation of biomaterials. This term appears to be fully justified for describing the mechanism we propose. However, il must be clear that our proposal of mechanism just applies for the family of solids and has not the ambition to be general. We had the chance that the solids were well crystallized, after a short time of reaction, contained a maximum of resonating nuclei, and that the number of reactive species was rather small and easily accessible. Depending on the nature of the metals in the framework, it can be anticipated that some situations will appear much more complex. It is for example the case for silicates, where the number of possible reactive species is so large (>100) that it seems impossible to do the same study as ours...But, al least, it exists now.

Our main papers on this point : J. Chim. Phys. **95**, 310-316 (1998) ; Colloids and Interfaces A. **158(1-2**), 299-311 (1999).

As soon as we had understood the formation of this class of solids, it was necessary to look at the various consequences that such a new knowledge implied. For the solid state chemist I am, the proved existence of these SBU incited to look at a possible generalization of this fact under several aspects. Three were privileged : (i) crystal chemistry concepts, (ii) a possible prediction of structures and (iii) a come back to chemistry with new ideas.

#### 2. Crystal chemistry consequences : the scale chemistry concept<sup>269</sup>

My initial idea to describe inorganic structures from polynuclear bricks instead of looking at the association of various polyhedra was legitimated by our *in situ* measurements which proved the reality of these bricks. Instead of limiting this type of description to zeolitic compounds, was it applicable more generally? My old knowledge of inorganic crystal structures, alimented by the pioneer works of the famous crystal chemists that already were Bruce Hyde, Sten Andersson and Mike O'Keeffe (Nature Phys. Sci. 237 (1972) 35; Inorganic Crystal Structures, Wiley, 1989; MSA Monographs, 1996) since the beginning of the sixties, was helpful.

Indeed, what is interesting is the topology adopted by these assemblies of bricks in their final structures. It rapidly

oxides/fluorides. For instance, whereas the ReO<sub>3</sub> structure is built up from the 3D connection of isolated octahedra which act as the brick, the same topology is adopted by NH<sub>4</sub>AlPO<sub>4</sub>F (or AlPO4-CJ2), where the brick is the tetramer composed of two phosphates and two Al in two different coordinations (Al<sup>V</sup> and Al<sup>VI</sup>). Moreover, the ReO<sub>3</sub> structure type is adopted by the fluoride Nb<sub>5</sub>F<sub>15</sub> and the mineral pharmacosiderite (an iron hydroxyarsenate) in which the formal SBU are an hexamer of corner-sharing square pyramids and a decamer Fe<sub>4</sub>As<sub>6</sub> respectively (Fig.I.10 top left). This homothety was verified on several other structure types. This lead us to propose the following rule :

### Whatever the chemical formula and the size of the building units, the topology of the structures remains invariant and, consequently, the larger the brick, the larger the pore.



**Fig.1.10.**- Some illustrations of the « scale chemistry » concept applied to several structure type ;(left) : famous oxide series with the  $ReO_3$ , hexagonal tungsten bronze,  $CaTa_2O_6$  and  $BaNb_2O_6$  topologies with, on their left, dedicated bricks ; (right) : example of the invariant sodalite structure from different bricks (top ; tetramer of tetrahedra ; middle : enneamer  $AI_5P_4$ ; bottom : various assemblies of tetrahedra serving as SBU in a series of indium sulfides discovered by Yaghi and O'Keeffe).

This concept has some consistency. For instance, the structural evolution that we noted from ULM-4 to ULM-3 by the increase of the length of the template is also observed to  $CaTa_2O_6$  and  $BaNb_2O_6$ , in which it is the size of the alkaline-earth cation which determines the structural type. This provides another general way for thinking about crystal structures.

It also implied that the search of large pores in inorganic porous solids must require large SBUs. Our experimental experience with alumino- and gallophosphates proved that, at least within this family, the largest pores were reached with cloverite (internal diameter : 16Å). However, it will be shown in the following that it is possible in other systems. An example will be provided later (§ 4) by VSB-1 and VSB-5 (VSB standing for Versailles Santa Barbara). Anyhow, this rule, despite interesting for crystal chemists, remains an *a posteriori* analytical tool for describing structures. It remains qualitative, is conditioned by new experimental data and does not present any predictive aspect whereas, based on the real existence of bricks, such a prediction becomes possible.

### **3.** Structural prediction consequences : the Automated Assembly of SBU (AASBU) method<sup>272</sup> (Angew. Chem. Int. Ed. Engl. **39**, 2270-2275 (2000)).

The SBUs exist during the reaction. Their geometry is accurately known from crystal structure determinations. This means that these SBUs can be used to construct a graph of corner-, edge- and face-connected polyedra embedded in a three-dimensional space. This was the foundation of our computer simulation program, named the AASBU method (AASBU stands for Automated Assembly of Secondary Building Units). Its key feature lied in the use of predefined topological building units and in the exploration of their auto- assembly in three-dimensional space through a sequence of simulated annealing plus subsequent minimization steps, with optional symmetry constraints, but leaving cell-parameters unconstrained. When it appeared, this approach was fundamentally different from the existing ones which always started from the prediction of assemblies of individual atoms. Starting from already formed assemblies shortens a lot the time of calculations (< 24h).

It has also the great advantage that the simulations are independent of the chemical nature of the elements of the secondary building units (SBUs). This allows to exclusively focus on their capacity to generate connections among each other, while automatically scanning structures related to one another through topological rela- tionships. The rules that control the possible assembly of the SBUs are encapsulated in a cost function consisting of a Lennard-Jones-like term plus a « force-field » that favors « sticky-atom » pairs. Note that this latter term has no direct physical meaning, serving simply to 'glue' together the SBUs at the linkage points during the subsequent simulation steps, with a possible merger at a later stage of the graph generation.

When the building unit and the Lennard-Jones potentials are defined, the candidate periodic structures are generated by a cascade of simulations that entails six major steps:

- (i) Periodic trial arrangements of the SBU are randomly generated by a simulated annealing procedure. The angular degrees of freedom for each SBU are sampled by a Metropolis Monte-Carlo algorithm. At each step, both the cell size and the distances between the SBUs are adjusted to relieve close interatomic contacts, leading to successive phases of cell contractions and expansions. As the simulated annealing proceeds, configurations of lower cost are stored.
- (ii) The trials arrangements are reduced to a set of unique arrangements corresponding to unique local minima. The redundant arrangements are removed.
- (iii) The resulting set of configurations is minimized with respect to the 'cost' function (energy).
- (iv) After the optimization step, the redundant arrangements are removed, leaving a list of unique arrangements of connected SBU.
- (v) For each original configuration of the SBUs, the sets of 'sticky' atoms at short separations are reduced to single atoms. This step generates realistic crystal structures, the space group of which are redetermined.
- (vi) The resulting structures are ranked by decreasing lattice energies and allow to distinguish betwen 'hypothetical' (unfavourable lattice energies) and 'not yet synthesized' for these virtual structures.

## The sequence of simulations provides a list of candidate structures together with their space groups, cell parameters, atomic positions and theoretical X-ray powder diffraction patterns, that can, for example, be directly compared with existing inorganic structures.

The feasibility of the method has been first demonstrated through the generation of networks of polyhedra of both known and not- yet-synthesized crystal structures among several large classes of solids, for example, perovskites, bronzes, zeolites, or spinels. Since no explicit limit regarding the nature, number, or size of the SBUs is involved, the method offers a boundless potential for exploration in terms of the topological diversity. This especially opens the way to the dedicated search for new and interesting structures, such as large-pore materials including cage or channel systems, identified through their expected properties (thermodynamic stabilities, adsorption capacities,...).



**Fig. 1.11.**- AASBU simulations using the SBU-6 hexamer generate lamellar and 3D structures, that include experimentally known topologies. For clarity the conventional + or - signs are used to represent the orientation of the building units(top) in the simulated structures.

AASBU simulations were first performed on the aluminophosphate system in various space groups, by using the known hexameric SBU-6, together with appropriate Lennard-Jones parameters to allow their assembly in threedimensional space. Figure **1**.11 presents some of the results which, among several 'reasonable' virtual possibilities, evidence some of the stucture types encountered during the experimental study of the system. Encouraged by these first results, we looked at the applications of the method when looking at other well known SBUs. The first attempt concerned the prediction of structures based on the well known sodalite cage. Most of the solutions remained 'hypothetical' but, in terms of lattice energy, one of them can be considered as 'not yet synthesized' (Fig. I.12). The simple cubic arrangement of sodalite cages generates a structure in which four different – and well known in the chemistry of zeolites – types of cages appear<sup>303</sup>.



**Fig. 1.12.** A virtual structure based on the sodalite cage-like SBU (top). The cubic arrangement, represented either in a polyhedral form or in a stick model, the lines joining two tetrahedra (middle) lets appear (bottom) four types of cages (from left to right : sodalite, D6R, eab and gmelinite) usually encountered in zeolites.

Another type of brick, already encountered during our study of the Al-P-O-F system, was submitted to the same treatment. It is the octamer  $Al_4P_4$  which appears in association with the classical SBU-6 in the ULM-5 type structure which exists with diamino- n-anes (n=6,7,8). It is also the only brick building up the large pore zeolite cloverite. Described with sticks joining two tetrahedra, the eight tetrahedra form a cubic cage (often named D4R) within which fluoride ions (probably associated with protons ; see *J. Am. Chem. Soc.***123**, 111-120 (2001)) are inserted.



Fig. 1.13. - Polyhedral representation of the D4R octamer existing in ULM-5 and cloverite structures.

The application of our AASBU method provides many possible structures. Some of them, presented next page in Fig. I.14, were discovered later by the group of Russell Morris, in Saint-Andrews.



**Fig. 1.14.** Some virtual structures based on the D4R cage obtained using the AASBU method. The two structures of the extreme left column correspond to known structures (ACO and cloverite types). The original D4R cages are highlighted in yellow.

Even if, most of the time, ignored by the community (my regret), it is clear that this method can be of great help in the search of new phases. It has several advantages :

- No single crystal : when a given SBU is concerned, the identification of new structures is very fast because obtained by just a comparison between experimental and theoretical X-ray powder diffraction patterns, without the need of a single crystal for providing the atomic coordinates which are already listed by the program ;
- (ii) Support to synthesis chemists: for the solid state chemist, and owing to the tremendous number of solutions given by the program, it is a great hope for the discipline. It indeed shows the incredible number of possibilities of new structures, 'not yet synthesized' according to our energy classification, compared the current number of known phases and their associated physical properties.
- (iii) Structure of activated samples: Beside the post-synthesis identification of new phases, one information provided by the AASBU method should be of interest toward chemists interested by the applications of porous solids. Indeed, the latter become useful only when the template and/or water molecules have evolved their structure (activation most of the time generated at high temperatures) and rendered the pores accessible for gas adsorption storage for example. The performances of adsorption are drastically conditioned by the quality of the activation. The adsorption properties are of course conditioned by the structure adopted by the activated sample and the explanation of the properties can be provided only when the high temperature structure is known. Unfortunately, heating often leads to a poor crystallinity of the activated product and render difficult any structure determination. The AASBU method overcomes this limitation. It suffices to introduce the geometry of the dehydrated SBU and the program provides the patterns of the few structures able to represent the activated form. Just a comparison with the experimental data provides the solution<sup>304</sup>. This was elucidated on several aluminum phosphates<sup>270,302,314</sup>.

#### Our main papers on this point :

Angew. Chem. Int. Ed. . **39**, 2270-2275 (2000) ; Chem. Mater. **13**, 1732-1738 (2001) ; J. Am. Chem.Soc. **123**, 9642-9651 (2001) ; Stud. Surf. Sci. Catal. **135**, 254 (2001) ; Stud. Surf. Sci. Catal. **135**, 267 (2001) ; J Am.Chem.Soc, **124**, 1040-1051 (2002) ; Angew. Chem. Intl. Ed. Engl., **41**, 972-975 (2002) ; Chemistry.Eur. J. **8**(18), 4102-4113 (2002) ; J. Am.Chem. Soc. **124**, 15326-15335 (2002) ; Solid State Sciences. **5**, 79-94 (2003) ; Solid State Sciences **8**, 241-247 (2006) and references therein.

#### 4. Chemical consequences : rational variations and creation of magnetic porous solids.

#### 4.1. Rational synthesis of new alumino /gallophosphates :

The tools that we created allowed a return to chemistry, with more rational ideas. Indeed, our previous studies on aluminum and gallium phosphates had established the relation between macroscopic conditions of synthesis

(temperature, time, pH, nature of amine) with the existence of a given SBU. Moreover, the importance of the nature, the steric hindrance and  $pK_a$  of the amine was highlighted in relation with the final structure based on the given SBU. It became therefore possible to rationally create new alumino/gallophosphates by an appropriate and *a priori* choice of the acido-basic properties and volume of the amine involved in the structure. Fig. **I**.15 shows some new topologies created by this way.



**Fig. 1.15** - Beside already known structures (ULM-3, -4 and -5), some structures rationally obtained by fixing <u>a priori</u> the chemical conditions suitable with the existence of a SBU-6, and by playing on the  $pK_a$  and steric hindrance of the amine.

#### 4.2. First evidence of magnetic porous solids:

At the end of the nineties, all the solids described in the literature were based on diamagnetic metals (AI, Ga, Si...). Transition metals, when used, served only as dopants. My old experience of solid state chemist had learnt me that

these diamagnetic metals, in fluorinated solids and oxides, could be replaced, keeping the same coordination, by 3d and 4f transition metals in order to introduce physical properties (magnetism, conductivity...). The challenge was to look at the possibility to do the same with porous solids, whereas it was not known at that time. It worked,

and we were the first to create potentially porous magnetic solids. Several metals, with various oxidation states, were tested.

a) Iron-based solids : 235

Their synthesis is rather difficult because extremely dependent on the chemical conditions (temperature and concentrations). However, beside the now well-known ULM-3 structure type, several phases were discovered and structurally characterized (Fig.I.16)





**Fig.l.16**.- Some of the new templated iron phosphates discovered in the group. The secondary building blocks are highlighted in the right bottom part of each figure. Their dimensionality vary from 1D (first row) to 3D. Most of the time, they are built up from  $Fe^{3+}$  cations, except the mixed valence ULM-10 synthesized in strongly basic medium (Color code :  $Fe^{3+}$  : green ;  $Fe^{2+}$  : orange ; P : yellow ; O : red ; F : purple ; Owdark blue ; C :black ; N : pale blue). Their magnetic ordering temperature is also mentioned to be compared to that of ULM-3(Fe) : 37K.

Despite the difficulty of synthesis, the crystal chemistry of this series of solids is very rich. Indeed, when looking at the structures in terms of SBUs, the chemical conditions strongly influence their nuclearity. Depending on the pH and the choice of the amine, the SBUs scan vary from SBU-2 through SBU-3, SBU-4, SBU-6 (with some variations of the coordinence of the satellites in the Fe trimers) and up to SBU-8.

Their magnetic characterization, performed both by susceptibility measurements and Mössbauer spectroscopy, evidences for all of them the onset of a magnetic ordering. When Fe<sup>3+</sup> is involved, all the solids are antiferromagnets at low temperature ( $37K > T_N > 4K$ ). Only ULM-10, synthesized in a strongly basic medium, contains iron in a Fe<sup>2+</sup>/ Fe<sup>3+</sup> mixed valence state, which leads to an interesting ferrimagnetic behaviour (Tc = 28K).

However, despite interesting on the front of new knowledge and feed of databases, the temperatures of magnetic ordering are rather - but not surprisingly - low for eventual applications ( $T_N < 40K$ ). Indeed, in the structures, the ordering temperatures depend on the capacity of long range superexchange or super-superexchange interactions provided by the metallic inorganic subnetwork. Here, the magnetic carriers form either chains or clusters in super-superexchange interaction, which means limited long-range interactions, and therefore, low Néel or Curie temperatures.

It was tempting to look further at this class of porous inorganic solids by changing the nature of the magnetic carriers in order to see if the phenomenon was more general than for trivalent metals.

b) Vanadium-based solids : Several groups at the same time were interested by this system, mainly Haushalter in USA and Beltran-Porter in Valencia (Spain). My main contribution to the topic concerned the vanadium (IV,V) phosphate templated with diaminopropane (DAP) (Fig.I.17)



#### **FIG.I.17.** The structure of $V_3P_2O_{13}(H_2O)_2$ , DAP<sup>162</sup> (V : green ; P : yellow). The SBU-5 is highlighted in dark green(V) and grey (P)

This time, the SBU is a pentamer  $V_3P_2$ . The metallic part consists in a trimer of vanadium polyhedra, the central one being a square pyramid and the two external ones being octahedra. It is a mixed-valence solid in which vanadium presents both  $V^{4+}$  and  $V^{5+}$  species, disordered within the SBU, as confirmed by EPR and NMR.

c) Nickel(II)-based solids. Toward first applications<sup>237,289,295,350,379,390,393,419.</sup> :

Once demonstrated by trials and errors that magnetic metal phosphates could exist with tri-, tetra-and pentavalent ions, it was tempting to look at the complete range of oxidation numers. All our attempts with hexavalent metals failed, but with divalent metals, the results were positive, particularly for Ni<sup>2+</sup>. He corresponding series was labelled **VSB-n** (for Versailles Santa-Barbara) to take into account our collaboration with Prof. A.K. Cheetham, from the University of California Santa-Barbara, who spent two years as an invited 'Blaise Pascal' professor in my Institute.

The results were surprisingly outstanding. The hexagonal structures of VSB-1 and VSB-5 exhibited tunnels with 24membered rings, a characteristic which represented, during a long time, the largest tunnels ever discovered (Fig.I.18).



Fig.I.18.- Structures of the nickel phosphates VSB-1 and VSB-5 with very large pores. The tunnels are mostly filled by water.

Compared with the previous solids, these nickel phosphates (fluorinated or not, depending on the pH of the solution) have one interesting particularity : instead of hosting amines as templates, the tunnels are filled with water,  $H_3O^+$  or  $NH_4^+$ , species which are easily extracted from the framework by heating, thus providing easy access to the pores for some guest species.

The easy accessibility to the pores incited us to look at properties in two directions : catalysis and adsorption. In terms of catalysis, we proved that VSB-1 is a good catalyst for the conversion of butadiene into ethylbenzene [289], VSB-5 being interesting as an hydrogenation catalyst [<sup>295</sup>]. More generally, they represent a new class of shape-selective catalysts, particularly for epoxidation of cyclic olefins [<sup>379, 419</sup>] with tunable properties because we showed that the nickel of the framework can be partially substituted by other transition elements [<sup>390,393</sup>].

In terms of adsorption, they represent good performances for hydrogen adsorption, but at 77K. Under 600 torrs, the uptake (140 cm<sup>3</sup> / cm<sup>3</sup>) is more than three times better than that of classical adsorbers like aluminosilicate ZSM-5 and active carbons (Fig.I.19)



Fig.1.19.- Comparison of the hydrogen uptake at 77K of VSB-5 compared to usual adsorbers ZSM-5 and activated carbon.

Inelastic neutron scattering proves that <u>molecular</u> hydrogen is first chemisorbed on the accessible Ni sites in pentagonal coordination at low pressure before being physisorbed when theses sites are saturated [<sup>350</sup>].

#### Our main papers in this series

C.R.Acad.Sci. Série IIC. 2,387-392 (1999) [237]; Chem. Comm.,859-860 (2001) [289]; Angew. Chemie, Intl. Ed. Engl. 40, 2831-2834 (2001) [295]; J. Am. Chem. Soc. 125, 1309-1312 (2003) [350]; J. New Mat. Electr. Sys. 6, 29-31 (2003) [354]; Chem.Mater. 16, 1394-1396 (2004) [377]; Angew. Chemie, Intl. Ed. Engl. 43, 2819-2822 (2004) [379]; Chem. Mater 16, 5552--5555 (2004) [390]; J. Phys. Chem. B 109, 845-850 (2005) [393]; J. Catal.. 239, 97-104 (2006) [419].

5. The titanium phosphates<sup>219,223,224,231,247,260,294,298,309,312,345,357,364</sup> : an academic topic generated by the demand of chemical industry.

The RHODIA company was in the nineties a strong producer of titanium-based products and of phosphates, but had difficulties for finding new solids based on Ti and P to be put on the market. Knowing the experience we had accumulated in the study of metal phosphates, they offered us a PhD thesis in Versailles for looking, with our

approach, at the possibilities of finding new solids (labelled MIL-n) in the system Ti/O/F/P for possible applications. This nice example shows that a suggestion of industry can lead to interesting academic research.

Our first surprise was to see that the chemistry of titanium in solution was practically unknown, and that the number of known titanophosphates was extremely small. Therefore we decided to apply the same strategy as that developped for aluminophosphates, with a combination of the trials and errors method and in situ studies for a better understanding of the titanium(IV) chemistry. It occurred in three steps : firstly, a study of titanium phosphates under hydrothermal conditions was undertaken to discover the possible topological arrangements ; secondly, an NMR study of the titanium fluorophosphates aqueous solutions allowed identifica- tion of the species in solution. The elucidation of the PNBU was performed by NMR *in situ* and *ex situ* analyses of crystallization. In a last step, rational design was successfully applied in particular to the synthesis of a mesostructured new titanium phosphate.

Our first observation was that the chemistry of titanium in water is limited by its very low solubility at almost all pH. Titanium is only soluble to some extent in strongly acidic medium, which imposes to work at very low pH to observe soluble species. This represents the main trend of titanium chemistry.

The second one concerned the drastic influence of pH on the dimensionality of the structures (Fig.I.20). The speciation of titanium in solution depends on several factors,  $[H_2O]/Ti$ ,  $[H_3PO_4]/Ti$  and [HF]/Ti as well as pH. In all these syntheses, the coordination state of titanium remains six. Therefore, controlling the formation of the network means controlling, as the first stage, the environment of titanium. It will contain,  $H_2O$ ,  $H_3PO_4$  and HF depending on composition ratios, and the actual charge of the species will depend on deprotonation of each ligand,  $H_2O$ ,  $H_3PO_4$  and HF.



**Fig.1.20.**- Inorganic networks of some titanium-based solids obtained under hydrothermal conditions as a function of the final pH. Solids are reported depending on the titanium octahedra connection mode (monomers, dimers, trimers, chains).

Acidity controls the state of deprotonation of the different kinds of species that we identified in solution. First,  $Ti(H_2O)_6^{4+}$  must be considered, then  $Ti(H_3PO_4)_x(H_2O)_{6-x}^{4+}$ ,  $Ti(HF)_x(H_2O)_{6-x}^{4+}$  and eventually  $Ti(HF)_x(H_3PO_4)_y(H_2O)^{4+}$ . As pH increases from 0, the titanium complex loses its protons and therefore is prone to condense. The partial charge method of Henry shows that, at pH = 0,  $Ti(H_2O)_{6-x}^{4+}$  has already lost two protons and exists in both forms:  $TiO(H_2O)_5^{2+}$  or  $Ti(OH)_2(H_2O)_4^{2+}$ . The existence of this titanyl bond has been investigated and it has been shown that the two forms with titanyl TiO and  $Ti(OH)_2$  interconvert in water. The presence of phosphate and fluorine in the complexation sphere of titanium modifies this equilibrium. The competitive fluorine/phosphate complexation was fully quantified during this study for explaining the various connectivities of the species.

The first mixture of titanium source, solvent, HF and  $H_3PO_4$ , produces a solution containing Ti surrounded by  $H_2O$ , F<sup>-</sup> and  $H_3PO_4$ . Without fluorides, at pH between 2 and 3,  $H_3PO_4$  starts to deprotonate, Ti–O–P bonds form. In the presence of F<sup>-</sup>, Ti containing species have already lost 2 protons and form a titanyl bond. Depending on F : P ratio, the fluorides may stay or not in the crystal, and if they stay inside, they decrease the titanium functionality creating terminal Ti-F bonds. Adding an amine in hydrothermal coditions leads to further deprotonation of phosphates, which therefore connect the network. The first pH controls the number of Ti–O–Ti bridges, non-connecting bonds, the F/P the number of "protected" Ti vertices, and the vertices remaining define the node functionality of each titanium. As the amount of amine defines the final pH, *i.e.* the protonation state of the phosphate, it defines the dimensionality of the network. Hydrolysis ratio of titanium, functionality control by F/P, dimensionality control by final pH and pore shape by amine selection, allow to



**Fig.1.21.** Left : Structure of  $\pi$ -TiP with the two (1) and (2) possible SBUs describing the structure ; right : the true PNBU which represents the same brick which leads to both the formation of the microporous and the hexagonal mesophase.

In this series, among the various solids that we isolated, two attracted our attention; the microposous  $\pi$ -TiP or Ti<sub>2</sub>O(PO<sub>4</sub>)<sub>2</sub>, 2 H<sub>2</sub>O and our new Mesoporous hexagonal titanium fluorophosphate309. Their conditions of synthesis were indeed very close leading, depending on the template, on either a microporous or a mesoporous phase. This feature incited us to look at their mechanism of formation using the same strategy (X-Ray powder diffraction coupled with *ex-* and *in situ* <sup>31</sup>P and <sup>19</sup>F NMR studies as a function of time (range 0-45 hours)). The solid crystallizes after 3 hours.

After the *ex-situ* identification of the various species, and their evolution *vs.* time, the study of both solids proved that it is the same PNBU which is the building block leading to both micro- and mesoporous phase H-TiP. Therefore, the crystallisations of  $\pi$ -TiP and H– TiP occur probably through a common step involving the same PNBU Ti<sub>2</sub>OF<sub>2</sub>(HPO<sub>4</sub>)(H<sub>2</sub>PO<sub>4</sub>)X<sub>5</sub> (X = OH, H<sub>2</sub>O). The final connection of the PNBU to produce the solid is however different since no template is present for  $\pi$ -TiP and micelles of surfactant are located within the pores in the case of the mesophase. In both cases, the PNBU is thought to be associated in solution with a counterion, H<sub>3</sub>O<sup>+</sup> or micellar CTA<sup>+</sup>, to create neutral pairs that eventually condense. However, this part of the mechanism of formation has still to be elucidated.

Finally, these results indicate that our investigation methodology is also successful for the formation of mesoporous compounds. It is an important result and, to the best of our knowledge, it is the first time that this phenomenon is demonstrated.

#### 6. Reasons for the abandon of the topic.

Despite interesting from the academic point of view, and even if we brought new contributions to the topic of inorganic porous solids, we decided to stop our research on this class of solids.

After ten years, we had enriched the crystal chemistry databases of similar solids by discovering new topologies. We had discovered solids with large pores. We proved that it was realistic to increase the number of possible metallic cations (mainly transition metals *3d*) which can be incorporated in the phosphate framework and, consequently, introduced *for the first time* the physical properties - like magnetism - usually encountered in dense oxides, fluorides

**Our main papers in this series :** The feature article in *Chem. Comm.* 2755-2765 (2003) [364] and the references therein gather all the results of this study. The other papers are *C. R. Acad. Sci. serie IIc*, **2**, 85 (1999) [223]; *C. R. Acad. Sci. serie IIc*, **2**, 147 (1999) [224]; *Inorg. Chem.*, **38**, 5370 (1999) [247]; *J. Mater. Chem.*, **9**, 579 (1999) [219]; *J. Mater. Chem.*, **9**, 1185 (1999) [231]; *Chem. Mater*, **12**, 444 (2000) [260]; *Solid State Sci.*, **3**, 623 (2001) [294]; *Inorg. Chem.* **21**, 5350 (2001) [298]; *Chem. Mater.* **14**, 180 (2002) [309]; *Chem. Mater.* **14**, 998 (2002) [309]; *Chem. Mater.*, **14**, 4939 (2002) [345]; *Chem. Mater.*, **15**, 2328 (2003) [357].

and sulfides. That was a noticeable contribution but, to my opinion, the most important one was to elucidate the mechanism of formation of this type of solids from various *in situ* methods and to highlight the tight correlation between the reactive species in the hydrothermal medium and the secondary building blocks which allow the macroscopic description of the structures, and to reconsider the relative importance of each experimental

parameter on the occurrence of given phase. What I consider as a breakthrough allowed not only to introduce rationality in the design of new structures, but also, by the edition of a special program, to predict the few possible structures which can arise from a given SBU and a given template. For the academic chemist that I was, it was a great intellectual satisfaction to have more understood how the solids form and to have improved my culture, useful for entering in the promising domain of hybrid porous solids, particularly – but not only ! - in terms of new applications ;

Indeed, since a long time, the domain of porous solids implies an economic dimension, due to the numerous applications used primitively in the domains of petroleum chemistry, catalysis, gas storage and separation and fine chemicals. Even if some interesting catalytic and hydrogen storage properties were evidenced for the porous nickel phosphates, it was not enough for expecting an interest of industries for our phases.



Fig.I.22-. Evolution wit time of my contribution to the topic of porous solids. After an overlap of my activities concerning both inorganic and hybrid porous solids between 1998 and 2005, our current works concern now exclusively hybrid porous solids (papers concerning inorganic frameworks appear in grey; in orange, those related to hybrids).

Even if their chemistry is rich, their principal default remains the difficulty to extract the template from their framework for obtaining an accessible porosity, essential for applications. Most of the time, activation unfortunately leads to a collapse of the structures, except for nickel phosphates. This was the main reason of our abandon of the theme.

Moreover, since 1997, we had simultaneously developped research on the newly discovered hybrid porous solids (or MOFs), which seemed to represent a new field to explore academically, conjugated with the multiple potential new applications expected for this class of solids beside the classical ones. My decision to stop the porous inorganic phosphates theme for privileging Metal-Organic Frameworks occurred in 2005, after the end of some PhD theses. However, the richness of the experience that we had accumulated with phosphates and the original strategy that we had developped were extremely useful. We immediately applied it to this new class of solids, thus providing an integrated approach to its knowledge an approach which remains original compared to the usual one of the community.

# **CORPUS. PART II.1**

### MILS POROUS SOLIDS WITH A HYBRID ORGANIC-INORGANIC FRAMEWORK (MILs: Materials of Institut Lavoisier).

## THE BREATHING EFFECT

### POROUS SOLIDS WITH A HYBRID ORGANIC-INORGANIC FRAMEWORK OR METAL-ORGANIC FRAMEWORKS (MILs: Materials of Institut Lavoisier).

A SHORT INTRODUCTION

Experimentally begun in 1997, it represents the last but, probably, the richer part of my scientific life. As mentioned before, the experience I accumulated on inorganic porous solids prepared me once more to an integrated approach of this new class of solids.

Indeed, conceptually, inorganic and hybrid porous frameworks, have close topologies (Fig.II.1). Both have walls and windows. In the first, the 3D network, built up from the 3D connection of polynuclear inorganic bricks (the so-called SBUs) encapsulate a template (amine). In the second, the brick is composed of inorganic and organic species (carboxylates, phosphonates...) exclusively linked by strong bonds, but as the organic moiety has a variable carbon chain between the coordinating functions, this introduces a potential tunability for the dimension of the pores, playing on the length of this chain. This tunability is impossible to realize with the inorganic porous solids. In hybrid solids, it is the molecule of solvent which acts as template. The approaches of both families are therefore quasi-identical.





However, beside tunability, some other differences: (i) in inorganic solids, the extraction of the template, most of the time (except for silicates, lead to a collapse of the structure whereas it is easy for hybrids in which the trapped species is the solvent; (ii) as we shall see, the number of possibilities for incorporated metals within the framework are much larger for hybrids. Joined with the very large number of possible ligands, it appears that the family of hybrid solids will be extremely richer than the inorganic one.

When I tackled this new theme, I was convinced that syntheses and structures, despite essential, were not sufficient to illustrate the extreme richness of this family, beyond chemistry. The variety of solids, the metallic substitutions authorized within the framework, the tunability of the size of the easily accessible pores opened the way for discovering new properties beside – without neglecting them - the usual ones like adsorption and gas storage.
For that, and simultaneously with my colleague Kitagawa in Kyoto, we discovered by chance a new state of crystallized matter : the giant and reversible flexibility (or « breathing phenomenon » ) of our solids, which can lead to a variation of the volume of the unit cell larger than 300% <sup>443</sup>. Far beyond the curiosity, I immediately understood that this phenomenon, due to its extreme sensitivity toward stimulii, could, after the structural explanation of the phenomenon, be of great help for, in a first step, deepening the understanding of the physical chemistry of these type of phases, in particular, by several *in situ* techniques and computer simulations, for deciphering the nature, diversity and intensity of the host-guest interactions which are practically unknown. Such an unusual feature, which corresponds for us to an important activity (63 papers) deserved in this report a dedicated part, where physical chemistry is predominant..

Moreover, it is worthy to note that, when I began the research, the known Metal-Organic Frameworks were rather scarce and mainly concerned divalent metals, probably because of their easy synthesis. Therefore, since the very beginning, and with the lessons of my previous experience, I adopted an integrated multi-facets strategy.

The strategy for an integrated approach :

- 1. Concerning synthesis
- a) identify the variety of oxidation numbers of the metals able to generate the hybrid solids ;
- b) extend, beside the classical solvothermal method, the ways of synthesis leading to MOFs ;
- c) determine on some examples the most important chemical parameters influencing the synthesis :
- d) try to elucidate, for some selected interesting solids, their mechanism of formation ;
- e) favour the reactions in aqueous medium instead of organic solvents, for their cheap cost ;

f) concentrate the studies on the solids resistant to humidity, one of the first criteria requested for by industrial colleagues for large-scale production and applications ;

- g) focus the attention on the quality of activation of the phases ;
- h) search the rational possibilities for getting pores as large as possible,

2. Concerning the structural aspects, and even if – for the moment – it is often easy to get single crystals, it seemed to me that, with the increasing complexity of this class of solids, the probability to grow crystals would decrease soon. So, I first developped *ab initio* structural resolution from synchrotron powder data, which was particularly useful when we tackled the dynamic aspects of the structures and their change with time under the action of an external stimulus (pressure, temperature, insertion). We created special apparatus able to follow in real time the evolution of the patterns;

3. Concerning the properties, our action focused on the various possibilities provided by the triple characteristics of porous solids : framework-pores-specific surface area for generating new properties beside the classical ones (adsorption, storage...). The goal was to show that this class of solids could present also, using an appropriate chemistry, the physical properties usually encountered in dense phases (conduction, magnetism, optical properties...) ;

4. As soon as properties are envisaged, their application at the industrial scale implied the mastery of a shaping of the material, adapted to the dedicated application. In this way, we created nanoparticles, thin films, monoliths of our solids beside the bulk production.

Table I summarizes both the extent of our chemical and structural contribution with a number of different metals (more than 120 new structure types), and the various physical aspects of the characterizations we performed on some of these solids for evidencing and explaining their various new properties.

### THE UNUSUAL FEATURE OF FLEXIBLE HYBRID POROUS SOLIDS : The « breathing » phenomenon ; explanation and properties.

Living matter, polymers are flexible, with various magnitudes of swelling, but they are structurally amorphous. If one except the thermal variations of the atoms or the reversible displacive phase transitions in crystallized solids, which correspond to small atomic displacements (< 0.5 - 1Å), the ordered matter can be considered as a first approximation as rigid. Therefore, independently in 2002, great was our surprise, Prof. Kitagawa and myself, when observing for the first time the noticeable flexibility in our solids, with several Å displacements.

### The fact :

In our case<sup>308,316,342</sup>, the phenomenon was initially observed using benzene-dicarboxylates (1,4-BDC) as ligands bonded to different trivalent metals [ $Cr^{3+}$  (MIL-53) and  $V^{3+}$  (MIL-47)]. As-synthesized in aqueous medium, they are mono-hydrated and isostructural. Their structure, solved by *ab initio* powder diffraction, consist of chains of metal octahedra sharing OH corners. These chains are linked together through BTC ligands and form a rhombic framework with lozenge-shaped tunnels in which the water molecules of solvent are inserted. The first evacuation of water by heating leads to an expansion of the unit cell and a volume increase of 38%. Followed by X-ray thermodiffractometry (Fig.II.2), this swelling, visible from the spectacular displacement of the Bragg peaks, occurs without any amorphisation of the structure. It leads to an arrangement with the same topology, but this time with empty large pores (LP) instead of the primitive narrow ones (NP). Rehydratation of the anhydrous LP form is reversible with  $Cr^{3+}$  (MIL-53) and provides again the shrinked NP form. Hundreds of cycles show the same reversibility (*« breathing »*) without any loss of crystallinity. Interestingly, MIL-47 ( $V^{3+}$ ), whose colour changes from green to blue during dehydration, remains in the LP form upon hydration. XPS experiments proved that vanadium(III) was oxidized into vanadium(IV) during heating with a simultaneous loss of the hydrogen of the OH groups within the chains ( $V^{3+}$ -OH becomes  $V^{4+}$ -O). This fact was sufficient to rule out the contraction.

This first simple observation induced four important features which justified our long study for explaining the phenomenon at the molecular level : (i) water, and more generally solvents, represent one stimulus generating the breathing ; (ii) the nature and oxidation degree of the metal influences the phenomenon ; (iii) both the rigid MIL-47 and the flexible MIL-53 with the same topology can serve as models for quantitatively looking by various techniques (NMR, IR, EXAFS, microcalorimetry) at the different host-guest interactions. They indeed govern the flexibility. Their respective strength provide different contributions to this new state of matter ; (iv) this understanding would allow the determination of the rules governing the occurrence of this phenomenon and the search for non classical properties.



Fig.II.2. - (left) : X-ray thermodiffractometric study of the dehydration-rehydration process vs. temperature of MIL-53(Cr). The corresponding structures are shown at each step; (right) : crystal structures of (a) the NP form and (b) the LP form of MIL-53(Cr); the same phenomenon is observed for another Cr(III) carboxylate (MIL-88)<sup>443</sup>; (c) and (d) represent their NP and LP forms respectively. The variation of the cell volume between the two forms is larger than 300%.

### The mechanical reasons:

Each carboxylate function of the benzene-dicarboxylate ligand (1,4-BDC) shares its two oxygens with two octahedra of one chain; therefore, the whole ligand is linked to two different chains of the structure of MIL-53(Cr). The flexibility of the edifice results first from the two oxygens of –COO which can act as '**knee-caps'** between the inorganic chain and the phenyl ring during the transition and allow the deformation of the structure (Fig. II.3).



Fig.II.3. - (left) : Illustration of the 'knee-cap' role of the axis of the two oxygens of the –COO function during the deformation of the structure; (right) : the different guest-guest and host-guest interactions responsible of the contraction of the framework when water is in the tunnels.

Moreover, the shrinkage of the structure when water is introduced is due to the onset of three different types of hydrogen bond interactions, sufficiently strong for inducing the movement (Fig. II.3 right). First, the inserted water molecules interact with themselves in a guest-guest interaction and form a chain at the center of the tunnel, chain which will act as the backbone of the movement. Evidenced by *in situ* NMR performed during the hydration on the isostructural MIL-53(AI)<sup>373</sup>, two other interactions, this time host-guest, are observed: one between the H of the inserted H<sub>2</sub>O and the oxygen of the carboxylate, the other between the oxygen of H<sub>2</sub>O with the hydrogen of the OH groups of the chains. These interactions occur along the small diagonal of the lozenge-shaped tunnel ended by two different chains of octahedra, and alternatively above and below the central water chain. This symmetrical interactions with two opposite inorganic chains make that the latter become closer during hydration. Then, with Al and Cr, the structure shrinks, and reopens during dehydration. However, it is not a general feature.

### Nature of the metal vs. breathing of the MIL-53 type

Indeed, when Fe<sup>473</sup> and Ga<sup>477</sup> are used instead of Al and Cr, it is the contrary. Dehydration occurs in two steps :





starting from the hydrated MIL-53(Fe) already in a NP form, the intermediate structure of an hemihydrate exhibits two types of tunnels and increases the shrinkage, before the complete dehydration corresponding to the closest variety of the NP form. One note during the *in situ* Mössbauer spectroscopy study, a specific signature of the quadrupolar splitting for each phase. The structure reopens only at 500K.

The existence of magnetic dipolar interactions between iron ions could be proposed to explain the permanent closure of the tunnels but the example of MIL-53(Ga) rules out such an argument. A careful comparison between all the members of the family, demonstrated finally that it is the distance between phenyl rings, responsible of  $\pi - \pi$  interactions which is a key factor. The variable strengths will contribute specifically to the occurrence of the NP and LP forms *vs.* temperature.

Anyhow, and far beyond the case of water, this first study highlighted the importance of the guest species acting as *stimulii* for the breathing behaviour. It was therefore important to look at the influence of the chemical nature of the stimulii on the extent of swelling, in relation with their interactions with the framework.

### Breathing, guests and strength of interactions

Most of the studies below refer indirectly to properties of adsorption. However, at variance to others, it was not with this aim of targetting performances that we looked at this aspect. **We just wanted to decipher the code, to understand from physical chemistry this new phenomenon** by developping complemetary and mostly *in situ* techniques able to provide the explanation. They included diffraction vs. time, temperature and pressure, quasielastic neutron scattering for studying the dynamic effects, NMR, IR, microcalorimetry. The end of the explanation required further modelization for being complete. It was done.

The guests could be gases, solvents or organic molecules. Greenhouse gases provided a remarkable sensor for explaining the strange and previously unknown phenomenon.

### a) $H_2$ and greenhouse gases

Among the gases, we focused our attention essentially on  $H_2$ , <sup>367</sup> the greenhouse gases  $CO_2$  and  $CH_4^{408}$  and sometimes light alkanes<sup>474,496</sup> for their numerous different characteristics and their effects on the simple structures of flexible MIL-53 and the isostructural rigid MIL-47.

Experimentally, two situations are observed. In the first, the adsorption curves exhibit a classical type I behaviour; no accident is observed in the curve of amount adsorbed vs. pressure (Fig. II.5a). This situation is encountered for all the solids with hydrogen (hysteresis at the desorption) and methane and only with MIL-47 adsorbing  $CO_2$ . The second belongs to **a new case of adsorption** in the field of hybrid porous solids. It is a two-step behaviour. After a fast adsorption at very low pressure, the curve reaches a 'plateau' in a certain range of pressure before increasing once more. Even at 70 kbars, the saturation is not reached. This phenomenon occurs only with MIL-53(Cr,AI) during  $CO_2$  adsorption (Fig. II.5b).





Such different situations using the same solid deserved to be explained. We therefore undertook a series of experiments combining for each gas *in situ* powder diffraction in real time at various pressures, with microcalorimetry and molecular simulations in order to provide complementary elements of explanations for such an unusual feature. Powder diffraction vs. pressure and temperature, performed at the ESRF Grenoble, used a new home-made set-up placed in the beam<sup>496</sup>. It is now in free access at ESRF. The gas is introduced at increasing

pressures in the tube containing the activated solid and the powder patterns are collected for each pressure. This gives the evolution of the cell parameters for each pressure with the possibility, if the product is sufficiently well

crystallized, to solve from powder diffraction the complete structure in order to provide structural informations about the location of the guests.

Quasi-elastic neutron scattering (QENS) permits access to the dynamics of diffusion. Microcalorimetry provides experimentally the thermodynamic elements, in particular the adsorption enthalpy, which indicates the strength of the guest-host ineractions. Finally, molecular simulations (DFT, Monte-Carlo, molecular dynamics) comfront experience and theory for the fit of the isotherms and give an image of the movements of the guests within the tunnels and their jumps from one adsorption site to another.

### a.1. Thermodiffractometry and localization of the guests.

The study of the hysteretic adsorption-desorption of  $CO_2$  at 300K was privileged because of the unusual shape of the isotherm. Performed on MIL-53(Cr), first in Daresbury and then at ESRF Grenoble for solving the structures, it quantitatively provides a structural explanation of the unusual aspect of the isotherm. Under vacuum the structure is open (LP type). When the  $CO_2$  pressure (3-4 bars) corresponds to 2  $CO_2$  molecules/unit cell, the 'plateau' is reached and the structure suddenly shrinks into its NP form. At higher pressures, the tunnels reopen. Moreover, from the <u>ordered</u> localization of the guests, the interactions become evident with the onset of  $CO_2$ -  $CO_2$  guestguest interactions forming the backbone and, from a consideration of distances, also the host-guest interactions which occur between the  $CO_2$  molecules and the OH groups of the chains.



Fig.II.6. - (left) : The crystal structures of MIL-53(Cr) at 300 K, in its LP form under vacuum and in a NP form when at least 2 molecules of  $CO_2$ /unit cell are adsorbed; (middle) : recall of the adsorption isotherm of  $CO_2$  (in blue) and  $CH_4$  (in red) in MIL-53(Cr) at 300K; (right) : two views of the localization of  $CO_2$  molecules within the tunnels. They clearly show the interaction between the  $CO_2$  guests and the OH groups of the chains, highlighted within yellow ellipses (see text).

This study is, to the best of my knowledge, the first explanation of what is physisorption in this type of solids. Indeed, it results from the interaction between the well known strong (- 1.4.  $10^{-35}$  C. m) quadrupolar moments of CO<sub>2</sub> with the dipoles of the OH groups, sufficiently strong to explain the retention of the NP form in an important range of pressures. At higher pressures, the structure reopens and the CO<sub>2</sub> molecules become disordered.

In situ IR spectroscopic experiments, performed in the same conditions as for the diffraction studies, provided an elegant signature of the dynamics of swelling during the hysteretic adsorption-desorption<sup>439,452</sup>. The evolution of the integrated intensity of the v2 bands between 645 and 665 cm<sup>-1</sup> give during the cycle the amount of adsorbed CO<sub>2</sub>. The shift from 1022 to 1017 cm<sup>-1</sup> of the v18a ring mode of the terephtalate entities signed the passage from the LP to the NP forms of the skeleton. At lower wave numbers (550-600 cm<sup>-1</sup>), (not represented here), the modification of the spectra caracterized the distortions of the framework under the action of the CO<sub>2</sub> molecules. The split of the v2

band into two components at 653 and 662 cm<sup>-1</sup> also reveals that the main interaction involves the formation of **electron donor-acceptor** complexes. Clearly,  $CO_2$ , which remains linear (no sign of carbonatation) acts as an electron acceptor while the OH group plays the role of donor. It was the first time that such an interaction between  $CO_2$  and OH was characterized in a solid.



Fig.II.7. - (left) : The crystal structure of activated LP form of MIL-53(Cr) at 300 K, with the adsorption-desorption cycle; (middle) : up : the hysteresis cycle deduced from the evolution with pressure of the intensity of the v2 band ; down : the fraction of LP form vs. P, cycle deduced from the evolution with pressure of the relative intensities of the v18a band ; (right) : corresponding evolution of the spectra.

Moreover the evolution vs. pressure of the intensities of the v2 and v18a bands provided both a new and independent measurement of the hysteresis cycle, in very good agreement with the previous one, and also the ratio between the NP and LP forms during the cycle.

However, a similar study performed with  $CH_4$  and  $H_2$  as guests show that there is **no breathing** for these species, both for MIL-53 and MIL-47 which remain in their LP form. The guests remain disordered in the tunnels. It was not surprising for the MIL-47 matrix because, as already mentioned, the oxidation of V(III) into V(IV) during the activation, hydroxyls are transformed in oxide ions, therefore suppressing the quadrupole-dipole interaction responsible of the breathing. As it does not exist also with MIL-53(Cr/AI) the strength of the interactions will be important for the breathing.

### a.2. Breathing or not breathing ? Thermodynamics of the interactions and dynamics of the guests.

The value of the enthalpies of adsorption provide an estimation of the strength of the interactions. We therefore measured them at 300 K by microcalorimetry at increasing pressures.

Concerning **hydrogen<sup>367, 465</sup>**, the enthalpies of adsorption are very weak (3-7 kJ.mol<sup>-1</sup>). Not only the solids do not breathe, but this low value explains why hydrogen is stored only at 77K. 15 kJ.mol<sup>-1</sup> would be necessary for observing adsorption at room temperature.

Despite non breathing, the type I adsorption isotherms obtained for **methane** reveal that, at 35 bars and 304 K, MIL-53 adsorbs ~6 mmol.g<sup>-1</sup> of  $CH_4$ , which is three times larger than for zeolites The enthalpies of adsorption of  $CH_4$ , relatively constant during pore filling, are centred around 17 kJ.mol<sup>-1</sup>, well above the liquefaction enthalpy of  $CH_4$ . This almost flat enthalpy profile (Fig. II.5 right) often corresponds to interactions between an adsorbate gas and relatively homogeneous surfaces. This 17 kJ.mol<sup>-1</sup> value means that (i) this energy is not strong enough for provoking the shrinkage of the structure and (ii) there is an obligation to determine more accurately the threshold in energy above which breathing occurs.

Noting that CH<sub>4</sub> is the first term of the series of **alkanes**  $C_nH_{2n+2}$ , we looked at the adsorption of these solids at 300 K for 2 < n < 9 <sup>474, 496, 516, 530, 548</sup>. Even if the increasing size and the conformational effects of the guests render more difficult their interpretation, the major feature is that, **from ethane, breathing occurs.** The microcalorimetric measurement of the enthalpies of adsorption show their linear increase with n (Fig. II.8). Their extrapolation

threrefore provides the values of the threshold : 20 kJ.mol<sup>-1</sup>, a value corroborated by independent DSC measurements of the dehydration of  $MIL-53^{484,532}$ .





The study of the kinetics<sup>474</sup> of the adsorption of alkanes revealed the presence of several regimes with an influence of both the alkyl chain length and the temperature. Finally, the observed very unusual temperature dependence of the loading capacity is probably due to a competition between standard adsorption thermodynamics and the temperature-dependent increase of the pore opening in the MIL-53 solids.

Moreover, depending on the NP or LP forms of the host, guests are either ordered or disordered in the tunnels, requiring to look by quasi-elastic neutron scattering (QENS) and NMR at **the dynamic aspects** of the gases adsorption in the NP and LP forms.

**The very high diffusion of H<sub>2</sub>** in MIL-47 and MIL-53, about 2 orders of magnitude higher than in zeolites, has never been observed in any nanoporous material<sup>465</sup>. In MIL-47(V), a 3D jump diffusion model is predominant, with a distribution of jump lengths being 4.3 to 22 Å for the highest and lowest H<sub>2</sub> concentrations, respectively, whereas, in MIL-53(Cr), a 1D jump model is observed. The jump length, around 7Å, corresponds to the distance between two OH groups of the chain. The significantly higher diffusivity in MIL-47 than in MIL-53 is in agreement with a lower activation energy for Mil-47 (0.6 kJ.mol<sup>-1</sup> instead of 1.6 kJ.mol<sup>-1</sup>).

The same type of comparison was done for CH<sub>4</sub> and CO<sub>2</sub>. **For methane**<sup>466</sup>, **a 1D diffusion model** corresponding to the motion of CH<sub>4</sub> along the tunnel was observed in both MIL-47 and MIL-53. The methane diffusivities are significantly higher in MIL-47(V) than in MIL-53(Cr) over the whole range of investigated loadings. This observation is consistent with the trend observed for the activation energy  $E_a$  measured for similar loadings : 3.0 and 8.0 kJ.mol<sup>-1</sup> for MIL-47(V) and MIL-53(Cr), respectively. This means that the  $\mu_2$ -OH groups in MIL-53(Cr) act as attractive sites and steric barriers, and both effects contribute to perturb the trajectory and thus decrease the mobility of CH<sub>4</sub>. Calculation of the probability density of methane in the tunnels of both MILs clearly show that the positions of CH<sub>4</sub> with the highest probability in the pore of MIL-53(Cr) (Figure II.9 top) are centered around the  $\mu_2$ -OH groups.



Fig.II.9. - (top) : 2D density plots at 250 K of the distribution of methane for 1  $CH_4$  /unit cell in MIL-53(Cr) (left) and MIL-47(V). White regions have a higher probability of containing  $CH_4$  molecules, black regions mean unfavourable positions ; (bottom) 2D free-energy maps at 250 K in MIL-53(Cr) (left) and MIL-47(V) (loading : 5  $CH_4$  /unit cell).

In MIL-47(V)), a broader probability distribution within the pore is obtained, but the regions around the  $\mu_2$ -O groups remain the most favorable. This is confirmed by the free-energy maps (Figure II.9 bottom). In MIL-53(Cr), lower-energy regions are centered around the  $\mu_2$ -OH groups as well as in the middle of the pore. In MIL-47(V), this latter region is much more favorable for the CH<sub>4</sub> molecules. Furthermore, minimum-energy pathways of CH<sub>4</sub> in the pores of both MILs can be approximately drawn by following the lower parts of the 2D free-energy maps (Figure 6). They are predominantly orientated along the direction of the tunnel and thus confirm a 1D diffusion mechanism in both cases. In MIL-53(Cr) (Figure II.9 bottom left), one can imagine a sequence of jumps between two consecutive  $\mu_2$ -OH groups (mean jump lengths : 5.6Å with time intervals of 7.3 ps).

This observation suggests that the diffusion of CH<sub>4</sub> is mainly ruled by the presence of the  $\mu_2$ -OH groups, which leads to 1D diffusion along the tunnel of the pore. As MIL-47(V) does not have  $\mu_2$ -OH groups, one would imagine a 3D diffusion but Fig.II.9 shows thet the diffusion remains roughly 1D with mean jump lengths of 8.3 Å with time intervals of 6 ps.

**Concerning carbon dioxide**, the dynamic aspects of the inserted molecules within the tunnels of MIL-47 and MIL-53 are drastically different.

• For MIL-47, which exists only in the LP form whatever the loading, only a very small contraction of the unit cell is observed (1%). QENS experiments coupled with molecular dynamic calculations show a purely 3D diffusion mechanism with non passage from one tunnel to the other<sup>509</sup>. The activation energy for 4 CO<sub>2</sub>/unit cell (6.4 kJ.mol<sup>-1</sup>) is significantly higher than those previously determined for CH<sub>4</sub> (3.0 kJ.mol<sup>-1</sup> and H<sub>2</sub> (0.6 kJ.mol<sup>-1</sup>). The density plots corresponding to the probability density of CO<sub>2</sub> within the pore of MIL-47(V) at 230K for two loadings (Fig.II.10), illustrate this **3D mechanism in the LP form**.



Fig.II.10. - Typical 2D probability density plots at 230 K showing the 3D microscopic diffusion mechanism of  $CO_2$  in MIL-47(V) at low (2  $CO_2$ /unit cell); left) and high (7  $CO_2$ /unit cell; right) loadings.

• For MIL-53, breathing occurs, with a large (38%) variation of the cell volume between the NP and the LP forms. A study, similar to above, was undertaken at 230K<sup>470</sup> for several loadings : 1.0, 2.5, 3.7, 5.2, and 7.4 CO<sub>2</sub> molecules per unit cell (u.c.), which cover the range of loading in which the MIL-53(Cr) framework exhibits the two reversible structural switchings. For a CO<sub>2</sub> concentration of 5.2 molecules/u.c., the activation energy for transport diffusion (9.7 kJ.mol<sup>-1</sup>) is higher than those previously reported in zeolites (5-6 kJ.mol<sup>-1</sup>). This confirms, in agreement with microcalorimetry, that the interactions between CO<sub>2</sub> and the  $\mu_2$ -OH groups at the MIL-53(Cr) surface are rather strong. The corrected diffusivities only show moderate variations with increasing CO<sub>2</sub> concentration, with values centered around 10<sup>-10</sup> and 10<sup>-8</sup> m<sup>2</sup>.s<sup>-1</sup> for the NP and LP forms, respectively.



### (b) LP (7 $CO_2/u.c.$ ) forms of MIL- 53(Cr). The white and black regions correspond to regions of lower and higher free energy, respectively.

The significantly slower diffusivity for the NP form is related to the highly orientational already evidenced ordered arrangement of the confined CO<sub>2</sub> molecules into the channel. In contrast, the diffusivity of CO<sub>2</sub> is faster in the LP form due to the larger space available within the pore and the weaker interaction with the CO2/MIL-53(Cr) pore wall. Free energy maps through a given channel were calculated at different loadings for both forms of MIL-53(Cr). They show that in the NP form (Figure II.11), the lower-energy regions are centered on the  $\mu_2$ -OH groups whatever the CO<sub>2</sub> concentration. This suggests that the slow diffusion of CO<sub>2</sub> is mainly caused by the strong interaction between the diffusive species and these OH groups. Further, the minimum-energy pathways of CO<sub>2</sub> in this NP form, which can be approximately drawn by following the lower parts of the 2D free-energy maps, shows that the CO<sub>2</sub> molecules are predominantly orientated along the direction of the tunnel. This observation suggests that, **in the NP form, a 1D single-file diffusion mechanism** takes place.

Despite larger pores, **the diffusion mechanism remains mainly 1D in the LP form**. As shown in Fig. II.11 right, the displacements of the CO<sub>2</sub> molecules are mainly restricted along the direction of the tunnel, and the most favorable interactions between CO<sub>2</sub> and the  $\mu_2$ -OH groups lead to a global 1D normal diffusion mechanism, even more valid at higher loading (7CO<sub>2</sub>/u.c.), where the interactions between the probe molecules tend to enhance the predominance of unidirectional diffusion by sterically restricting motion.

### a.3. Computer simulations vs. experiments.

For such a new phenomenon and its various consequences, the observation is by far not enough. We explained above its reasons but for being complete, one must also verify that a modelization of this novelty is possible and - of course - in close agreement with experience. This had not been done before, except for the molecular dynamics calculations in relation with the above QENS experiments, for which programs already existed. This represents one of our breakthroughs.

With such a challenge, the first difficulty was to derive for the force field based simulations a set of accurate potential parameters able to capture the associated structural transition implying a unit cell volume change up to 40% experimentally observed for the MIL-53 structure. This permanent experimental/modeling interplay allows a full validation of the derived flexible force field, pre-requisite for further understanding the microscopic key features that govern the spectacular breathing of such a material.

Multidisciplinary computational approaches, including quantum (Density Functional Theory)<sup>459</sup> and force field based simulations (Monte Carlo/Molecular Dynamics)<sup>448, 459, 465, 466, 470, 483, 542</sup> or macroscopic thermodynamic models<sup>459</sup> (see also *J. Am.Chem. Soc.* **2008**, *130*, 14294 and *ChemPhysChem.* **2011**, *12*, 247)) have been further conducted to get insight into this guest assisted breathing phenomena. The conclusions drawn from this modeling effort were supported by a series of experimental measurements (manometry, microcalorimetry, Infrared, *in situ* X-ray diffraction....) realized on the MIL-53(Cr,AI)/CO<sub>2</sub> system.

Our first contribution was the derivation of a specific flexible force field for the MIL-53(Cr) framework which, combined with an Hybrid Osmotic Monte Carlo (HOMC) scheme, successfully captured the low pressure domain of the CO<sub>2</sub> adsorption isotherm, while it failed to reproduce the re-opening of the structure at intermediate pressure, leading to an incomplete description of the experimental adsorption isotherm. Only recently<sup>567</sup>, from the above knowledge gained on the key structural parameters of the MOF framework that govern the guest assisted structural transition, we produced a reparameterization of our previous flexible force field which not only fairly describes the experimental CO<sub>2</sub> adsorption isotherms at 300K in the <u>whole</u> range of pressure, always using HOMC simulations (Fig. II.12 left), but is also valid for the LP  $\rightarrow$  NP  $\rightarrow$  LP transformations as a function of temperature and external pressure, as described farther.



Fig. II.12. - [left] HOMC simulated (dashed line) and experimental (solid line)  $CO_2$  adsorption isotherms at 300 K for the MIL-53(Cr) solid ; - [right top] Calculation of the evolution with time of the cell volume of MIL-53(Cr) for different values of the number of CO2 molecules within one unit cell; [right down] the evolution of the cell volume vs. the number of  $CO_2$  molecules within the cell. The black line is simply a guide for the eye.

This allowed also to simulate the temporal variation of the cell volume as a function of the number of  $CO_2$  molecules within the tunnels. This important result, not directly accessible by experience, explains the existence of the plateau during adsorption. Indeed, even for molecules having a high enthalpy of adsorption, breathing occurs only for a minimum number of guests in the cell, a minimum which corresponds to the establishment (for reasons of proximity) of strong guest–guest interactions within the tunnel. These  $CO_2$ – $CO_2$  interactions act as a backbone for the adsorbed species and allow the double interaction between the oxygen atoms of the adsorbate and two hydrogen atoms on the hydroxyl groups on opposite chains. This symmetry and a threshold intensity of the interactions is essential for the occurrence of the contraction. This last remark regarding intensity is crucial and explains why MIL-53 does not breathe with methane. Its enthalpy of adsorption is too low and, mainly due to the spherical and apolar characters of methane, rules out the development of strong guest–guest interactions which could lead to a contraction.

### b) Solvents and other organic molecules

Even if we had a preference for syntheses in aqueous medium, we were sometimes obliged to use organic solvents which often change the results of the synthesis. It was the case for MIL-53. In a DMF medium, we indeed obtained a new solid : MIL-68<sup>370</sup>, with the same chemical formula than MIL-53, but this time rigid with hexagonal and triangular tunnels. The question was therefore, on the contrary, to see if the introduction of solvents like DMF in a swelling structure was able to change its topology or not MIL-53(Fe),  $H_2O^{473}$  (NP form) was used as test material. When put in an organic solvent, the exchange between it and the initial  $H_2O$  guest is immediate and complete, leading to the LP form. Therefore, we performed a series of experiments realized under the synchrotron X-ray beam, where an aqueous solution of the solvent (10%) is introduced drop by drop in a stirred suspension of MIL-53(Fe),  $H_2O$  in water. At each drop, a diffraction pattern is collected (Fig. II.13 left), up to the time when the exchange is complete, thus providing a picture showing quantitatively the evolution of the NP:LP ratio *vs.* time ratio during the exchange (Fig. II.13. right).

Surprisingly, as soon as a few guest molecules penetrate the tunnels, they weaken the strong H<sub>2</sub>O-host hydrogen bonds and the volume adopted by all the cells in the grains of MIL-53 that are in contact with the added solvent adopt the volume of the fully exchanged sample, despite the fact that the majority of guest molecules in the tunnels are still water molecules. This means that, since the beginning of the exchange, the two extreme structures coexist. We called that the **« forceps effect ».** Indeed, this striking structural effect looks like the operation of forceps: as soon as the entrance of the tunnel is opened, the rigidity of the chains of octahedra obliges the whole structure to adapt and follow the effect of the stimulus. It may be thought that the volume therefore increases as a first order transition that affects progressively all the grains in contact with the solution of guest. This is in agreement with the curves describing the decay of the hydrated material and the growth of the final phase since they cross at very close to 50 %, suggesting a direct conversion of one phase to the other without the formation of any significant amount of an intermediate, disordered phase.

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Fig. II.13. [left] Scheme of the exchange experiment under the X-Ray beam of Daresbury synchrotron; [right] Contour plots of diffraction data measured during the uptake of lutidine by MIL-53(H<sub>2</sub>O) from the (a) detector at  $2\theta = 1.495^{\circ}$  (b) detector at  $2\theta = 4.34^{\circ}$ . The d-spacing (Å) is related to the energy, E (keV), by E = 6.11926 / (d.sin $\theta$ ).

Moreover, the X-ray powder pattern obtained with the fully exchanged sample allows the determination of the localization of the solvent within the tunnels and, therefore, to inform about the principal interactions governing the expansion of the unit cell.



Fig. II.14. Comparison of the theoretical evolution of the cell volume vs. d/D (black squares) with the experimental ones (red, green and blue filled circles) associated with the changes of symmetry and space groups during the swelling. The discontinuities and small deviations from the theoretical curve illustrate the influence of host-guest interactions in the phenomenon. The increase of swelling of the transient water-methanol phase at 0, 25 and 40 minutes is shown as orange stars.

The same experiment was repeated with many solvents, protic and non-protic, polar and non-polar. First, the cell volumes of the fully exchanges samples was determined. The particularly simple topology of the MIL-53 type easily permitted also to establish the evolution of the theoretical volume of the cell (see insert of Fig. II.14). The later

were calculated as a function of the ratio between the two diagonals of the lozenge section of the tunnel (the third parameter being considered, in agreement with experience, as constant). The fit between this theoretical curve and the different experimental values of the volumes is excellent, whatever the change of space group which however keeps the same topology (Fig. II.14).

Note that, with alcools, the situation is rather different because, instead of observing the two extreme structures since the beginning, there is a limited zone of solid solution in which water and alcool coexist in the same tunnel and both participate to the swelling.

This study shows that the *d* distance, characterizing the short diagonal, provides a qualitative estimation of the relative importance of the guest-guest ( $I_{G-G}$ ) and host-guest ( $I_{H-G}$ ) interactions *vs*. the extent of swelling (Fig. II.15).



Fig. II.15. [left] *Scheme of the different interactions occurring in the hydrated MIL-53 structure* [right] *Relative predominance of the two types of interactions as a function of <u>d</u>.* 

Fig. II.16 provides some illustrations of the localization of the guest molecules within the tunnels, particularly those possessing a phenyl ring. This underlines some new features which participate to the breathing.



Fig. II.16. [first row] Final structure of m-xylene at 300K and of the two different localizations of quinone at different temperatures; [Second row] Insertion of two N-donors: pyridine and lutidine with various situations of predominance of the various guest interactions.

The examples above exhibit another type of guest-guest interactions, completely different from those existing during the adsorption of  $CO_2$ . This time,  $\pi - \pi$  interactions are concerned, both guest-guest and host-guest.

The case of quinone <sup>482</sup> is particularly significant for the influence of temperature on the relative strengths of interactions; which can lead to reversible displacive phase transitions, as it is the case for the quinone guests. At 300K (Fig.II.16), they exhibit a perfect  $\pi$ – $\pi$  stacking, nearly parallel to half of the four organic walls and identical from one cell to the other. It governs all the interactions. Suddenly, at 350K, a reorganization of half of the four organic walls is clearly observed. Within the same tunnel, the double chain is still nearly parallel to half of the four organic walls, while the double chain is tilted in order to be nearly parallel to the second half of the four organic walls in the nearest neighbouring tunnels. This phenomenon corresponds to a **"flip flop effect**", Indicating qualitatively a decrease of host-guest interactions, whereas the guest-guest ones remain almost the same. Unfortunately, the accuracy of our structure determination is, despite a change of space group, not good enough for correlating this transition with some tiny variations of the position of the phenyl rings of the skeleton.

The comparison between the structures of pyridine- and lutidine-inserted phases is also of interest. Both of them present the same  $\pi$ - $\pi$  stacking as above. In both of them, the host-guest interactions occur between the nitrogens of the molecule and the OH grpups of the chains. From the examination of intermolecular distances, in MIL-53 pyridine, the shorter distance (2.68Å) between the guest and the chains indicates that the host-guest dominates, at variance to what happens with lutidine, where the the guest-guest ones are the stronger. This can be explained : with pyridine, N atoms point direcly toward the OH groups ; the CH<sub>3</sub> groups linked to N in lutidine serve as screens for the interaction and weaken it. Moreover, **a pronounced confinement effect** appears for pyridine when trapped in the tunnels. It is clear when comparing to the organizations of molecules in MIL-53 and in solid pure pyridine and lutidine. They are similar for lutidine, with the same type of stacking. On the contrary, they completely differ in pyridine. It is only because strong host-guest interactions exist with MIL-53 that the stacking appears, whereas it is not the case in pure pyridine. These interactions therefore act as an internal pressure for the alignement.

### The effect of other stimulii.

### Temperature alone:

The solid model was MIL-53(Al) due to its diamagnetic behaviour which allows multiple NMR characterizations. Experimentally, it was studied by colleagues.

Indeed, Liu *et al.* (*J. Am. Chem. Soc.* **2008**, *130*, 11813), using neutron powder diffraction and inelastic neutron scattering techniques established that anhydrous MIL-53(AI) showed a temperature-driven reversible structural transformation. Due to a marked hysteresis, the LP  $\rightarrow$  NP transition is complete below ~125 K, as is the NP  $\rightarrow$  LP transition above ~325 K. This experimental finding was further confirmed by a complementary experimental exploration based on electron spin resonance measurements (*J. Phys. Chem. C.* **2010**, *114*, 19443). Our recent computer simulation study<sup>567</sup>, using our programs (described above), allows to define the volume of MIL-53 as a function of temperature. It fairly justifies the observed hysteresis during the transition (Fig. II.17).



Fig. II.17. Simulated unit cell volume of the empty MIL-53 as function of the temperature at 0.1 MPa (from <sup>567</sup>)

#### Pressure alone :

The question was to know what was the effect of pressure on the breathing. We observed the reversible LP-NP transition in bare MIL-53 at room temperature from mercury porosimetry experiments by applying an isostatic pressure (ca. 50 MPa) all around the sample's microcrystals, using a mercury intrusion device <sup>533</sup>. The LP  $\rightarrow$  NP transition occurs at 55 MPa. The calculated free-energy of the transition is 3.5 kJ.mol<sup>-1</sup>) in agreement with DSC measurements described above ((5 kJ.mol<sup>-1</sup>).



Fig. II.18. Experimental unit cell volume of the empty MIL-53 as function of the applied pressure (from <sup>567</sup>)

By applying an external pressure at room temperature, using a home-made clampered cell allowing to impose pressures up to 1 GPa, the transition is observed with a large hysteresis (Fig.II.18) from neutron diffraction patterns (D1B ILL Grenoble) collected every hour for each pressure. In good agreeement with porosimetry, the LP  $\rightarrow$  NP transition occurs at 53.5 MPa (whereas it requires much more (137 MPa) for the 'rigid' MIL-47<sup>559</sup>). Decreasing pressure from 300 MPa leads to the NP  $\rightarrow$  LP change with a large hysteresis in pressure (50 MPa). Our simulation program with the new force field parameters nicely agree with the experimental data, both for temperature and pressure <sup>567</sup>. Note that a similar conclusion was recently drawn by Boutin, Fuchs and Neimark using the stress option of their osmotic thermodynamic model (see *J. Phys. Chem. Lettr.* **2011**, *2*, 2033 and refs. therein).

### The (T,P) phase diagram of the MIL-53 structure <sup>538</sup>:

Another way for evidencing more accurately these phase transitons was to mesure vs. temperature the adsorptiondesorption curves using Xe as probe  $^{499}$ , and to perform after a complete  $^{129}$ Xe NMR study of the transition  $^{524}$ 



Fig. II.19. - Xe adsorption (full symbols) and desorption (empty symbols) isotherms measured at 195 K (lozenges), 220 K (squares), 273 K (triangles), 292 K (circles) and 323 K (stars). Inlet: low-pressure region of isotherm at 220 K.

Xe adsorption-desorption isotherms were measured in the 0–1.2 bar pressure range at different temperatures: 195, 220, 273, 292 and 323 K  $^{499}$ . Below 300 K, the isotherms present one or two steps and hysteresis loops (Figure II.19). At 323 K, the adsorption isotherm presents no step and can be described by the Langmuir equation on the whole set of data. The amount adsorbed at saturation depends on the channel form. For a given form, it increases when temperature decreases.

The calculated isosteric heat of adsorption varies with the Xe concentration from 16-20 kJ/mol for the open LP form to ca. 30 kJ/mol for the closed NP form of the channels.

The <sup>129</sup>Xe (polarized or not) NMR study was undertaken *vs.* temperature and pressure<sup>524</sup> from a careful analysis of the chemical shifts of the various peak conributions during both adsorption and desorption. These chemical shifts are known to be extremely sensitive to their environement. Their study is a measurement of the local xenon amount in the tunnels and, consequently, represent the first spectroscopic quantification of the extent of transformation from large to narrow pores in MIL-53 materials.

Two types of lines are evidenced when pressure and/or temperature are varied. They are the signature of the LP form (line a in the legends of Fig.II.18) and NP form (line b).



Fig. II.20. – [left]: Chemical shift variation (squares) of line a (blue signature of the LP form) and line b (red; NP form) and linewidth variation (triangles) of line a as a function of **pressure**. Adsorption, solid symbols; [right] : Percentage of open (blue) and closed (red) channels as a function of pressure at Xe adsorption (solid symbols) and desorption (open symbols).

The appearance of line b) induces a large variation of the linewidth of line a). At variance to experiments performed with other guests, the NP  $\rightarrow$  LP is never complete. However, on the whole, <sup>129</sup>Xe NMR confirms the results obtained by other techniques : the LP form is the high temperature and low pressure form of MIL-53. It is the contrary for the NP form. All the results agree with the existence of a strong hysteresis and quantify its extent.

Gathering all the experimental and theoretical described above, and using the osmotic thermodynamical model of Boutin and Fuchs - which seems universal for describing the breathing of MIL-53 -, we are now able to **predict** the P,T phase diagram of MIL-53, and its breathing for different guests introduced in its tunnels.



Fig. II.21. -(T,P) phase diagram of the MIL-53 structure [left]: The LP  $\rightarrow$  NP transiton with differents guests [CH<sub>4</sub> (black & grey); xenon (yellow); carbon dioxide (black & red)] [right]: the T,P phase diagram of MIL-53 when it hosts these three guests. The domain of NP form appears in a color specific for each guest. The grey region corresponds to the domain of existence of the LP form.

The multiplicity of the techniques developed for understanding and explaining this new state of solid matter (structural, spectroscopic (NMR), thermodynamics, kinetics...) have provided many informations and allows us to consider that this new phenomenon is elucidated, at least in the case of the MIL-53 topology which was an ideal case owing to its structural simplicity. However, in the present case – which is almost unique for the moment - , the breathing effect is considered as a bistable system oscillating between a closed and an open form.

Two questions arise now:

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LOOKING AT A STRUCTURE, IS IT POSSIBLE TO <u>PREDICT</u> IF IT WILL BREATHE OR NOT?
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✤ IS BISTABILITY THE GENERAL PHENOMENON, OR IS THE MIL-53 EXAMPLE A FIRST MANIFESTATION OF A MORE GENERAL PHENOMENON, REFLECTING MULTISTABILITY?

### Some empirical structural rules for possible breathing 468, 485.

I propose them from my experiences, after having looked at many structures.

a) the first concerns the inorganic brick (SBU). Independently of the nature of the ligand, it seems that the only bricks which permit swelling are those which possess a mirror plane, with the carboxylates in symmetrical position above and below it. This allows their in-phase rotation. It is the case of the dimer of [Zn<sub>2</sub>(1,4-BDC)<sub>2</sub>(DABCO)] and of the trimer of MIL-88 (see below). Otherwise, the solid is rigid. It is the case for MOF-5 (Fig.II.22). This will be an *a priori* indication when new clusters are discovered. Experiments related to dynamic effects can then be performed.



Fig. II.22. – [left]: Structure of rigid MOF-5, showing the impossibility for the ligands to give in-phase rotations around the tetrameric cluster; [right] : Examples and counter examples showing the need of mirror planes within the cluster for allowing flexibility.

b) Even if it needs to be validated on many other examples, It seems that the ratio C/M (*C* : number of the carboxylate functions surrounding rhe cluster ; M number of metallic atoms within the cluster) is a good indicator of

the possibility of the brick to potentially allow swelling. From the few examples in the litterature, it seems that C/M must be  $\ge 2$  for such an effect.

- c) Breathing effects can only occur with ditopic carboxylates. Between two clusters, the kneecaps provided by the O-O axes of the different carboxylates ought to be parallel for possible in phase rotations. This condition obviously prohibits the use of tri-or tetratopic ligands for expecting swelling. This is typically the case of MIL-103<sup>407</sup> which uses tritopic 1,3,5 benzene trisbenzoate and MIL-102<sup>430</sup> formed with the naphtalene 1,4,5,8-tetracarboxylate.
- d) The existence of odd cycles in the structure, both at the level of the cluster and/or at the level of the topology of the skeleton, is unfavourable for dynamic effects, owing to their rigidity (case of MIL-68, MOF-5 for instance). A particularly illustrative example is provided by MIL-101 <sup>409</sup> which, despite favorable conditions (trimeric brick, ditopic ligand) does not breathe only because most of the windows of the cages are pentagonal. But, at variance to the other rules, it cannot be predicted because the topology is known *a posteriori*.
- e) Breathing occurs only if all the conditions above are satisfied simultaneously. In this case, adsorptiondesorption phenomena can exhibit *hysteretic effects* (gate effect, multiple-step adsorption...) depending on the nature of the guest and on the relative *energies* of host-guest and guest-guest interactions.

### Is the breathing effect a bistable system?

Until very recently, the very few examples described in the literature prevented for a definitive answer. The most spectacular case of this bistability was provided by our MIL-88 series <sup>385,443</sup>, also iron or chromium dicarboxylates, but with a completely different structure. In this series, which goes for the moment from terephtalate to diphenyl-dicarboxylate, the inorganic brick is a trimer of metallic octahedra linked by a central  $\mu_3$ -O oxygen (Fig.II.23); it satisfied the mirror-plane condition for breathing. The structures were experimentally determined. Simultaneously, our AASBU method, applied to hybrid solids, allowed, from the knowledge of the terephtalate to predict with a high accuracy the structure of the others <sup>411,418</sup>.

The 3D structure consists in the assembly of the inorganic trimers with the different organic linkers in such a way that two types of pores appear : tunnels and bipyramidal cages in which the guests are located. As synthesized, the solid guests water (form *As* in Fig.II.23). Dehydration provides the dry form with very contracted cages, but rehydration leads to a drastic increase of the cell volume (from 60 to >300% depending on the ligand)  $^{443,452}$ .



Fig. II.23. - [top]: Evolution of the shape and size of the bipyramidal cage of MIL-88 with diphenyl-dicarboxlates as linkers ;

### [down] : [001] projection of the whole structure showing with dimensions the dastic swelling of the structure.

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t represents the completely opposite case of what happened with MIL-53 : here, the LP form is filled by the solvent and the pores of the NP form are empty. This gives a presumption for different behavious between the two solids. Even if the adsorb organic molecules in the same way, the adsorption, for instance, is completely different. The adsorption istherms of  $CO_2$  and  $CH_4$  are not of type I, and show unusual parabolic shapes, on which we currently apply the methods which served for the characterization of MIL-53. At 50 MPa, 25 and 2 mmol.g<sup>-1</sup> are adsorbed for  $CO_2$  and  $CH_4$  respectively, but it remains a bistable system.

The proof **that breathing is not a bistable but multistable** was proved very recently with the example of cobalt 1,4benzene dipyrazolate <sup>534</sup> with DMF and water molecules as guests. My young colleague J.R. Long Isolated this solid and solved the structure. When he looked at its adsorption properties after activation, he had the surprise to see that **the isotherm of adsorption of nitrogen occurred in FIVE steps**.



Fig. II.24. – [top]: Structure of Co 1,4- benzene dipyrazolate (CoBDP); [down] : the isotherm of adsorption of  $N_2$  in activated Co(BDP).

Knowing our works on breathing, he asked me to undertake a cooperation on this solid for explaining this strange result using our *in situ* methods. We solved the different structures and evidenced a change of coordination for, square planar in the low pressure forms and tetrahedral for the as-synthesized (Fig.II.25). It was the first step. We are currently using all our methods for a full explanation of this new phenomenon.



Fig. II.25. – [top]: The evolution of the structure of Co 1,4- benzene dipyrazolate (CoBDP) with pressure.

This first example proves that BREATHING IS A GENERAL PROBLEM, characteristic of multistability and not only a bistable system. This is an exciting development both for chemists and for experts in simulation who will be obliged to adapt their current programs to this new reality.

# **CORPUS. PART II.2**

## HYBRID POROUS SOLIDS: AN INTEGRATED APPROACH, FROM CHEMISTRY TO APPLICATIONS.

## HYBRID POROUS SOLIDS: AN INTEGRATED APPROACH, FROM CHEMISTRY TO APPLICATIONS.



The ideal for an academic chemist is not only to create, characterize and transform matter with specific properties at the laboratory scale but also, when it is possible, to understand how the matter forms, from what he can predict some other phases and properties. The best is of course, at the end, to propose products useful for the society, which requires upstream a massive production.

Anticipating the richness of this new class of solids, we tried to do so, step by step, keeping in mind the procedures we had developped for inorganic porous solids.

### THE VARIOUS FACETS OF A GLOBAL STRATEGY.

Gradually, by our increasing contacts with industry, we learnt that, for an industrial development – if any -, two criteria were important for the companies : low cost of the product and stability both with temperature and humidity. Combined with our academic preoccupations aiming at investigating a maximum of possibilities for synthetizing new solids, flexible or rigid, our chemical strategy became simple : start from various cheap precursors, favour reactions in water, and obtain solids with pores as large as possible.

### 1. A chemical strategy.

What was the situation of the literature when we began this part of our work ? At that time (1997), just a few years after the breakthrough of Robson, only a few solids had been described and most of them were based on divalent cations (Zn, Cu) probably because of their high reactivity and their easy synthesis in organic solvents at low temperature. The challenge, at that time, was to increase the dimensions of the pores by introducing ligands with longer sophisticated chains, and keeping the same inorganic cluster.

With my past of solid state chemist, and my habit to conjugate chemistry, structure and properties (mainly magnetic), I decided in a first step to explore (i) solids containing paramagnetic cations, (ii) the possibilities for metals (paramagnetic or not) with higher/lower (sometimes multiple) valences for providing also hybrid porous solids, a special attention being paid to  $AI^{3+}$  and  $Ga^{3+}$  for the useful informations they can give from NMR, as already seen for inorganic porous solids. Up to now, we have introduced in hybrid structures 34 elements of the periodic classification, including all the 3d and 4f metals, their oxidation number varying from M<sup>I</sup> to M<sup>IV</sup>.

It represents the first indication of the inorganic chemical richness of this class of solids; we demonstrated it. Obviously, it is without comparison with the immense possibilities offered by organic chemistry for the ligands, but the combination of these two large possibilities evidences the fact that the **hybrid solids** represent a new and **quasi-infinite class of solids**. Such a screening of metals, beside the enlargement of the databases, aimed also at potentially providing materials with the physical properties (magnetism, conductivity, luminescence) usually encountered in inorganic dense phases.

Concerning the organic linkers, we first chose alkyl diphosphonates, as a prolongation of what we had done with porous metal phosphates. Both the difficulty of preparing them when increasing the length of the alkyl chains, and the weak interest of the resulting phases made that we rapidly moved, through some carboxyphosphonates<sup>283</sup>, to alkyl and aryl polycarboxylates, a richer class of precursors. We also rapidly understood that using alkyl chains was not favourable for getting large pores, due to their flexibility which tends to minimize the lattice energy, to increase the density and therefore to minimize the size of the pores. This explains why the majority of our new phases, flexible and rigid, contains linkers with phenyl rings.

This notice will not - of course - provide a boring list of each of them. It will restrict to the most appealing topologies for illustrating our approach, at various steps.

**1.a.** Our first objective was not to get pores as large as possible, but to identify the largest number of **new** structure types, among which one could select the most promising ones in terms of stability, large pores, easy accessibility to them, and facilities of metal substitution. This is the reason why, at the very beginning, we principally used short and robust linkers like 1,n ( $2 \le n \le 4$ ) benzene-dicarboxylates (BDC) or 1,3,5- benzene-tricarboxylate (BTC) as models. The extension of the pore volumes could intervene after, by increasing the size of the linkers keeping the same topology.

A large number of our solids were synthesized hydrothermally in aqueous medium (typically 150-200°C, autogenous pressure). Obviously, when discovering a new field, the use of the trials and errors method is required, what I sometimes call (however with respect for the richness of the method!) « *happy fishing* ». At the beginning, systematic screening is imperative, varying the chemical conditions (time, temperature, pH, concentrations ...) for looking at their various influences on the result. As the autoclave used in hydrothermal synthesis is a 'black box', it was only *a posteriori* that we could estimate these influences.

### **1**.b. The influential macroscopic parameters. Examples.

• *Temperature* : The most illustrative example concerned the cobalt(II) succinate with an alkyl chain. Initiated when looking at the difference between hydrothermal and non-hydrothermal syntheses<sup>285,368</sup>, all the other parameters being fixed, this study showed a drastic structural evolution of the solid when the temperature is increased<sup>368 and refs</sup> therein . Between 60 and 250°C, seven different phases appear. The most interesting feature was the evolution of the dimensionalities of both the whole structure and of the inorganic subnetwork (Fig. II.2.1). At 60°C, the Co succinate is one-dimensional, with an alternation of single octahedra (0D) and linker in the chain. The same situation occurs at 100°C with, this time, trimeric clusters of edge-shared octahedra. By increasing the temperature - and now, in hydrothermal conditions – one note an increase of both the dimensionalities of the whole architecture (from 1D to 3D), and of the inorganic subnetwork (from 0D to 2D). At 250°C, the structure is 3D, linkers acting as pillars between two-dimensional inorganic sheets.

For this parameter, this led to three important conclusions: (i) in terms of porosity, high temperatures favour threedimensional solids and therefore the appearance of noticeable cages and/or tunnels, justifying *a posteriori* the recourse to hydrothermal conditions; (ii) the topology of the inorganic brick which will determine the final structure drastically depends on the temperature of synthesis, rendering difficult (but not impossible in some cases) to reach the mechanisms of formation (*vide infra*); (iii) in terms of potential physical properties, which require the establishment of long range interactions for their propagation, high temperatures are favourable since important dimensionalities for the inorganic subnetwork, most of the time responsible of these properties, occur in this range of temperature.



**Fig.II.2.1**.- Five of the seven structural evolutions with temperature in the cobalt–succinate- $H_2O$  system, with increasing dimensionalities of both the framework and of the inorganic subnetwork. For each temperature, two views are proposed : stacking of the layers (left) and a projection of the latter (right). Cobalt is represented as pink octahedra, and succinate as balls and sticks. The column in the middle evidences the dimensionalities (D for the framework, d for the inorganic subnetwork). The corresponding formula of each structure appears on the right with the corresponding references.

This last remark about the influence of temperature on the dimensionality of the resulting frameworks was very fruitful for the evolution of our research and oriented our syntheses.



**Fig.II.2.2**.- Use of temperature for getting MILs with various dimensionalities of the inorganic framework, generating different physical properties : 0D (MIL-59) ; 1D (MIL-53) ; 2D (MIL-71) and even 3D for MIL-73.

### • Combined influence of time and pH:

The study of the system Aluminum – 1,3,5- benzene-tricarboxylate (BTC) [or trimesate] in water at a constant temperature of 180°C, highlighted the complex role of these parameters in the syntheses. Limiting the reaction to 12h (time at which the system has reached its equilibrium) and  $0 \le pH \le 4$ , three aluminum trimesates with completely different structures are evidenced (Fig. II.2.3).

At short times (3-5h), increasing pH gives the succession MIL-100<sup>504</sup> (with a very small domain)  $\rightarrow$  MIL-96<sup>426</sup>  $\rightarrow$  MIL-110<sup>479</sup>. Increasing time to 12h leads to a complete transformation of the diagram : MIL-100 has disappeared at very low pH and surprisingly, it is now MIL-110 which is stable in this range whereas it only appeared at short times at ca. pH 3.5. With time, MIL-96 increases its domain fof stability (Fig. II.2.3).

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**Fig.II.2.3**.- First row : Domains of existence of the three Al trimesates ; Second row : their structures ; Third row : the types of building blocks in each of them (carbon : grey ; oxygen : red, Al has different colors).

This system served to us as an example of the need, far beyond the discovery of a new phase, of a complete investigation *vs.* T, t and pH for each system, what we did for every of them.

This, however, takes a long time. Owing to the strong international competition, it rapidly appeared that we had to improve the kinetics of discovery for better participating to the challenge. This implied new methods, in particular **high-throughput investigations**, that we developped in collaboration with Prof. Norbert Stock (Kiel university), one of my former post-docs, when looking at the influence of the ratio of concentrations between the precursors of the studied system.

• Influence of the ratio of concentrations:



**Fig.II.2.4**.- Nature of the phases which appear in water at  $110^{\circ}$ C in 1 day, varying NH<sub>2</sub>-BDC/Fe ratio at various pH imposed by the introduction of NaOH.

It was studied for the system Iron(III) – amino 1,4-benzene-dicarboxylate (NH<sub>2</sub>-BDC) [or aminoterephtalate] – NaOH or HCl - water<sup>467</sup>, at 110 and 160°C during 1 day.

MIL-101 type only appears in a very narrow domain. Increasing the NH<sub>2</sub>-BDC/Fe ratio ( $\rho$ ) without adding HCl leads to a mixture of MIL-101 and the stable flexible MIL-53 which is more and more favoured. In more acidic medium, MIL-101 does not appear and is replaced by the other flexible solid MIL-88, mixed with MIL-53. At higher temperatures,

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and whatever the respective concentrations, only MIL-53 exists. This informs on the respective stability these three phases. MIL-88 and MIL-101 are metastable, and MIL-53, despite its flexibility, is the thermodynamic phase in water medium.

Note that high-throughput experiments allowed also our unique incursion for looking at the solvent effect, since we were focused on aqueous reactions. Clearly, it has an important effet on the nature of the phases, but my group was too small for looking at this aspect. However, this study showed that the stability of the phases spectacularly depends on the solvent used: in DMF, without addition of NaOH, MIL-101 is the stable phase. At higher pH, MIL-88 predominates ; in methanol and acetotnitrile, only MIL-88 appears.

### **1**.c. Do faster and better for large amounts... The microwave solvothermal synthesis.

The above studies aimed at the optimisation of the process using classical hydrothermal synthesis for obtaining pure phases. This required at least one day for each solid to get 1 gram of solid. *When the potentially interesting solids have been selected* (which means large pores, active cations), some experiments need large amounts of product for rendering a new experiment feasable. This means about one month dedicated only to preparation of samples. It is the case, for example, for the preparation of samples for neutron diffraction (10-25g required, <u>coming from the same batch</u>) and for *operando* measurements during adsorption.

This implied to find a new way of preparation. In collaboration with Dr. Jong-San Chang from KRICT (South Korea), another post-doc of mine, we were among the two first<sup>429,436</sup> to develop the use of **microwave solvothermal synthesis** for such a purpose.



**Fig.II.2.5**.- Left column : Principle and realization of the microwave solvothermal synthesis ; Middle column : evolution with time of the X-ray powder patterns of MIL-101 during reaction times in the range 1 mn  $\le t \le 40$  mn, showing the excellent crystalinity of the product ; Right column : STEM photographs of the resulting solids (the bar scale is 200 nm).

The results, performed on MIL-101 which presents very large pores (*vide infra*), are at least surprizing, in the good sense. Indeed, even **after only 1 mn**, **the solid is crystallized** in the form of nanoparticles (10nm). The reaction is complete after 40 mn, with a yield close to 100%, a mean particle size of 200 nm, and a crystallinity better than that resulting from classical ways. The extreme rapidity of the reaction has allowed us to transform the first home-made reactor into a vessel producing continuously the desired product. We are currently able to **produce in the plant 100kg of raw MIL-101/day** (see J.-S. Chang *et al., Mic. Mes. Mater.* **2012** (in press)).

### **1**.d. The chemistry of functionalization.

Once the synthesis and parent structure of a series of new potentially interesting MILs optimized (case of the flexible MIL-53 and rigid MIL-100 and -101), functionalization of a part of the sructure can be envisaged. Beyond their academic interest, these functionalizations, which can occur during synthesis using modified synthons, or post-synthesis, aim at a modification of the original structure for **tuning** its **properties**. We did not do that systematically, but only for structures which presented an interest for their evolution of properties <sup>480,490,512,535,545,551,565</sup>. For example, MIL-53 is one of them. The functionalisation by four methyl groups of the phenyl ring of the terephtalate induces its rotation by 83° from its original position and renders this solid non-porous, for any gas.



**Fig.II.2.6**.- Left: Perspective view of the chromium terephtalate ; Right: perspective view of the Cr tetramethyl-terephtalate. The functionalisation by four methyl groups of the phenyl ring of the terephtalate induces a rotation by 83° from its original position and renders this solid non-porous, for any gas.

Another example, concerning this time the functionalization of MIL-101 on its inorganic part, will be described in the paragraph of catalysis.

### **1**.e. The chemistry of activation.

Once the preparation of pure products optimized, their pores are filled by solvents and, sometimes, some excess of the linker molecules. For becoming active for the measurements of various properties, the post-synthesis inserted species must be <u>completely</u> eliminated. This **activation** represents an essential step for obtaining the real properties and the intrinsic values deduced from the measurement.

Unfortunately, this step is often neglected by many authors who assume without any verification that the guest has evolved the pores just by heating at 150°C. From my experience, it is not enough because, if the solvents have indeed left the structure at this temperature, the excess of linker, more strongly bonded to the skeleton, requires also a repeated chemical treatment allowing the dissolution of this linker by organic solvents before exchanging the latter by water. It is the case of crude MIL-101, for example, which needs several washings with ethanol and  $NH_4F$  solutions and further exchange with water<sup>464</sup> for obtaining the completely empty cages. A colleague, who wanted to be the first to announce the exceptional adsorption capacities of this compound neglected activation and published results ... three times lower than ours... This clearly shows that a careful verification of the quality of the activation is necessary before any other measurement. We do that systematically both by IR spectroscopy and NMR<sup>479, 487, 550</sup>.

All these requirements being fulfilled, my group extracted from his series **90 new structure types**, among which 10 of them were considered as potentially interesting for new properties and applications, either for their large pores, for their stability toward temperature and humidity, their tunability or the nature of cations inducing hitherto unknown properties (Fig.II.2.7).



**Fig.II.2.7**.- Some of the most potentially interesting MIL structures for applications.

### 2. A structural strategy. Why?

Even if such a topic seems trivial at first glance for those who think that it is sufficient to get single crystals for solving (*now, most of the time, automatically*) a crystal structure, I decided to include this part in my integrated approach for several reasons.

As I already noticed, since the beginning, I was persuaded that this new class would be so rich that all the possible tools for its better knowledge had to be developped, and my strategy was thought on the long term. Indeed, the richness of this family of solids and the chemical facility to obtain phases in a single crystal form made that - at least for the moment – in the immense majority of the papers describing structures, they were obtained from single crystal determinations which do not need a good knowledge of crystallography techniques for being solved. However, with time and the increasing sophistication of the syntheses, the increasing complexity of the architectures, the number of systems leading to the obtention of single crystals is decreasing continuously. More and more, powders are obtained with the impossibility, for a large number of colleagues, to determine the structure from their powders. Currently, I should be curious to know how many powders corresponding to perhaps interesting new products remain in the drawers of the desks of my colleagues... We soon anticipated this eventuality by using intensively the new developments of crystallography for overcoming this limitation.

### **2** 2.a. Solve structures *ab-initio* from X-Ray powder diffraction.

We had a great investment in that point because the structural information is absolutely essential for explaining the properties. Indeed, at variance to the determination from a single crystal which is now almost automatic and occurs within half a day, the solution from powder diffraction data is always a challenge. One knows the beginning, never the end, even for some experts ! But at least, no powders in the desks. This technique is used when nothing is known for the structure : neither symmetry, nor space groups (difficult problem for powders) and obviously nor atomic coordinates within the cell. Everything must be determined from the powder data before any refinement of the atomic positions. Note that there is a strong distinction between this method and what is called the Rietveld refinement from powder data. In the latter, the approximate coordinates are this time known and the program just refines the positions for a better fit of the diffraction intensities observed in the experimental pattern. The two methods are successive for a good resolution of the structure and accurate crystal data.

In my former life of inorganic solid state chemist, I had the chance to meet the rare pioneers of this young domain which appeared in the late 60's (P.E. Werner, D.Louër and J. Langford and, further, A. Le Bail). They initiated me and this technique became for me a common and useful tool for solving structures when crystals were not available. I improved my knowledge by my long frequentation in Grenoble (France) of the Very Large Neutron and Synchrotron Facilities in which this type of resolution is frequently performed. All my coworkers currently use also this technique, whereas, even now, only a few groups are familiar with this type of calculations in our community.

Nevertheless, as all the techniques, it has its limitations even if they are rare. Le Bail proved that a resolution from powder data remains possible if the cell volume is lower than 300,000 Å<sup>3</sup>, but such cells are so scarce... As it will be seen further, it arrived to us twice. Exceptionally, other methods were then necessary for solving the problem as explained further in detail for solving the structures of the mesoporous MIL-100 and MIL-101, the cell volumes of which being ca. 400,000 and 700,000Å<sup>3</sup> respectively.

Indeed, the knowledge of the organisation of matter is a crucial point. In solid state sciences, without such an information, research and explanation of the properties are limited. Far beyond the determination of structures at room temperature from powder data, these *ab initio* calculations are a powerful tool when solids are submitted to external stimulii like temperature, introduction of guests under pressure or light. Often, these stimulii provoke phase transitions in the original structure. Our best example was provided by the dehydration of powdered MIL-53, H<sub>2</sub>O *vs*. temperature<sup>342</sup>. The diffraction patterns are completely different (see Fig. II.1.2) and it was our knowledge of *ab initio* calculations which elucidated the two structures, opening the way for the thorough study of the breathing phenomenon, previously described in detail. It was also the case for demonstrating that this feature is not a bistable process, but a multistable one, from the example of CoBDP with its five steps in the breathing.

The mastering of this powerful technique helped us a lot for the development of our works. At least 50% of our structures were determined from powders, sometimes after preliminary experiments in the case of the structural study of metastable solids.

One interesting illustration was provided when we looked *in situ* at the crystallization *vs.* time of one of our solids, using synchrotron radiation working in an energy dispersive mode (EDX) at Daresbury (UK). For that, a special apparatus was designed locally : the autoclave (with transparent windows for X-Rays passage) contains the reactants at 200°C and is put into the X-Ray beam. Then, intensity diffraction data on some Bragg peaks are collected at regular intervals of time in order to appreciate the kinetics of crystallization (Fig.II.2.8).



**Fig.II.2.8**.- Left : the designed autoclave for the EDX experiment ; Middle : principle of the experience ; right : evolution with time of the intensity of some detected Bragg peaks which indicates first that the reaction is finished after only 2h and that, during the first minutes of the reaction, an intermediary metastable phase appears.

Not only the evolution of the intensities show a complete reaction within two hours, but also reveals the existence between 0 and 20 mn of an unknown transient metastable phase which disappears after this time. Knowing after this experiment the chemical conditions of existence of this phase it became easy to prepare it in large amounts and perform after a classical *ab initio* structural determination of this intermediary solid which, without this experiment, should remain unknown up to now.

However, *ab initio* calculations are not an universal tool. It does not work every time, either for too large dimensions or because there are within the powdered solid some special features (micro-twins, defaults...) which prevent from any resolution without the recourse to complementary techniques able to produce new informations for overcoming the problem. More and more, the mesoporous MIL-101 was the center of our preoccupations on this point.

### **2**.b. Other sources of structural information.

### 2.b.1. Diffraction on tiny single crystals.

It represents a hope for users. Indeed, my own experience has convinced me that, beside its usefulness, X-Ray powder diffraction needs a long practice for being efficient, and I can understand that many groups are rather reluctant to invest time in this technique. Until recently, single crystal diffraction on classical diffractometers needed to possess crystals with at least 10  $\mu$ m in size for obtaining good diffraction data.



**Fig.II.2.9**.- Photograph of a tiny crystal (1  $\mu$ m) stuck on a fiber glass; before data collection at ESRF.

My long frequentation of the Very Large Facilities informed me that C. Riekel (ESRF. Grenoble) was developping a new set-up for collecting diffraction data of good quality on single crystals with ca. 1  $\mu$ m in size. This was theoretically possible with synchrotron radiation and its high flux. It was a great challenge, mainly for structural biologists who have many difficulties to get single crystals of their compounds.

Anyhow, knowing since a long time the crystalline quality of our solids, he proposed us to test his set-up on some of our solids. The first was MIL-110<sup>450</sup> represented Fig.II.2.7. This led to a paper in Nature Materials, describing both the set-up and the structure. Other determinations followed <sup>487, 504,505,529,554</sup>. It is considered as a breakthrough for structuralists but, even if it represents a hope for the community, it is clear that the limited access to the diffractometer of ESRF prevents from a common utilization by many colleagues.

### 2.b.2. Electron microscopy.

When a colleague has too small single crystals or powders whose structure cannot be solved directly using *ab initio* methods, there is only one way to get preliminary informations and trends about some crystallographic characteristics of his product : electron diffraction techniques which represent, all over the world, a limited number of experts. Maryvonne Hervieu (Caen, France) and Gustav Van Tanderloo (Antwerpen, Belgium) are two of them and their talent helped us when our difficulties were too strong.

It was the case for the mesoporous MIL-101 for which unconventional methods (see below § 4) provided solutions which needed to be confirmed.



**Fig.II.2.10**.- Some electron microscopy photographs of MIL-101 illustrating the various possibilities of information provided by this technique. In the STEM mode, it gives the shape (here an octahedron), the size and the crystallographic orientation of the single crystal particles (top left and right). In diffraction mode, the set of dots, obtained for various orientations, informs on the symmetry and cell parameters of the solid, of great help for the beginning of a further ab initio determination. Finally, in high resolution mode, the pictures provide the mysterious organization of groups of atoms at the nanometer scale. Once decifered the code and the atomic arrangements, simulation images compared to the experimental ones verify that the solution is correct.

The problem with hybrid porous solids is that most of them are unstable under the very energetic electron beam and very often lead to an amorphization of the structure when exposed to it. Taking great care of the experimental conditions of data collection, they successfully obtained<sup>415</sup> images which provided a definitive confirmation of what was proposed (Fig.II.2.10). To the best of my knowledge, it is up to now the only study on Metal-Organic Frameworks involving electron microscopy but it at least provides to the community an example of what is possible for decoding a structure in the worst conditions.

### 2.b.3. Dynamic aspects of the structures and quasi-elastic neutron scattering.

The examination of many papers describing the structures of MOFs is often disappointing. Looking at the results, authors are mostly interested by the organization of the framework, and not by what happens within the pores. This means that they only consider that solids are fondamentally static (even if they refine the thermal vibration factors...) whereas the dynamics of guests is also of utmost importance. Very often, colleagues conclude by facility (instead of deeply looking at the Fourier syntheses) that the guests species are disordered within the pores. It results in mediocre or bad reliability factors at the end of the refinements which are often criticized by crystallographers.

This neglected **apparent disorder** is however the first evidence of the **dynamic effects** existing in structures. It is particularly true for hybrid porous solids when adsorption phenomena are considered. This incited us to look at this aspect for having a complete structural view of the solids we isolated. For that, **quasi-elastic neutron scattering** [QENS] (and to a lower extent pulse field gradient NMR diffusion experiments) is the tool of choice. Coupled with molecular dynamics simulations which elucidate the diffusion mechanism at the microscopic scale, it provides detailed molecular-level information on the diffusion of various adsorbates in nanoporous materials. Moreover, it has proved to be a very powerful tool in (i) investigating the dependence of the self- and transport diffusivities for various guests on loading, including hydrocarbons in zeolites and (ii) measuring the corresponding activation energies of jumps.

We focused our attention on the diffusion of H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub> and C<sub>6</sub>H<sub>6</sub> within the pores of rigid MIL-47 and flexible MIL-53 with the same topology (see Part II.1) and defined the various diffusivity parameters for each guest in both structures. **For H<sub>2</sub>, a supermobility, 100 times larger than for zeolites is observed**<sup>483</sup>. It can be explained, as in carbon nanotubes, by a flat smoothness of the potential energy surfaces, but also by a necessary critical balance between the guest-guest and host-guest interactions, leading to similar energetic profiles for both contributions within the pore of both MILs. Further, 1D and 3D microscopic diffusion mechanisms have been elucidated for MIL-53 and MIL-47 respectively, depending on the chemical features of the MIL surface, specifically the  $\mu_2$ -OH groups in MIL-53(Cr) acting as steric barriers.



**Fig.II.2.11**. – Left : Comparison between experimental (+) and fitted (solid lines) QENS spectra obtained for  $H_2$  in MIL-47(V) for different concentrations: (a,e) 0.91, (b,f) 2.14, (c,g) 3.43, and (d,h) 6.0 molecules/u.c. (T : 77 K, Q : 0.27 Å<sup>-1</sup>). The theoretical lines correspond for the spectra on the left to 3D diffusion (a-d), and for the spectra on the right to 1D diffusion (e-h). Right: (Top) Typical illustration of the 3D microscopic diffusion mechanism of  $H_2$  from the 2D probability density plot in MIL-47(V); (down) the same for the 1D diffusion in MIL-53(Cr).

For CH<sub>4</sub>, high mobility was found at low loading with a self-diffusion coefficient at infinite dilution (4.2(8).  $10^{-7}$  m<sup>2</sup>.s<sup>-1</sup>) at room temperature, 10 times larger than those observed in other MOFs or in zeolites with large pores such as NaY<sup>466</sup>. Furthermore, it was possible to show that the global diffusion mechanism of CH<sub>4</sub> does not strongly depend on the chemical features of the MOF material. A 1D diffusion model corresponding to the motion of CH<sub>4</sub> along the tunnel was thus observed in both MIL materials.

In MIL-53(Cr), CO<sub>2</sub> exihibits a 1D diffusion process both in the large pore and narrow pore forms<sup>500</sup> whereas, in the large pore MIL-47(V), 3D diffusion is observed<sup>509</sup> with an unprecedented non-monotonous variation of the transport diffusivity coefficient, indicating that, in this solid, CO<sub>2</sub> molecules do not behave like an ideal gas. In the same large pores structure, a corkscrew motion of is evidenced<sup>564</sup> for C<sub>6</sub>H<sub>6</sub>. The same study is currently on the way with long-chain n-alkanes<sup>568</sup>.

### 2.b.4 . Spectroscopic techniques.

The above techniques using diffraction are very fruitful but their accuracy makes that, if the obtained results are of good quality for chemists, they represent however a mean structure, inherently to the method. In special occasions, this information is not performant enough and need more accurate informations for providing the best knowledge of the structure. The local probe character of various techniques gives this missing information.

It is obvious with NMR, for which we have described in the first part of this notice the numerous aspects that it provides. We already had a large recourse also to IR for evidencing the sites of adsorption and their type of acidity. As we have isolated many Fe-based MILs, Mössbauer spectroscopy is systematically used for informing both in the nuclear and the magnetic states, the first being related to coordination and valence state when mixed valence are present, the second defining some magnetic characteristics, in particular the accurate determination of the temperatures of magnetic ordering, of the hyperfine magnetic fields in relation with magnetization and of an eventual structural disorder between the cations. We used only once EXAFs experiments during our approach of the mechanisms of formation<sup>425</sup>.

With the mastery of so many tools, we became sure of our structural results when trying to explain from them the properties of the corresponding solid.

However, in the same way as that used with inorganic porous solids (Part I), and even if we had isolated many solids, the question remained open concerning their formation.

### 3. A tentative approach of some ways of formation.

Initially inspired by our previous experience on inorganic porous solids, we tried to elucidate the mechanisms of formation of some MILs. However, from our chemical knowledge of these solids, it rapidly appears that the problem would be much more complex than for inorganic solids. Indeed, we had proved the extreme sensibility of the inorganic moieities toward temperature. At variance to ULMs, the increase of this parameter indeed modifies to a large extent both the shape and the nuclearity of these bricks. This implied that, if we were able to elucidate some mechanisms, it would be for some solids and only at a given temperature, which restricts very much the generality of this type of information. The following must then be considered as a small contribution to solve the difficult problem of the formation of these hybrid solids.

One of the numerous chemical problems we had to face up was the influence of the nature of the precursor on the final result, and in particular, an eventual relation between the structures of the inorganic bricks of the precursor and of the resulting compound. In most of the cases, when halide, sulfate, nitrate salts are used, there is no relation. However, starting from the acetate, the relation is obvious. Both solids contain the same SBU : a trimer of metallic octahedra (M = AI, Cr, Fe, Ga...) connected by a  $\mu_3$ -O oxygen. From these observations, two questions arose :

- In the case of acetates, is the trimer destroyed during the reaction and built up again at its end ?
- In the general case, what is the reactive inorganic brick ?

This required two types of experiments : *in situ* EXAFS for the first, *in situ* NMR for the second. The latter implied to choose aluminum-based solids with different topologies. Anticipating a variety of answers and for seek of comparison, we performed NMR measurements on three solids already described during the study of the influence of pH and time : MIL-96, MIL-100 and MIL-110.

For the *in situ* EXAFs experience<sup>425</sup>, the chosen product was iron(III)-based muconate MIL-89, the structure of which is close to the flexible MIL-88 type (Fig.II.2.12). The first step of the experiment was to perform *in situ* X-Ray powder diffraction. The solid is first in an amorphous state ; crystallization begins to occur after 3 h and is complete in 60 h. The EXAFS data were then collected at regular times between 0h and 60 h. the most



**Fig.II.2.12**. – Left : Powder X-Ray diffraction patterns of the the solids isolated from solvothermal reactions used to prepare MIL-89. Asterisks indicate Bragg peaks due to unreacted trans-trans muconic acid ; Middle : the structure of MIL-89 and its trimeric building unit. The terminal green atoms are either OH<sup>-</sup>, F<sup>-</sup> or H<sub>2</sub>O statistically distributed on these sites ; Right : EXAFS spectra of iron at various times and their Fourier transforms, which show the invariance of the trimer which remains unaffected all along the reaction.

striking feature is the invariance of the EXAFs signal, confirmed after calculation of its Fourier transforms. At 0 h, it corresponds to the trimer in the muconate precursor. At 4 hours, when the onset of crystallization occurs, the signal belongs to the trimer in MIL-89. It persists up to the end of the reaction. This means that, in the conditions of synthesis, **the trimer of the precursor directly serves as the reactive building block** for the formation of MIL-89, without reorganization. This indicates the strong stability of this SBU, which was used in other syntheses. In this case, the mechanism of formation of the hybrid porous solid can be just considered as an exchange between the acetate and the muconate ligands. This property was later used for the production of thin films acting as sensors.

This was probably the most simple case, but rather rare, due to a choice of the precursor. With the other salts it did not apply. So we entered in the complexity by applying during a long time the *ex-* and *in situ* NMR methods already developped locally for the study of our inorganic porous solids. They revealed that the general case is much more complex than above.

Our choice<sup>565</sup> concerned the trio of samples MIL-96<sup>426</sup>, MIL-100<sup>504</sup> and MIL-110<sup>479</sup>. They appear successively during the synthesis of MIL-96 showing their mechanistic relations. All are trimesates (BTC). For them, both the solution and solid parts of the reactive mixtures were studied along the synthesis process. *In situ* speciation in solution of both inorganic and organic parts during hydrothermal crystallization were monitored using <sup>27</sup>Al and <sup>1</sup>H NMR spectroscopy. The nature and morphology of the various intermediate solid phases, at different reaction times, were monitored by means of *ex situ* powder X-ray diffraction (XRD) and scanning electron microscopy (SEM), in relation with the solution speciation. As seen in more details below, this multi-modal approach allowed assignment of the <sup>27</sup>Al NMR signals. Beside the dominant signal of the aluminum monomer (0-1 ppm), two additional small resonances at 4 and 7 ppm appeared at times depending of synthesis conditions. They are assigned to two different types of Al dimers, a corner shared  $\mu_2$ -O and an edge shared  $\mu_2$ -O, stabilized by two and one trimesate ligands respectively. These units can be found in MIL-96 and MIL-100 structures for the first and of MIL-110 for the second one. Depending of the nature of the solid intermediate product, the structure of the soluble species is proposed, and a scheme of the reaction pathways occurring in solution is provided. The final structure strongly depends on the nature of the species formed in solution.

The first step was to identify by *in situ* X-Ray powder diffraction (XRPD) the nature of the phases which appear during the reaction at 180°C as a function of time (Fig.II.2.13).



**Fig.II.2.13**. – Top: nature of the different phases appearing during the synthesis of MIL-96 using in situ XRPD; zones with two colors correspond to biphasic domains with the evolution of their predominance; down : the same for the synthesis of more simple MIL-110. In all the syntheses, the first pattern to appear was crystallized trimesate BTC (in blue in the picture).

A similar study by scanning electron microscopy (SEM) allowed to observe the evolution of the morphologies of each phase *vs.* time, a good way for a further easy recognition of crystals of each phase in a mixture (Fig.II.2.14). They indeed exhibit very different and typical habitus (hexagonal platelets for MIL-96, octahedra for MIL-100, needles for MIL-110).



Fig.II.2.14. – Evolution with time of the morphologies of the different phases during the synthesis at 180°C.

Whereas <sup>1</sup>H NMR spectroscopy was not very informative, the *in-* and *ex-situ* <sup>27</sup>Al NMR studies at 180°C with time were of particular interest for the identification of the reactive species existing during the crystallization of the phases in the aluminum trimesate system.



**Fig.II.2.15**. – Evolution with time of the <sup>27</sup>Al NMR signals (see text) in the solution above the 3 phases at 180°C.

For MIL-96, the main signal at 1.4 ppm (in grey in Fig.II.2.15) decreased continuously along the synthesis period, while the shoulder at 3.9 ppm (in red) increased first during the first two hours, and then decreased progressively until depletion around 13 h of reaction. After ca. 4 h of reaction a third signal around 7 ppm (in blue) appeared and its intensity increased continuously up to 11 h of reaction and then suddenly decreased. In the 10-12 h period the amount of Al (4 % of total Al) in solution increased, maybe as a consequence of partial dissolution of some solids. After 13 h and till the end of the experiment (23 h) almost all aluminums were transformed into solid state, and less than 4 % of total aluminums were left in solution. Furthermore, during all this period no major change happened to the spectra indicating the end of the reaction. At the end of the *in situ* experiment, lowering the temperature led to a slight shift of both signals from 6.9 and 1.1 ppm at 180 °C to 6.2 and -0.1 ppm respectively. XRPD confimed that the final solid recovered at the end of the NMR experiment was pure MIL-96. This is consistent with the *ex situ* study of Fig.II.2.13.

For MIL-100, <sup>27</sup>Al NMR spectra showed some significant evolution (Figure II.2.15b)). Between 0 and 5 h of heating at 180 °C no major changes were visible except a slow and progressive increase of the 0.3 ppm signal. The shoulder at 3.8 ppm remained small and stationary, and accounted for only ca. 3 % of total Al. Around 6 h of reaction, a sudden shift of the main signal to 0.45 ppm took place accompanied with a decrease of its intensity and an increase of those of the resonance at 3.8 ppm. At the same time, the total amount of aluminum in solution augmented quickly reaching a maximum of almost 100 % of total Al, and subsequently decreased slowly. One hour later, the third signal at ~ 7 ppm appeared and grew continuously till the end of the experiment at 18 h. At about 12 h a second shift of the main signal occurred from 0.45 ppm to 0.6 ppm. At this moment minor changes were observed on signal intensity evolutions particularly for the 0.6 and 7 ppm signals. The latter increased further, while the former continued to decrease, but a bit faster. This would indicate that the species corresponding to 7 ppm signal was formed directly from consumption of the species responsible for the 0.6 ppm signal. At the end of the experiment, a large fraction of aluminum remains in solution (~ 50 % of total Al), in contrast to MIL-96 synthesis. The signal at 4 ppm disappears when lowering the temperature to 25°C, indicating its instability at this temperature, while those at at 0.6 ppm and 6.7 ppm observed at 180 °C resonate now at -0.1 and 6.2 ppm at 25°C. At this reaction time, MIL-100 was entirely transformed into MIL-96 and MIL-110, in agreement with XRPD.

For MIL-110, only two signals were present during overall the synthesis. During the first 2 hours of reaction, the signal initially at 3.6 stabilized at 4.0 ppm with an increase of its intensity, and in the same time those originally at 0.4 ppm shifted at 0.8 ppm accompanied with a decrease of its intensity. During this period, the total amount of aluminum in solution increased up to complete solubility. After, the situation was inverted, where the signal of ~ 1 ppm increased and those of 4 ppm decreased slowly and progressively. Along the following 16 h of reaction, no major changes occurred, ^roving the stability of MIL-110. Coming back to 25°C, and as for MIL-100, the signal at ~ 4 ppm disappeared. At the end of the *in situ* experiment, XRPD indicated that MIL-110 was the only crystallized product. Fig.II.2.16 summarizes the above results.



**Fig.II.2.16**. – Comparison between NMR observation in solution and the nature of the solid product along the synthesis course of MIL-96, MIL-100, and MIL-110 according the in situ and the ex situ studies.

The three *in situ*<sup>27</sup>Al NMR studies showed almost the same features. This meant that identical species were present in the solution whatever the synthesis. Their amount and timing of appearance vary depending on the

intermediate or final solid product. The four signals observed at 0,  $\sim$  1,  $\sim$  4, and  $\sim$  7 ppm correspond to four distinct Al containing species for which an identification was required.

• Observed in all the studied solutions and during all the syntheses, the signal **at 0 ppm** is assigned to the uncomplexed cation  $Al(H_2O)_6^{3+}$ , the main Al species in aqueous solution;

• The resonance at ~ **1 ppm** appeared during the increase of the temperature. Its presence is correlated with the presence of BTC in solution. It is therefore assigned to the primary complex  $Al(H_2O)_5(H_2btc)^{2+}$ . This complex is labile and undergoes fast chemical exchange with the uncomplexed monomer.

• The presence of the signal at ~ 4 ppm related to the MIL-110 formation, while the other at ~ 7 ppm appeared during the formation of MIL-96 and to a lesser extend of MIL-100. Therefore, the 4 and 7 ppm signals could correspond to some building units structurally present first in MIL-110 and, on the other side, MIL-96 and MIL-100. When compared, these two last structures exhibit indeed similar structural features: the trimer Al<sub>3</sub>( $\mu_3$ -O)(H<sub>2</sub>O)<sub>2</sub>(OH)(*btc*)<sub>2</sub> which does not exist in MIL-110. Furthermore, the two species corresponding to 4 and 7 ppm are kinetically related: the 7 ppm signal appears always after the 4 ppm signal and could correspond to a further aggregation of species. Knowing that the structure of MIL-110 presents the dimer Al<sub>2</sub>( $\mu_2$ -O)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(*btc*)<sup>-</sup> (edge-sharing bi-octahedral motif), the 4 ppm signal might be its signature. In these conditions, the sub-unit Al<sub>2</sub>( $\mu_2$ -O)(H<sub>2</sub>O)<sub>2</sub>(*btc*)<sub>2</sub><sup>-2</sup> (vertex-sharing bi-octahedral motif) would be more likely related to the 7 ppm signal. Based upon these observations, the resonances at 4 and 7 ppm were assigned to the dimeric complexes Al<sub>2</sub>( $\mu_2$ -OH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>(H<sub>2</sub>DO<sub>6</sub>(H<sub>2</sub>DC)<sup>-3+</sup> respectively.

NMR experiments performed in the same conditions <u>but without btc ligand</u> confirm the above assignments of signals at ~ 1, 4 and 7 ppm. Indeed, they confirmed the absence of such signals at 180 °C up to 25 h in the solutions. Only the signal of monomeric Al was present in highly acidic solutions (HNO<sub>3</sub>). In absence of nitric acid, a weak shoulder appeared at ~ 2 ppm, much broader than the signal at 4 ppm.It corresponds as already known, to dimeric Al<sub>2</sub> species . All the observed signals are within the range of hexacoordinated aluminum carboxylate chemical shifts in aqueous solution.

Once assigned these signals and their sequential evolution in the different syntheses studied, one can propose a scheme for the first chemical reactions and equilibria taking place in the reactive solutions (Figure II.2.17). The monomeric complexes ( $Al(H_2O)_6^{3+}$  and  $Al_1$ -*btc*) are present in all solutions and all along the course of the syntheses whatever the phase and the reaction time. These complexes constitute the main precursor species at the early stages of the synthesis leading to the reactive dimeric Al species.



**Fig.II.2.17**. – The primary Al-btc complexes formed during the early stages of MIL-96, MIL-100, and MIL-110 syntheses

Only in the case of syntheses of MIL-96 and MIL-100, the Al dimer with one *btc* ligand,  $Al_2-(btc)_1$ , is the first to appear during the first hour of heating preceding the other dimer with two *btc* ligands,  $Al_2-(btc)_2$ . It was not detected along the course of synthesis of MIL-110 up to 25 h of reaction at 180°C. From these observations, one can conclude that the dimer  $Al_2-(btc)_1$  is the precursor for the second. Only when *btc* concentration is increased enough,  $Al_2-(btc)_2$  is formed. Due to the low solubility of the trimesate precursor in acidic solution,  $Al_2-(btc)_2$  is less favored in the highly acidic synthesis medium of MIL-110. Furthermore,  $Al_2-(btc)_2$  appears to be more stable than  $Al_2-(btc)_1$  because, when returning to room temperature, the latter is never observed while  $Al_2-(btc)_2$  remains observable, even if the amounts are much lower at room temperature than at 180°C.

Lowering the temperature leads therefore to the dismutation of  $Al_2^{-}(btc)_1$  into  $Al_2^{-}(btc)_2$  and the Al monomer. The connection mode between the two Al of the dimer is definitely contrasted. With  $Al_2^{-}(btc)_1$ , the two Al octahedra share an edge with two  $\mu_2^{-}OH$ , while in  $Al_2^{-}(btc)_2$  they share a vertex with one  $\mu_2^{-}OH$ . Such a situation allows only two *btc* bridging two Al octahedra with vertex-shared  $\mu_2^{-}OH$  (7 ppm), but one *btc* bridging two Al with edge-shared  $\mu_2^{-}OH$  (4 ppm). The edge-shared dimer allows only flexibility around the edge and restricts bridging of the two octahedra to only one *btc* bridge. The vertex-shared dimer allows bridging by two *btc*.



**Fig.II.2.18**. – Formation of MIL-96, MIL-100, and MIL-110 crystals integrant units: i) reaction of the dimeric  $Al_2$ -btc complexes and the monomeric  $Al^{3+}$  cation leading to ii) nanoaggregation and condensation/networking and iii) crystallization.

At variance to what happened for inorganic porous solids, the two kinds of dimeric complexes  $Al_2-(btc)_1$ and  $Al_2-(btc)_2$  could not be regarded as SBU because with only such units, the structure of each respective phase cannot be built up. Nevertheless, they could be considered as prenucleation building units (PNBU) in this sense that they are precursor species of the corresponding SBU. Figure II.2.18 shows how each possible SBU of each phase can be obtained from the observed dimeric *btc* complexes in solution. In each case, only monomer cation  $Al^{3+}$ , of octahedral geometry, is needed to join the dimer *btc* complexes to form the structural units in the crystal (the integrant unit). For MIL-110, the basic unit from which the structure is built, the octameric unit  $Al_8(OH)_{15}(H_2O)_3(btc)_3$ , can be formed from combination of three dimers  $Al_2-(btc)_1$  and two  $Al^{3+}$  cations. MIL-100 is constructed from an assembly of the trimer  $Al_3O(H_2O)_2(OH)(btc)_2$ , which can be decomposed into one  $Al^{3+}$  cation and one dimer  $Al_2-(btc)_2$ . MIL-96 structure can therefore be described as an assembly of the  $Al_{12}O(OH)_{18}(H_2O)_3(btc)_6$  unit, which is constituted of six  $Al^{3+}$  cations and three dimers  $Al_2-(btc)_2$ . These various condensations are pH-dependent because the amount of BTC in the solution depends on the syntheses.

The formation of crystals observed here proceeds through successive steps:
1) the initial formation of complexes (PNBU) distributed as a function of composition and temperature.

2) the second is the aggregation, in other words a density fluctuation by lowering the dielectric constant of the solvent, allowing condensation in the solution into units that will appear in the crystal to come.

3) the interconnection of these units into a network.

4) the last stage is the transformation of this network into a crystal by clicking the network into a periodic lattice.

### This reflects in this case a supersaturation/aggregation/nucleation/crystallization phenomenon.

These two first studies clearly show that the situation for elucidating the mechanisms of formation of hybrid porous solids is much more complex than it was for porous metal phosphates. The chemical conditions determine the nature of the complexes in solution which, after some condensations, will lead to the final solid. The units present in the crystals are not present as such in the solution. This implies that, depending on the metal, on the ligands, on the temperature and pH, many different situations can occur, leading to numerous SBUs. Our work was just an example of a much more general phenomenon.

This implies too that the hypothesis that we did for establishing the AASBU method for the prediction of new structures of porous metal phosphates (i.e the invariance of the SBU in the solution and the final solid) is not yet valid, from above. For extending this method to hybrids, the mechanisms of formation cannot be evoked. It can only be adapted considering the associations of one inorganic brick (extracted from known examples), - whatever its origin - with a given ligand for providing a virtual library of possible structures.

### 4. Computer-assisted prediction of porous hybrid structures.

It represents an extension of the AASBU method (see in part I), applied to the realm of hybrid organic–inorganic frameworks and demonstrate its capacity to produce hybrid candidate crystal structures that are built from predefined organic and inorganic counterparts.

Indeed, hybrid frameworks offer ideal features for computational developments: although the isolated metal ion, taken alone, lacks directional information, the inorganic unit derived from the metal atom and the organic ligand does. Once the inorganic and organic units are defined, one may assume that there are a limited number of arrangements that are compatible with periodicity and symmetry. With predefined organic and inorganic building units, AASBU simulations are used to perform their automated assembly in three dimensions aimed at exploring the possibilities of connection. The simulations yield a virtual library of candidate hybrid frameworks that are assorted by their space group, cell parameters, and atomic positions.

Our initial efforts were aimed at validating the AASBU approach in the field of hybrid frameworks by simulating existing architectures. In the second instance, we aimed at predicting structures that have not yet been synthesized, both to tackle the issue of polymorphism by limiting the domain of structures that are possible for a given metal– organic-ligand pair, and to aid the often-difficult task of crystal structure determination. This last point was crucial, as seen below.

In our approach, the inorganic and organic counterparts may be treated as two different building units, or encapsulated in a single hybrid building block. Both approaches were explored. The preliminary step consists of the elaboration of a suitable library of SBUs, directly extracted from known and typical hybrid frameworks (Figure II.2.19). The inorganic unit is modeled by a rigid body,  $\{M_xL_y^{inorg}\}$  (M: *metal centers*; L<sup>inorg</sup>: *ligand atoms of the inorganic units*). The organic unit is treated as a flexible body,  $(C_nL_m^{org})$  (C: carbon skeleton, L<sup>org</sup> : ligand atoms of the organic units such as oxygen atoms of carboxylate functions). The computational assembly is further controlled through the use of predefined "sticky-atoms": all ligand atoms on both the organic and inorganic units, L<sup>inorg</sup> and L<sup>org</sup>, are defined as equally possible linkage points.

The rules that control the possible assembly of the organic and inorganic building units during the subsequent

simulation steps are encapsulated in a forcefield that includes "sticky- atom" pairs. They are parameterized on an atom-atom basis by a simple Lennard–Jones expression for the energy of interaction between pairs of atoms i and j, as defined in Equation (1):

$$E_{ij} = \varepsilon_{ij} \left[ (r_{ij}^*/r_{ij})^{12} - 2 (r_{ij}^*/r_{ij})^6 \right]$$

The main steps are the following :

1) periodic trial arrangements of organic and inorganic units are generated by using a simulated annealing Monte Carlo procedure within the imposed space group and the imposed number of organic and inorganic units per asymmetric unit. At this stage, the stored configurations correspond to unconnected organic and inorganic units in 3D space.

2) Each unique arrangement is minimized with respect to the total cost function. This is a key step at which the assembly of inorganic and organic units (or alternatively hybrid building blocks) through the predefined linkage points is performed, which possibly leads to periodic connected hybrid arrangements. At this step, the flexibility of the organic unit is crucial to make adequate connections to the inorganic units.

3) Sticky-atom pairs, L<sup>org</sup>...L<sup>inorg</sup> and L<sup>inorg</sup>...L<sup>inorg</sup>, are reduced to a single atom. Realistic predictions of crystal structures are thus produced with a list of candidate hybrid structures (space group, cell parameters, atomic positions) and the theoretical X-Ray powder pattern of the proposed arrangement. The symmetry of each candidate hybrid structure is redetermined *a posteriori*.

4) The stability of the hybrid candidates is estimated using an Ewald summation. It allows a **classification** by ranking the solutions by decreasing lattic energies into **reasonable** (which means an energy close to that of known structures), **not-yet synthesized** (for those less stable, but with an energy slightly below the reasonable ones) and **unlikely** ones.

We validated the method with the simulation of existing and well-characterized hybrid frameworks (Fig.II.2.19). The characteristics of the simulated structures were in excellent agreement with the experimental data.



**Fig.II.2.19.** - Left: Examples of mono-(a), di-(b), and tetrameric (c) metal clusters and organic carboxylate ligands commonly found in hybrid frameworks. Right: For each organic/inorganic combination, an example of existing very open framework is shown with the comparison between experimental and simulation data.

An attractive feature of the simulations is indeed the generation of new topologies. Typically, while assembling one {MO<sub>6</sub>} octahedron and one BDC molecule, not only the experimentally known MIL-53 structure was predicted but

also a series of not-yet-synthesized topologies ranging from lamellar to 3D extended structures (Fig.II.2.20). This opens the way for tackling an eventual polymorphism for these new architectures.



**Fig.II.2.20.** - Topological relationships between three simulated hybrids that were obtained by assembling one BDC mole- cule and one octahedron per asymmetric unit. The three structures are built from the same plane (top and side view in a), which range from lamellar (b and c) to 3D networks (d).

This possibility was tested using the trimeric inorganic brick existing in MIL-88, for which we had proved by *in situ* EXAFS the invariance from the precursor to the final solid. The synthesis used either 1,4–benzene dicarboxylate (BDC) and 1,3,5–benzene tricarboxylate (BTC) as ligands. In our conditions, two powdered phases were isolated with a very complicated X-Ray powder diffraction diagram and isotherms of adsorption indicating the existence of large pores. Moreover, all our attempts for getting single crystals failed. Knowing the M/L ratio, this represented an ideal case for testing our modified AASBU method



**Fig.II.2.21.** – First Row : (a) The trimer of  $\mu_3$ -O corner-shared octahedra; (b) The X-Ray powder diffraction pattern of the unknown phase, (c) the base motif of the resulting hypothetical structure : a large supertetrahedron of trimers linked by trimesates; (d) a  $C_{60}$  moiety at the same scale; Second Row : the three reasonable virtual structures obtained from the calculations; except for the unknown topology labelled HEX, the two others have a known zeolitic topology and only the last, circled in red corresponds to the experimental X-Ray powder diffraction pattern.

Whatever the ligand, only three 'reasonable' solutions were extracted from the simulation (Fig.II.2.21), with different topologies, different space groups and different cell parameters. They all have a zeolitic topology with large pores, the HEX form being unknown. When calculating the theoretical X-Ray powder diffraction pattern for each of them, only the one corresponding to the MTN form is in excellent agreement with that obtained experimentally

when the position of the Bragg peaks is concerned. The intensities are rather different because the simulation takes only into account the framework and not the guests. A further Rietveld refinement led to an excellent fit between observed and calculated intensities.

### The result is rather striking on many points :

• the cubic unit cells are very large :  $\approx$  400,000 Å<sup>3</sup> with the trimesate ion and  $\approx$  700,000Å<sup>3</sup> with the terephtalate ligand, which means in the range of proteins ; the two solids, labelled MIL-100 and MIL-101 respectively represented the two first examples of crystallized mesoporous solids (the other known mesoporous solids [MCM-41, SBA-15...] were inorganic with pores diameters in the range 20Å <  $\phi$  <500 Å, but were amorphous) ;

• such unit cells and their accurate associated data were obtained without any recourse to diffraction on single crystals; they were not available;

• *ab initio* powder diffraction would have failed to solve the structure since, as already mentioned, such determinations are possible only when cell volumes are <  $300,000 \text{ Å}^3$  (see above);

• paradoxically, the crude solution just came from a comparison between two X-Ray powder diffraction patterns : the experimental and one of the theoretical 'reasonable' ones, the latter being provided from the simulation of an initial association between an inorganic cluster (which, in the present case, existed in the solution, a situation already encountered with porous phosphates of Part I) and a ligand.



**Fig.II.2.22.** – Left: Perspective view of the topology of MIL-100 and MIL-101 described in terms of association by corners of the supertetrahedra of Fig.II.2.21; the two types of cages are highlighted in yellow for the large cages and in blue for the small ones; Middle : isolation of each type of cage ; the coloured circles represent the free space within each cage and the numerical values of their diameters; Right: the two cages represented in terms of sticks and balls, the balls being the center of each supertetrahedon. Note that, with this mode of illustration, the small cage with its 20 vertices is one of the five Platonician polyhedra: the pentagonal dodecahedron, to which Plato associated the Universe.

The association of the supertetrahedra led to a very complicated structure inside which two types of cages could be distinguished : the large one with 28 vertices, 16 faces (12 pentagonal and 4 hexagonal), a useful pore diameter of 34 Å and windows openings of 16Å (hexagonal faces), the small one having 20 vertices, 12 pentagonal faces, a useful pore diameter of 29 Å and windows openings of 12Å.

Experimentally, in MIL-100, the pores are filled with only water molecules, easy to evacuate. In MIL-101, beside water, an excess of unreacted terephtalate was observed, which required in the latter case a very careful activation process. Surprisingly, once activated, these structures are thermally stable up to 400°C and stable for months in water.

I hesitate to confess that this structural result astonished the community who qualified our paper as a 'tour de force' (M. Zaworotko, USF) and deserved a 'Perspective' in *Science* after the publication of MIL-101 in 2005 in this journal. The paper was cited more than 800 times at the end of 2011.

This opened the way for an alternative and unconventional route for solving complex structures. One must however note that this approach is not this time – at variance to the situation described for porous inorganic phosphates - the consequence of the knowledge of the mechanims of formation , but only results from the observation and use of the geometrical characteristics of inorganic clusters, either published by others or discovered by us. In this latter case, even if we do not know the reactive species during the reaction, we know at least the initial parameters (ratio of concentrations, pH ...) leading to this inorganic cluster for a given metal at a given temperature, i.e. the relation

existing between these initial conditions and the formed cluster. The use of the AASBU method then allows to create, for a given inorganic brick, a virtual library of possible structures with their unit cell, space group, atomic coordinates and theoretical X-Ray powder diffraction pattern to which one can compare the experimental pattern of a new phase, as we did for MIL-100 and MIL-101, for an eventual qualitative identification and further refinement.

This virtual library allowed us to generate <u>rapidly</u> the structures of the frameworks with functionalized ligands. It was particularly useful when we wanted to see the various structural changes induced by the grafting of new functions on the phenyl rings of the ligands. Another consequence was to experimentally seek for new and unusual inorganic bricks with various nuclearities and connectivities in order to build up new possible *'not-yet synthesized'* architectures with reasonable latice energies (Fig.II.2.23-24)



**Fig.II.2.23.** – (a): *Titanium(IV)* tetramer with connectivity 9; (b) Cobalt(II) hexamer with connectivity 9; (c) titanium(IV) octamer with connectivity 12.

A nice example was provided by the very rare hexamer corresponding to an octahedron of Archimedean square antiprisms sharing edges (Fig.II.2.24). With its 12-connectivity, it provided a very open mesoporous framework which was later found experimentally.



**Fig.II.2.24.** – Top left : *Zirconium(IV)* hexamer of square antiprisms with (Down left) a 12-connectivity; Right : the resulting mesoporous architecture (pore diameter : 23Å) with a fcc network.

This step – and particularly the discovery of MIL-100 and MIL-101 - was of utmost importance for the further development of our research. Not only we mastered the chemistry and the structures, but we opened the way for predicting *'reasonable'* nano- or mesoporous architectures, some of them being discovered later. We created numerous solids, following our strategy. The next step of our integrated approach was to transform them into materials with a great variety of properties.

### 5. Porous hybrid solids... For what ? Their properties and their domains.

We had successfully applied the first steps of our integrated approach by creating or predicting cheap porous solids with large and tunable pores, with a good stability toward temperature and humidity. With the tools we had created, we had then to complete our strategy by transforming our solids into materials and, if possible, into **multifunctional materials**. This required to look first at their properties, but also, when it is needed, at their possibilities of shaping, according to the envisaged domains of applications of interest for the society.

For evidencing properties, **we used** the three unique characteristics of the porous solids : **the framework, the pores and the internal surface**. Depending on the desired property, we played specifically on one (and sometimes two) of these characteristics to introduce, tune and optimize the corresponding property.

The domains on which these properties apply concern the current most important societal problems : **environment**, **energy savings**, **energy and health** (Fig.II.2.25). My past of solid state scientist made that, on some of them, my works were pioneering, in particular for the domains of energy and health.



**Fig.II.2.25.** – Scheme of the various properties evidenced for our hybrid porous solids, with the domain in which they are concerned. The coloured triangles refer to the structural characteristics on which we played for creating the property (see the right side of the figure).

### 5.a. Properties related to the domain of environment. Evidence and explanations.

### 5.a.1 : Adsorption of greenhouse gases $CO_2$ and $CH_4$ :

It is a common preoccupation of most of the colleagues of the MOF community since the first attempts on methane by Kitagawa in 1997. We looked also at this property, mainly focusing on  $CO_2$  and  $CH_4$  but, at variance to others who tried to find the best performances of adsorption in a race to records, we used this physisorption as a sensitive tool for explaining the « breathing phenomenon » thoroughly described in Part II.1 and most of our results, using flexible solids, are already described and explained in this part. We shall not recall them but focus here on our main results on rigid MILs.

Obviously, the two materials of reference were MIL-100 and MIL-101. Their very large pores and large windows openings provided favourable factors first for a significant adsorption of  $CO_2$  and  $CH_4$ . We used a combination of complementary methods (gravimetry, manometry, microcalorimetry and FTIR) for elucidating the phenomenon.

A preliminary task was to activate carefully the as-synthesized materials owing to their large cages able to retain some terephtalic acid in excess. If the activation was easy and complete for MIL-100 by increasing temperature, as proved by *in situ* NMR <sup>550</sup>, it was much more difficult in the case of MIL-101 <sup>464</sup>. Indeed, in the as-synthesized compound a significant amount of non-reacted terephthalic acid is present both outside and within the pores of MIL-101a. To avoid this, a first activation treatment has been performed using hot ethanol and results in the MIL-101b solid. The last compound denoted MIL-101c was obtained starting from MIL-101b dispersed in an aqueous solution of NH<sub>4</sub>F at 333 K for 10 h; after cooling, the precipitate was filtered and washed five times with hot water (333 K) to remove traces of NH<sub>4</sub>F. The final activation occurred at 423K both to eliminate the H<sub>2</sub>O guests but also to extract the terminal water molecules of the trimer, leading to a direct access to the metallic cations (Fig.II.2.26) with the creation of cationic unsaturated sites (CUS).



**Fig.II.2.26.** – The original trimer (left) dehydrates at 423K with the formation of CUS (yellow : metal ; grey : carbon ; red : oxygen ; blue : water, F<sup>-</sup> or OH<sup>-</sup>).

**For MIL-100**, the methane isotherm shows a gradual increase with pressure and no obvious plateau indicative of total pore filling. One can note that approximately 119 cm<sup>3</sup><sub>STP</sub> cm<sup>-3</sup> of methane are adsorbed at 3.5 MPa which is below the capacity of the MIL-53(Al, Cr) solids (~150 cm<sup>3</sup><sub>STP</sub> cm<sup>-3</sup>) and far below the DOE target of 180 cm<sup>3</sup><sub>STP</sub> cm<sup>-3</sup> for methane storage.

Carbon dioxide also adsorbs gradually with increasing pressure and again shows no notable plateau region in the isotherm. The upturn in the isotherm above 6.5 MPa occurs as the sample approaches the supercritical point of this fluid. The amounts adsorbed are quite important, around 18 mmol g<sup>-1</sup> at at 5MPa and 303 K for the MIL-100 in the present study although this is not quite as high as the best MOF which to date would seem to be MOF-177, with 33.5 mmol g<sup>-1</sup> at 298 K and 4.2 MPa. However, in terms of volume adsorbed per volume of sample, then the uptake reaches around 280 cm<sup>3</sup><sub>STP</sub> cm<sup>-3</sup> at 5 MPa which approaches the performance of MOF-177 (320 cm<sup>3</sup><sub>STP</sub> cm<sup>-3</sup>).

The enthalpies of adsorption of methane tend to a value of around -20 kJ mol<sup>-1</sup> extrapolated to zero coverage, close to that observed in MIL-53 structures. This value reflects the moderate interaction of this gas with the surface. For CO<sub>2</sub>, the observed value around -63 kJ mol<sup>-1</sup> is the highest value reported so far for the adsorption of carbon dioxide on a MOF sample and shows the relatively large interaction of this probe molecule with the surface. For a better information, an infra-red spectroscopy study was undertaken. The 3 bands observed in spectrum of CO adsorbed at 100K on activated MIL-100 indicate the presence of Lewis acid sites due to the presence of an anionic vacancy around the metal. The spectra of MIL-100 after CO<sub>2</sub> adsorption present a strong band at 2351 cm<sup>-1</sup> with another weak band at 1271 cm<sup>-1</sup>. This band is normally infrared inactive for the free CO<sub>2</sub> molecule. This characterizes the formation of CO<sub>2</sub> coordinated species on Lewis acid sites ( $O=C=O...Cr^{3+}$ ). To check such an assignment, another CO<sub>2</sub> adsorption experiment has been performed on MIL-100 whose Lewis acid sites have been previously poisoned by water added at room temperature. The 2351 cm<sup>-1</sup> band does not appear, confirming the coordination of CO<sub>2</sub> molecules on the metal centres of the dehydrated solid with **no formation of carbonate species**. The strong interaction confirms the microcalorimetry results and explains their rapid decrease with increasing coverage. Adsorption of CO<sub>2</sub> can therefore be understood by an initial strong interaction followed by the filling of the residual porosity, implying much lower interactions.



**Fig.II.2.27.** – Adsorption isotherms and enthalpies of adsorption of  $CO_2$  and  $CH_4$  at 303K for MIL-100 (top) and MIL-101.

**For MIL-101,** the adsorption of methane corresponds to a capacity of ~135 cm $^3_{STP}$  cm $^3$ , slightly below that of MIL-100 (~150 cm $^3_{STP}$  cm $^3$ ). The enthalpies of adsorption of methane are comparable to those of MIL- 100 (i.e. close to - 20 kJ mol<sup>-1</sup>) at zero coverage.

Unlike for methane, significant differences are now observed in the carbon dioxide isotherms for the MIL-101 materials activated. The capacity at 5 MPa and 303 K is dependant on the activation method and increases from 28 mmol g-1 for MIL-101a and 34 mmol g<sup>-1</sup> for MIL-101b up to a record value of 40 mmol g<sup>-1</sup> in the case of MIL-101c. This leads to an enormous volume of carbon dioxide per volume of adsorbent adsorption capacity, with **a record value of 390 v/v** for MIL-101c, far above the previous value in the open literature of 320 v/v. It clearly demonstrates the higher loading capacity of MOFs both in mass or in volume to volume compared with zeolites or carbons. The enthalpy of adsorption of CO<sub>2</sub> is close to -45 kJ mol<sup>-1</sup> at zero coverage.

Turning to IR spectroscopy, the spectrum of CO adsorbed in MIL-101 samples only presents a single band at 2196 cm<sup>-1</sup>, assigned quantitatively to  $Cr^{3+}$  Lewis acid sites with a concentration of 1000 µmol g<sup>-1</sup>, three fold lower than that observed in MIL-100 showing that accessible Lewis acid sites are stronger and more abundant in MIL-100 than in MIL-101 materials. Since the configuration of the trimers of chromium octahedra is similar in both structures, the lower acidity of the MIL-101 materials implies the presence of extra framework impurities persisting inside the pores even after serious activation. It suggests that terephtalate impurities, in strong interaction with the CUS, remain in MIL-101 whatever the activation procedure. The IR spectra and TGA profiles confirm this tiny presence.

The IR study of carbon dioxide on MIL-101 shows at 2348 cm<sup>-1</sup> the  $v_3$  (CO<sub>2</sub>) band, also sensitive to the poisoning by water preadsorption. Its low intensity is in accordance with the low amount of free CUS Cr<sup>3+</sup>, shown above. As the frequency of the  $v_3$ (CO<sub>2</sub>) stretching band varies with the strength of the interaction (the higher the  $v_3$  frequency, the stronger the coordination), the results indicate that the coordination of CO<sub>2</sub> molecules on Cr<sup>3+</sup> sites is also weaker in MIL-101 than in MIL-100. We can thus understand the lower initial interactions observed by microcalorimetry for the MIL-101 series of samples.

The Henry's constants have also been estimated for  $CO_2$  and  $CH_4$  both for MIL-100 and MIL-101. As with microcalorimetry, they indicate first that methane interactions are weaker than those of  $CO_2$ , whatever their structures and compositions.

Perspectives for  $CO_2/CH_4$  coadsorption. The results obtained with the single components can be input into mixture adsorption predictions. Starting from a  $CO_2/CH_4$  50%–50% mixture, this calculation suggests 77% adsorption of carbon dioxide of  $CO_2$  on MIL-100 and 74% in MIL-101c. A similar calculation, taking into account the enthalpies of adsorption at zero coverage, gives close values : 78% and 74% respectively. It thus seems that the enthalpies of adsorption can also be used for such mixture calculations.

However, if one considers MOF materials with respect to potential applications, then one should take a closer look to the isotherm shape and not only at their capacity. If one wishes to purify a gas stream of contaminants at low

concentration and pressure (<1 bar), then an isotherm of the pure component of sharp "Type I" shape would be of interest at low pressure which rules out the use of MOFs for such applications. However, for other pressure swing adsorption (PSA) type processes, a more gradual, ideally linear, uptake at higher pressures is required and large pores MOFs such MIL-100 or MIL-101 could represent an alternative to carbons or zeolites. The aim in this latter case is for the isotherm slope to be steeper for the component that one wishes to recover. In most cases, then the slope between atmospheric pressure and the final process pressure is considered. An example of this is oxygen purification from air.

### 5.a.2 : Adsorption of the greenhouse gas $H_2S^{491,542}$ :

At variance to above, the studies concerning  $H_2S$  are more scarce. However, the removal of  $CO_2$  and  $H_2S$  from natural gas, coal/biomass gasification and reformate gas is of main interest in the use of gas and especially in the hydrogen production processes.  $CO_2$  and particularly  $H_2S$  are harmful pollutants:  $H_2S$  can cause corrosion and usually damages the transition-metal used in fuel cells. Acid gas recovery is also of great importance for the purification of both biogas (initial feed contains 1-5% of  $H_2S$ ) and natural gas (initial feed contains some ppm up to 20% of  $H_2S$ ). Moreover, regulations limit the amounts of sulfur species in fuels below 10-15 ppm.

Sulfur compounds present in gases are commonly removed by gas-liquid absorption techniques in aqueous amine solutions. These processes are highly energy-greedy, the amine solutions being of very limited lifetime. Alternatively, adsorption processes such as PSA (Pressure Swing Adsorption) appear to be less energy demanding but the crucial point of such technology relies on selecting adsorbent material combining large adsorption capacity and good separation ability with a full regeneration at low energy cost. Chemisorption is one way to perform the gas separation of a mixture containing sulfur species but this procedure needs specific reactivation of the adsorbents. Indeed, the physisorption appears to be the most suitable way to separate  $H_2S$  from syngas or natural gas as the adsorbent is expected to be more easily regenerable. Such a process usually allows for reaching a very low amount of sulfur compounds in feed. The Metal-Organic Frameworks materials can be very promising as adsorbents in order to capture sulfur compounds such as thiophene derivatives and  $H_2S$ . We then looked at the behaviour of some of our solids (MIL-47(V) and MIL-53(Cr)) in presence of  $H_2S$ .



Figure II.2.28 a,b reports the  $H_2S$  adsorption isotherms of MIL-47(V) and MIL-53(Cr) at 303 K for pressures up to 1.8 MPa with a zoom area for low pressures up to 60 kPa for the MIL-53(Cr) (insert in Fig. II.2.28c). MIL-47(V) exhibits a quasi-usual type I shape isotherm: an initial Henry domain for pressure below 25 kPa and a second linear zone for pressure up to 30 kPa. The saturation capacity for this material is 14.6 mmol.g<sup>-1</sup>. In contrast, the situation for MIL-53(Cr) is close to the two-step behaviour which happened with  $CO_2$ : first a plateau with a saturation capacity of 3.7 mmol.g<sup>-1</sup>. The second step starts at 0.12 MPa, the saturation being 13.1 mmol.g<sup>-1</sup>.

The IR spectra, first recorded at 298 and 220 K in the range 0-40 kPa  $H_2S$  pressure, display weak bands in the 2500-2600 cm<sup>-1</sup> range assigned to the v(SH) bands of the adsorbed  $H_2S$  species. From the plots of the integrated intensity of these bands vs the pressure introduced into the cell at 220 K, the optical isotherm for MIL-47(V) can be obtained

(Fig.II.2.29). It is similar to that deduced from the gravimetric measurement. The same agreemnt occurs for MIL-53(Cr).



**Figure II.2.29.** Variation of the areas of the  $v(H_2S)$  band versus the  $H_2S$  pressure introduced into the cell at 220K for MIL-47(V) (a) and MIL-53(Cr) (b). Insets: Infrared spectra in the  $v(H_2S)$  range.

During our IR study of breathing of MIL-53, we had noted that the LP and NP has their IR signature (v(18a) in the region 1000-1100 cm<sup>-1</sup>). We looked once more the situation when  $H_2S$  was introduced (Fig.II.2.30).



**Figure II.2.30.** - Adsorption of  $H_2S$  in MIL-47(V) (a) and in MIL-53(Cr) (b) at 298 K. Intensity of the v(18a) mode in function of the pressure introduced (bottom). Insets: spectra of the v18a band recorded upon  $H_2S$  pressure.

Whereas no modification of intensity is noted at 1024 cm<sup>-1</sup> for MIL-47 (always in the LP form), for MIL-53, a shift is observed from 1021 cm<sup>-1</sup> (LP form under vacuum) to suddenly 1017 cm<sup>-1</sup> (signature of the NP form) under very low pressure. Above 2 kPa, the LP form progressively reappears. With H<sub>2</sub>S, MIL-53 breathes.

In terms of host-guest interactions, IR spectroscopy provided also some decisive informations.

### For MIL-47

• (i) In MIL-47(V), in which there is no OH groups joining two V, as proved by the absence of any v(OH) band in the 3400-3800 cm<sup>-1</sup> range, the spectrum displays a strong band at 902 cm<sup>-1</sup>. This band, not perturbed upon H/D exchange, is therefore assigned to the v(V = O) mode of the asymmetric V-O-V bond sharing two consecutive VO<sub>6</sub> octahedra. It is worth noting that its wavenumber shifts toward lower values when the solid is exposed to H<sub>2</sub>S. Such a downward shift indicates the formation of the following adduct V = O...H-S-H, in which H<sub>2</sub>S plays the role of an acidic molecule. It corresponds to the v(SH) band at 2592 and 2585 cm<sup>-1</sup> in these species.

• (ii) by comparison with liquid solvents such as benzene and toluene in which exist hydrogen bonded species involving  $H_2S$  and  $\pi$  electrons of the aromatic ring, characterized by the asymmetric v(SH) mode, the position of this v(SH) at 2592-2585 cm<sup>-1</sup> with, at higher  $H_2S$  pressure, a shoulder at 2560 cm<sup>-1</sup>, suggests the formation of a  $H_2S$  liquid-like phase inside the channel of MIL-47(V).

• (iii) Molecular simulations performed for the MIL-47(V) system at a loading of 10 H<sub>2</sub>S molecules per unit cell, confirm these experimental findings. One can observe from the radial distribution function (rdf) plotted for the H(H<sub>2</sub>S)-O( $\mu_2$ -O) pair shows a distinct peak centered at a distance of 2.15 Å characteristic of a predominant interaction between the proton of H<sub>2</sub>S and the  $\mu_2$ -oxygen atoms of the MIL-47(V) framework. Such a relatively strong interaction is consistent with the high adsorption enthalpy values of 27.1(calc.) and 29.5 kJ.mol<sup>-1</sup> (exp.). Our structural simulation from these data evidences a typical arrangement of H<sub>2</sub>S in the MIL-47(V) at high loading.



**Fig.II.2.31.** -Illustrations of the preferential arrangements for  $H_2S$  simulated at 303 K in MIL-47(V) (a), MIL-53(Cr) NP (b) and MIL-53(Cr) LP (c) solids. The distances are reported in Å:  $S(H_2S)-O(\mu_2-OH)$  in green,  $H(H_2S)-S(H_2S)$  in red,  $H(H_2S)-O((\mu_2-O)$  in purple,  $S(H_2S)-O$  (carboxylate) in light blue and  $S(H_2S)-H(phenyl)$  in yellow.

Our simulations also evidence that additional interactions can occur between  $H_2S$  and the phenyl rings of the organic linkers (Figure II.2.31a). The rdf for the  $H(H_2S)$ - $S(H_2S)$  pair was further compared to those calculated for  $H_2S$  in the liquid state in order to highlight the effect of the confinement on the arrangement of the  $H_2S$  molecules. The first peak is shifted to shorter distances, confirming stronger hydrogen bonds between  $H_2S$  and therefore, **a confinement** by the pores of the MIL-47(V) form. Figure II.2.31a also shows that the weakly bonded  $H_2S$  molecules are arranged in such a way to form **dimers**, consistent with a liquid-like behavior. One should notice that these molecules are characterized by a rather high orientational disorder within the channel.

### T For MIL-53

• (i) In addition to two weak v(OH) bands at 3610 and 3580 cm<sup>-1</sup>, the spectrum of MIL-53(Cr) activated at 473 K displays two bands at 3654 and 924 cm<sup>-1</sup> assigned to v(OH) and  $\delta$ (OH) mode, respectively, for the  $\mu_2$ -hydroxyl groups bridged over two chromium atom). Introduction of H<sub>2</sub>S into the cell at room temperature (pressure from 4 to 33 kPa) perturbs both bands: the v(OH) band broadens and downward shifts from 3654 to 3490 cm<sup>-1</sup>, whereas the  $\delta$ (OH) band upward shifts from 924 to 980 cm<sup>-1</sup>. Such perturbations characterize the formation of H-bonded complex Cr-OH...SH<sub>2</sub> in which the hydroxyl group and the sulfur atom of H<sub>2</sub>S plays the role of H-donor and H-acceptor, respectively. The magnitude of the band shift ( $\Delta$ v(OH)) [164 cm<sup>-1</sup>] can be related to the acidity of the hydroxyl groups: the higher the shift, the stronger the acidity. Here, the measured  $\Delta$ v(OH) is lower than the one reported for H-bonded complexes between H<sub>2</sub>S and bridged hydroxyls in MFI zeolite ( 600 cm<sup>-1</sup>). Therefore, the **Brønsted acidity** of the Cr-OH groups in MIL-53(Cr) is **very low**, in agreement with previous results relative to the acidity measurements using CD<sub>3</sub>CN and CO as probe molecules<sup>439</sup>. Furthermore, adsorbed H<sub>2</sub>S species are evidenced

in the spectra by two v(SH) bands at 2575( $v_s$ ) and 2585 cm<sup>-1</sup> ( $v_{as}$ ) which intensity increase is related to the decrease of the  $\delta$ (OH). The two SH bands are thus assigned to a 1:1 complex with the Cr-OH group. It corresponds to the most predominant adsorption mode appearing during the first uptake (NP form). Further, one also notes a low asymmetric tail occurring from 2570 to 2520 cm<sup>-1</sup>. This low frequency component suggests the presence of H-bonds due to H<sub>2</sub>S-H<sub>2</sub>S interactions.

• After the second uptake, the intensity of the low wavenumber v(SH) component at 2565 cm<sup>-1</sup> is more intense whereas the  $\delta$ (OH) band is not perturbed. At this stage, the v(OH) band is observed at 3525 cm<sup>-1</sup> and the  $\delta$  (OH) one at 975 cm<sup>-1</sup>. The corresponding  $\Delta$ v(OH) shift of 130 cm<sup>-1</sup> is significantly lower in the NP structure (164 cm<sup>-1</sup>), showing a weakening of the strength of the hydrogen bond between the H<sub>2</sub>S and Cr-OH group in the LP form, where confinement effets are not so strong. As suggested by the increase of the low v(SH) component at 2565 cm<sup>-1</sup>, this phenomenon could result from the condensation of H<sub>2</sub>S molecules in the pores of the LP form.

• As for MIL-47, molecular simulations further bring some informations concerning the microscopic arrangements of  $H_2S$  and their predominant interactions. First, we explored the preferential adsorption sites for  $H_2S$  in the NP form, when the first plateau is reached, e.g., for almost 4 guest molecules per unit cell. The rdf calculated for the  $S(H_2S)$ - $H(\mu_2$ -OH) pair confirms the presence of weak hydrogen bonds between the protons of the  $\mu_2$ -OH group and the sulfur atoms of the adsorbed  $H_2S$ , with a mean characteristic  $S(H_2S)$ - $H(\mu_2$ -OH) distance of 2.71 Å. The rdf plot shows that the  $\mu_2$ -OH-SH<sub>2</sub> interactions correspond to the formation of 1:1 complex. Furthermore, the rdf for the  $H(H_2S)$ - $S(H_2S)$  pair evidence that the H-bonds between the  $H_2S$  molecules are slightly stronger when they are confined within the pores of the NP structure than in the MIL-47(V) form. Note that these H-bonds are much weaker than those previously pointed out for  $H_2O$  in the same MIL-53(Cr) solid. The  $H_2S$  molecules form dimers within the channel with some disorder, however weaker than in MIL-47(V). This host/guest geometry significantly differs with the one obtained for  $H_2O$ , where a highly 1D ordered arrangement was pointed out. In addition to their interactions,  $H_2S$  tends also to significantly interact with the oxygens of the carboxylate groups as shown in the rdf for the  $H(H_2S)$ -O(carboxylate) pair.

• The structural situation of the guests significantly differs when one analyzes the most probable arrangements of  $H_2S$  in the LP form for a loading of 10 molecules per unit cell, roughly corresponding to the adsorbed amount experimentally obtained at the second plateau of the isotherm. As compared to the NP form, one can notice from the rdf plot that although the mean distance  $S(H_2S)-H(\mu_2-OH)$  is slightly shorter (2.62 Å in LP vs 2.71 Å in NP), the corresponding free energy profile calculated following the methodology described previously shows a shallower well as compared to the NP form. This trend is also supported by lower simulated adsorption enthalpy in the LP (-23.4 kJ.mol<sup>-1</sup>) than in the NP (-32.5 kJ.mol<sup>-1</sup>) form, in good agrement with experimental results (-26.0 kJ.mol<sup>-1</sup> and -32.0 kJ.mol<sup>-1</sup>, respectively). Here also, the  $\mu_2$ -OH-SH<sub>2</sub> interactions agree with the formation of a 1:1 complex. Further, the interactions between  $H_2S$  and the oxygens of the carboxylate groups are much less frequent than in the NP structure. Finally, one observes that while some weak hydrogen bonds between  $H_2S$  molecules are still present, they appear significantly weaker than in the NP form.

The reversibility of  $H_2S$  adsorption at room temperature on both samples, which does not occur with MIL-100 and MIL-101(Cr), was also established from experiments on  $CH_4$  adsorption before and after  $H_2S$  treatment at 303 K with regeneration using primary vacuum <sup>491</sup>.

The H<sub>2</sub>S interactions are rather weak and decrease following the sequence: MIL-53(Cr) NP > MIL-47(V) > MIL-53(Cr) LP. This behavior suggests that H<sub>2</sub>S desorption is more difficult in MIL-53(Cr) NP than in MIL- 47(V), emphasizing that this latter solid would be more appropriate for application in separation/purification processes for purifying gases containing H<sub>2</sub>S as polutant. Preliminary simulations based on H<sub>2</sub>S and CH<sub>4</sub> adsorption data on MIL-47(V) suggests a high H<sub>2</sub>S selectivity toward CH<sub>4</sub> whatever the molar fraction of H<sub>2</sub>S in the gas phase under 1.0 and 0.2 MPa, pressure which are relevant to Pressures Swing Adsorption (PSA) in industrial processes.

# 5.a.3 : Adsorption of hydrogen <sup>367,426,430,433,472,505,513,517,545</sup>.

This section, which could have also appeared in the energy chapter to come, concerns indirectly environment. Indeed, the applications of hydrogen storage with its combination to oxygen is a necessary ingredient for fuel cells as one substitute to fossil energies in the future, since the only product of reaction is non polluting water.

The physical chemistry of this physisorption was already strongly evoked in the part dedicated to the breathing

phenomenon. Its study is extended here to rigid solids. The problem is double : find materials able to store large amounts of this gas at a temperature as close as possible to 300K, and to ensure after an efficient  $H_2$  storage for alimenting the fuel cells installed for instance in cars. The Department Of Energy (DOE) has fixed the minimal criteria fror such an application.

The difficulty for satisfying these requirements comes from the  $H_2$  molecule itself : light weight, apolar molecule and high speed of displacement (500m.s<sup>-1</sup> at 77K). Stopping this « bolide » implies sufficiently strong interactions of  $H_2$  with the walls of the framework for doing so. This strength is first reflected by the initial slope of the adsorption isotherm before any quantitative other data ; the steeper the slope, the stronger the interaction.

Before speaking about mesoporous MIL-100 and -101, we just recall in a few words what happened for the flexible MIL-53 structure type with a Langmuir surface area close to 1500 m<sup>2</sup>.g<sup>-1</sup>. It was a hysteretic adsorption-desorption process with adsorbed amount of 3.8 wt% under 1.6 MPa at 77K with a medium slope indicating weak H<sub>2</sub>-framework interactions (3-4 kJ.mole<sup>-1</sup>). Unpublished neutron diffraction data proved that the initial sites of adsorption were close to the inorganic part of the hybrid (Fig.II.2.32).



**Fig.II.2.32.** – (a) Hysteretic adsorption-desorption isotherm at 77K of MIL-53(AI) compared to those of other MOFs ; (b) adsorption sites of  $H_2$  (yellow parts) on the framework (in blue) of MIL-53(AI).

The same study with the rigid mesoporous solids MIL-100 and MIL-101. MIL-100 has a Langmuir surface area of 2800 m<sup>2</sup>.g<sup>-1</sup>, and the amounts of H<sub>2</sub> adsorbed are 0.15 wt% under 7MPa at 300K and 3.28 wt% under 2.65 MPa at 77K, close to activated carbons. MIL-101b has a Langmuir surface area of 5600 m<sup>2</sup>.g<sup>-1</sup>, and the amounts of H<sub>2</sub> adsorbed are 0.43 wt% under 8 MPa at 300K and 6.1 wt% under 8 MPa at 77K (several times larger than MIL-53), despite the presence of a slight excess of terephtalic acid remaining in the pores.



**Fig.II.2.33.** –(*left*) adsorption isotherm at 303K (dark symbols) and 77K (open symbols) of MIL-100(Cr); (b) the same with MIL-101 (MIL-101a refers to the as-synthesized product and MIL-101b to the activated sample.

Despite these much larger surface areas, the capacity increase of 90% relative to MIL-53 is smaller than expected. This confirms that surface area is not the only criterion for hydrogen adsorption. Indeed, one would expect that in systems with ultramicropores, that is, pores of up to three times the size of the probe molecule, volume filling should also occur. However, the ratio between capacity uptake and Langmuir surface area is almost constant for these

mesoporous compounds, suggesting that such a relationship is probably valid for compounds having similar structural properties.

Clearly, the very large empty space generated by large cages is useless for gas storage. To retain hydrogen in the tunnels and cages of porous solids, one needs strong interactions between the walls and the  $H_2$  molecules, provided that the pores are sufficiently large to accommodate  $H_2$  molecules.

With this in mind, it is interesting to compare the results obtained with MIL-100 and MIL-101 with those of MIL-53 which has a very similar composition to MIL-101. MIL-53 does not exhibit any H<sub>2</sub> sorption capacity at room temperature, whereas MIL-100 and MIL-101 do. The presence in MIL-100 and MIL-101 of fluorine atoms and of unsaturated chromium sites after removal of the terminal water molecules provides possible sites for strong interaction which may explain the present hydrogen-storage properties observed at 300 K. To understand more deeply the differences in hydrogen adsorption of these large-pore samples, micro- calorimetric experiments were performed at 77 K and low pressures of  $H_2$  (< 1 bar) on both samples. Surprisingly, the enthalpy of adsorption in MIL-101b at low coverage is much higher, close to -10 kJ mol-1 (range : -9.3 to -10.0 kJ.mol<sup>-1</sup>), than that of MIL-100 of around -6 kJ.mol<sup>-1</sup> (range : -5.6 to -6.3 kJ.mol<sup>-1</sup>). According to Bathia *et al.*, the thermodynamic requirement for an adsorbent capable of storing hydrogen at ambient temperature is a heat of adsorption of hydrogen of -15.1 kJ.mol<sup>-1</sup>. So, what could be the nature of the interaction between hydrogen molecules and the framework that gives rise to such high values for MIL- 101, the highest so far reported for MOFs (MOFs are usually in the range - 4-7 kJ.mol<sup>-1</sup>)? Looking carefully at the structures, two possibilities arise : (i) after dehydration, both mesosolids have unsaturated metal sites (i.e., five-coordinate chromium sites). However, IR experiments have shown that the strongest Lewis metal sites are poisoned in MIL-101 by coordinated BDCH<sub>2</sub> moleties, whereas this is not in the case for MIL-100. This observation rules out the possibility of the unsaturated metal sites being the strongest interaction sites for hydrogen in MIL-101. (ii) The possible presence of strong adsorption sites within the microporous supertetrahedra (ST). If their internal diameters are close to 6.6 and 8.6 Å, respectively, benzene rings of BTC moieties in MIL-100 lie at the faces of the STs and leave almost no space for gas molecules to enter the cavities of the STs. On the contrary, in MIL-101, the BDC moieties lie at the edges and leave the STs open to H<sub>2</sub> molecules. Therefore, in our opinion, the most probable hypothesis is that the microporous STs of MIL-101 are the sites of strongest interaction in MIL-101, probably at each corner close to the trimers of chromium octahedra. The structure is however too complex for getting accurate informations from neutron powder data.

In spite of good intrinsic performances, MIL-100 and -101 only adsorb at 77K and the amounts of adsorbed  $H_2$  decrease rapidly when temperature increases leading relatively low hydrogen uptakes at room temperature. In an attempt to increase the temperature of noticable adsorption in these phases, we introduced in the large cages Chevrel clusters with fluorinated external shells, expecting stronger interctions between  $H_2$  and the highly electronegative fluoride ions.  $[Mo_6Br_8F_6]^{2^-}$  was chosen<sup>507,517</sup>. X-ray powder diffraction, thermal analysis, elemental analysis, solid-state NMR, and infrared spectroscopy have evidenced the successful loading of the cluster. In a second step, the hydrogen sorption properties of the model cluster loaded metal organic framework (MOF) system have been analyzed and compared to those of the pure MOF sample, through a combination of adsorption isotherms (77 K, room temperature), thermal desorption spectroscopy, and calorimetry (calculated and experimental) in order to evaluate the hydrogen storage efficiency of the cluster loading. The conclusion is rather disappointing even if, at pressures beyond 0.35 MPa, the volumetric hydrogen storage capacity was increased by up to 20% by the inclusion of the metal clusters while the enthalpy of adsorption increased by 10% leading to release at higher temperatures. At room temperature and 8 MPa, the hydrogen storage capacity of the MIL-101-Mo<sub>6</sub>Br<sub>8</sub>F<sub>6</sub> is over twice that of MIL-101.

### **5**.b. Properties related to the domain of ENERGY SAVINGS. Evidence and explanations.

The decrease of fossil sources creates a societal problem. Beside the search of new sources of energy, scientists and engineers are also looking for processes which could reduce the energy costs in current technologies by appropriate innovations requiring less energy for equal or better yields. In this perspective, hybrid porous solids are concerned in two domains : advanced water adsorbents and new ways for separation of gas mixtures. Both domains use large consumptions of energy, either for regenerating the sorbents or for distillations either at low or high temperatures.

### 5.b.1. Adsorption of water and dehumidification properties<sup>555</sup>.

It seems trivial, but water sorption technologies are widely used commercially in many contexts, including industrial or indoor desiccant applications such as desiccant dehumidifiers, gas dryers, adsorptive air conditioning systems, fresh

water production, adsorption heat transformation. In recent years, the potential for energy savings through improved efficiency has received increased attention, particularly as low-grade thermal energy or solar energy could be utilized. Currently, silica gel and zeolites are the most widely utilized commercially, often formed into corrugated honeycomb rotors. As these sorbents typically must be heated above 450K during the desorption step, these sorbents are far from ideal in terms of energy consumption. There are additional issues with the level of dehumidification that these materials are able to achieve. Improved energy efficiency requires advanced water adsorbents that can be regenerated together with the removal of a large amount of water vapor from humid conditions. If such materials could operate at or below 350K, they could utilize readily available waste heat, leading to further energy savings.

Based on this requirement, the exceptional hydrothermal stability and large sorption uptakes known for MIL-101 and MIL-100 – both stable in liquid water for months - encouraged us to assess their applicability for water sorption applications after some studies on various MILs <sup>387,409,420,447,462,490,50,522</sup>. Reports of other groups dealing with MOFs as water adsorbents began in 2010 and are still scarce, despite the fact that there is a particular need to evaluate the low temperature desorption properties of hybrids, i.e., below 350K for application to energy-efficient dehumidication systems.

Activated MIL-101(Cr) and MIL-100(Fe) possess unique sorption properties for water vapor at 280K and 350K the water sorption isotherm in MIL-101(Cr) and MIL-100(Fe). They show a unique shape with an initial adsorption step  $(p/p_0 \ 0.2; p_0:$  saturation vapor pressure), indicating the presence of the coordinatively unsaturated metal sites followed by strong uptakes due to two capillary condensation steps in the mesoporous cages. It is the same for in MIL-100(Fe). This isotherm shape makes the MOF adsorbents special compared to zeolites and silica-gel adsorbents. It is also consistent with their structural features showing two mesoporous cages with two microporous windows. The capillary condensation steps are accompanied by hysteresis loops, which confirm such a condensation mechanism. Adsorption isobars of water vapor in MIL-101(Cr) (BET surface area : 4150(100) m<sup>2</sup>.g<sup>-1</sup>) and MIL-100(Fe) (BET surface area : 2300(100) m<sup>2</sup>.g<sup>-1</sup>) dehydrated at 430K for 12 h clearly reveal the dependence of sorption uptakes on adsorption temperature and water vapor pressure. These materials exhibit very high equilibrium uptakes : 1.5 g.g<sup>-1</sup> for MIL-101(Cr) and 0.84 g.g<sup>-1</sup> for MIL-100(Fe) above 2.4 kPa (p/p<sub>0</sub> : 0.57) at 300K. However, their uptakes decrease to less than 0.20 g.g<sup>-1</sup> above 330K and below 4.8 kPa (p/p<sub>0</sub> : 0.24).

As expected, water sorption isotherms at 300K show outstanding water sorption uptakes of MIL-101(Cr) and MIL-100(Fe) at relatively high partial pressures,  $p/p_0$  0.5, i.e., 1.61 g-H<sub>2</sub>O per g of dry adsorbent for MIL-101(Cr) and 0.873 g H<sub>2</sub>O per g of dry adsorbent for MIL-100(Fe). They are 2.5–5.0 times higher than those of zeolite NaX (0.336 g H<sub>2</sub>O), silicoaluminophosphate SAPO-34 (0.330 g H<sub>2</sub>O) and silica gel (0.327 g H<sub>2</sub>O) which are currently used as commercial water adsorbents. MIL-100(Cr) and MIL-100(AI) present similar sorption uptakes to that of the isomorphous MIL-100(Fe). To the best of our knowledge, the equilibrium uptakes (1.50–1.70 g.g<sup>-1</sup>) in dehydrated MIL-101(Cr) at 300–310K and  $p/p_0$ : 0.5 is one of the highest values among those ever reported in solid adsorbents.

In order to explain the large water uptake observed in these materials, we measured  $N_2$  physisorption isotherms at 77K using a volumetric gas sorption apparatus on samples activated at 30°C under vacuum. Despite the low activation temperature, more than 90% of their total pore volumes (based on activation at 420K for 1 day) were recovered in both cases. This implies that these materials can be almost fully dehydrated at 300K, in contrast to conventional porous materials requiring high temperature dehydration before use. This property is of great importance for energy-efficient dehumidification.

Besides water sorption capacity and hydrothermal stability, sorption kinetics of water vapor and the degree of regeneration (or reversibility) are also important factors that should be taken into consideration for industrial applications. High sorption rates of water vapor allow faster rotation cycles of the adsorbent- coated rotors used in dehumidification systems, improving performance. In this respect, dynamic sorption properties of MIL-101(Cr) and MIL-100(Fe) in a N<sub>2</sub> gas flow with controlled humidity 60% were scrutinized and compared to commercial adsorbents such as NaX, SAPO-34, and silica gel. It should be noted that the mode of dynamic sorption properties of MIL- 101(Cr) and MIL-100(Fe) at 300K can also be easily switched by changing the partial pressure of water (humidity). For example, both the MIL-101(Cr) and MIL-100(Fe) absorb appreciable water at relative humidity (RH) 65% while they could be desorbed at RH 1% at constant temperature. This corresponds to a room-temperature pressure-swing dehumidification cycle. Dynamic sorption rates of adsorbents of less than 10 min are preferred since adsorbent-coated honeycomb rotors are normally used for desiccant dehumidification systems. Such systems operate by a rotational phase change of adsorption at room temperature and desorption at elevated temperature with a speed of generally 5–30 RPH (revolution per hour).



**Fig.II.2.34.** - Water desorption profiles of adsorbent materials at 70° C in a dry  $N_2$  flow: a) MIL-101(Cr), b) MIL-100(Fe), c) silica gel, d) SAPO-34, and e) NaX. Test conditions: temperature-programmed desorption after adsorption at 300K and RH 60% for 1 h,  $p/p_0$  :0.6; ramping rate of desorption: 50°C/min<sup>-1</sup> from 30°C to 65°C and 7.5°C/min<sup>-1</sup> to 70°C and flow rate of  $N_2$  of 200 mL.min<sup>-1</sup>.

The desorption rates for these materials at 30°C are not sufficient for practical dehumidification, so a slight increase of the desorption temperature to 70°C may be necessary to enhance kinetics (Fig.II.2.34). From desorption profiles of the fully hydrated materials, the order of desorption rates is MIL-101(Cr) > MIL-100(Fe) > silica gel > SAPO-34 > NaX for 10 min. The water desorption capacities for 10 min are 1.55 g.g<sup>-1</sup> for MIL-101(Cr) and 0.8 g.g<sup>-1</sup> for MIL-100(Fe), much higher than the others. Additionally, ten regeneration cycles of these MILs between adsorption at 30°C and desorption at 70°C do not exhibit any decrease of sorption capacities.

Two main reasons explain the easier desorption of water compared to hydrophilic purely inorganic porous solids : (i) the amphiphilicity of these MILs, due to the presence of both organic and inorganic moities in the structures ; (ii) MIL-100 and MIL-101, while crystalline, are mesoporous. Thus, most of the water molecules do not directly interact with the surface of the pores, favoring easier desorption. In MIL-100, the large cages (diameter 24–29 Å) are accessible through microporous windows ( $\phi$  : 5–8.5 Å) and the terminal water molecules of the trimers point toward the center of the windows, which likely slows down the diffusion of water vapors. The diffusion of water is easier in MIL-101 because the windows are larger ( $\phi$  : 12–16 Å) and the terminal water molecules point this time toward the center of the large cages (29–34 Å).





*In situ* IR spectra show the existence of many complexes during the process. The spectra recorded at increasing temperatures under  $N_2$  flow indicate that the terminal water molecules coordinated to trivalent cations (1:1 complex, bands at 5280, 3700, and 3605 cm<sup>-1</sup>) are removable from the framework by heating above 150°C under flowing gas or 100°C under vacuum. It is assumed that the remaining water molecules above 70°C may be also those that strongly interact with coordinated water molecules (1:2 complex, bands at 5306 and 3680 cm<sup>-1</sup>). According to the degree of dehydration between 30 and 70°C, the IR spectra reveal mainly the presence

of both hydrogen-donor (band at ca. 3000 cm<sup>-1</sup>) and electron-donor water molecules (3680 cm<sup>-1</sup>) in moderate interactions with the terminal water molecules *via* H-bondings. These H-bonded molecules may exist as extra water multimers forming  $H_2O...(H_2O)_n$  chains under a humid  $N_2$  flow. The intensity of the 5200–5220 cm<sup>-1</sup> band, characteristic of the multimer species, depends on the water uptake.

The enthalpy profiles of water adsorption, measured by microcalorimetry, present two regions. Below about 0.3 g.g<sup>-1</sup> of water adsorption, the profiles correspond to a gradual decrease in energy interpreted as the continual adsorption on the coordinatively unsaturated metal cation sites (CUS) and pore surface with a gradual reorganization of water-adsorbed monolayers. The second region above 0.3 g.g<sup>-1</sup> corresponds to the enthalpies of the capillary condensation in the mesopores, with enthalpies of adsorption close to the evaporation enthalpy of water (-40.7 kJ.mol<sup>-1</sup>). In terms of amounts, MIL-100(Fe), for example, reaches more than 690 g H<sub>2</sub>O per kg dry sorbent per cycle in the following conditions : adsorption at 15°C in humid air (RH 65%) and desorption at 70°C in less humid air (RH 20%).

The present results imply that these cheap, biocompatible and non-toxic (see health section) materials can be favorably applied to evaporative humidifiers and efficient and environmentally friendly production of potable water, especially drinking water.

# 5.b.2. Inexpensive selective separations in gas mixtures<sup>408,432,502,522</sup>

As already said, separations processes have high energy costs. The challenge currently consists in finding new solids which avoid this default for instance in performing the separation at room temperature. We participated to this challenge in two domains of importance for applications : (i) the  $CO_2$ -CH<sub>4</sub> and (ii) the propane-propene separations at room temperature.

# • the $CO_2$ -CH<sub>4</sub> separation <sup>408,432,502</sup>

Due to its different adsorption behaviours toward  $CO_2$  and  $CH_4$  guests (2 steps behavior for the first, type I isotherm for the methane) the flexible MIL-53(Cr) solid was used for testing the power of this structure type as a selective adsorbent.



**Fig. II.2.36.**  $-CO_2$  ( $\blacklozenge$ ) and  $CH_4$  ( $\blacklozenge$ ) adsorption isotherms at 303 K on the MIL-53(Cr) compared to the relative Raman intensity of  $CO_2$  ( $\Box$ ) and  $CH_4$  (O), and the simulations ( $CO_2$ : full line;  $CH_4$ : dashed line). Gas compositions  $CO_2$ - $CH_4$ : 0-100 (a), 25-75 (b), 50-50 (c), 75-25 (d), and 100-0 (e); red:  $CO_2$ ; blue  $CH_4$ 

The study of the coadsorption of  $CO_2$  and  $CH_4$  in MIL-53(Cr) used a large variety of techniques (gravimetry, X-Ray diffraction, Raman spectroscopy, breakthrough experiments, hybrid Monte-Carlo (HMC) simulation). It shed some light onto a complex behavior.  $CO_2$ -rich and equimolar  $CO_2$ - $CH_4$  mixtures lead to a breathing of the structure, i.e., an LP to NP transition and then back to LP form as the pressure increases.  $CH_4$ -rich mixtures (>75%  $CH_4$ ) always maintain the solid in the LP form as with pure  $CH_4$ . The closing and opening of the structure is entirely controlled by the partial pressure of  $CO_2$ .  $CH_4$  only has an influence on the extent of the transition.

The structure can fully shrink when the  $CH_4$  content is low (<25%). For equimolar mixtures, the closing remains partial.

Experimental results suggest that  $CH_4$  is probably not adsorbed at all in the NP-form when it is filled with  $CO_2$  (likewise,  $CH_4$  does not adsorb in the NP form filled with  $H_2O^{432}$ ) in accordance with molecular simulations, which show that  $CH_4$  is expelled from the structure when the LP to NP transition occurs. The exclusion of  $CH_4$  from the NP structure lets us expect a very high  $CO_2$ - $CH_4$  selectivity in breakthrough experiments, carried out under conditions in which the NP form should dominate. However, experimentally measured selectivities were much lower, probably due to a kinetic barrier for the LP to NP transition which is not completed during the breakthrough experiments.

Structural metastability, probably also dependent on the heterogeneity of the sample, is an inherent feature of MIL-53(Cr) upon coadsorption of  $CO_2$  and  $CH_4$ . The phase rule predicts that the NP and LP form of MIL-53(Cr) can only coexist at one given pressure and composition. In practice, however, coexistence of the two phases is observed over a large range of conditions, which makes the system difficult to predict because the final coadsorption state depends on the starting point of the system, especially in breakthrough experiments where the contact time with the gas mixture is low.

Concerning the use of MIL-53(Cr) in a PSA system, the step of the  $CO_2$  adsorption isotherm at intermediate pressures looks very promising because it could potentially translate into a high working capacity between, for example, 0.2 and 1.0 MPa. Yet, other features make the system a little bit less attractive: the selectivity for  $CO_2$  at high pressure is rather low and the large hysteresis means that the regeneration (the desorption) of the column occurs at a lower pressure than desirable. The ideal solid would be flexible at intermediate pressure, but have a narrow hysteresis loop to facilitate desorption. This would be possible by decreasing the LP-NP barrier, which paves the way for the line of future research.

**Quantitative separation is however possible at room temperature**. When performing the same experiments with MIL-53,  $H_2O$  (the hydrated form of MIL-53, which exists in the NP form as previously characterized) the isotherms at 300K are completely different. The sigmoïd shape for  $CO_2$  is characteristic of a 'gate' effect : very small adsorption up to 10 bars and then important adsorption. On the contrary, the adsorption of  $CH_4$  is so small up to 20 bars that one can consider as a good approximation that methane is not adsorbed at all, providing a good selectivity for the mixture in the pressure range 10-20 bars at 300K.



**Fig. 11.2.37.** – Comparison of the adsorption isotherms of  $CO_2$  and  $CH_4$  when anhydrous MIL-53 (dark symbols) and MIL-53,  $H_2O$  (grey symbols) are used as hosts of the gases. Note than in the later case,  $CH_4$  is almost not adsorbed at all up to 20 bars, providing an excellent selectivity for the mixture (from <sup>432</sup>).

2,000 m<sup>2</sup>.g<sup>-1</sup>), stability in air for months (even in boiling water) but, more importantly, the existence of cationic unsaturated sites (CUS) which are well known to strongly modify interactions with gases and liquids in zeolites and amorphous mesoporous solids. Moreover, as interactions are also dependent on the oxidation of the metal, the possibility for iron to adopt several valences is beneficial for eventual redox properties, even if mixed valence MOFs are up to now extremely rare.

With this in mind, we carefully came back to the activation of MIL-100(Fe) vs. temperature. As already noticed, a classical activation performed at  $150^{\circ}$ C generated Fe<sup>3+</sup> CUS by elimination of the terminal water molecules of the

trimer. However, after activation at higher temperatures, the colour of the resulting solid surprisingly changed from orange to dark brown, a well known fact indicating the onset of a mixed valence  $Fe^{II}$ :  $Fe^{III}$ . We therefore undertook a study of this new feature in the range 150-250°C by using many different and complementary techniques for its characterization with the idea – for the first time – to correlate the reducibility of CUS with preferential sorption properties on selected gas adsorbates.

Several points were examined: (i) the invariance of the framework structure, (ii) the efficiency of evacuation from adsorption isotherms, and (iii) the respective influence of temperature, time and pressure on the coordination and the nature of the metallic species. Due to the large dimensions of the cell, the last point could not be solved by conventional X-ray diffraction. Only *in situ* spectroscopic studies (IR, Mössbauer) provided structural informations.

Even under hard conditions, the skeleton is preserved despite some slight variations of the intensity of the Bragg peaks. Moreover, the shape of the  $N_2$  adsorption isotherms is not strongly affected when increasing temperature from 100 to 250°C (12h); it is also the case for the BET surface area (2300±50 m<sup>2</sup>·g<sup>-1</sup>) and pore volume (1.2 cm<sup>3</sup>·g<sup>-1</sup>). *In-situ* IR shows the onset of Fe(II) CUS above 150°C but that temperature (in He flow) is not sufficient for providing efficient activation and Fe reduction. It had to be coupled with secondary vacuum during 12h to enhance the phenomenon.

The oxidation state of iron with activation temperature of the as-synthesized MIL-100(Fe) was examined by both IR and Mössbauer spectroscopy. *Operando* IR spectroscopic analyses after adsorption of CO and NO as probe gases quantify both the oxidation states of iron and the amount of CUS either in a He flow or under high vacuum (Figure II.2.38). Pre-adsorption of NO effectively distinguishes CUS Fe(II) and CUS Fe(III).



# **Fig. II.2.38.** – Concentrations of CUS Fe present in MIL-100(Fe) activated under high vacuum at different temperatures, measured by IR analysis upon CO adsorption,

The reduction of iron leading to CUS Fe(II) starts above 150°C and increases with the activation temperature up to 0.85 mmol/g (18 mol% of the total amount of iron sites) when activated at 250°C for 12 h. *In-situ* IR analysis confirms this fact and points out that it is possible to induce significant amounts of CUS Fe(II) and CUS Fe(II) within the structure of MIL-100(Fe) by thermal activation in an inert gas flow or under vacuum.

<sup>57</sup>Fe Mössbauer analysis of the as-synthesized MIL-100(Fe) *vs.* temperature also quantifies the proportions of Fe(III) and Fe(II). At -196°C, the broad quadrupolar doublet of the as-synthesized MIL-100(Fe) is consistent with the presence of octahedral Fe(III) ions showing different degrees of distortions, the highest one being assigned to Fe(III)-F/OH. At T < 150°C under high vacuum (<10<sup>-5</sup> Torr), only Fe(III) sites are present. Increasing

amounts of Fe(II) are observed at higher temperatures. Their content, negligible after degassing at 150°C, reaches 14 mol% of Fe(II) (with respect to total amount of iron) after degassing at 260°C/90h . Above this temperature, X-ray thermodiffractometry shows that the framework begins to collapse. At 260°C, the Fe(II) partial presence suggests unambiguously that it originates from the loss of the X ligand according to the scheme  $\text{Fe}^{3+}$ -X<sup>-</sup> into  $\text{Fe}^{2+}$ -Q rather than the direct reduction of CUS Fe(III). The 14 % contribution corresponds to more than 40% of the Fe-F site



The heat of adsorption of CO (-28 to -39 kJ.mol<sup>-1</sup> when only Fe(III) CUS are present) increases up to -51 kJ.mol<sup>-1</sup> for the partially reduced sample activated at  $250^{\circ}$ C under vacuum. This confirms the strong interaction of CUS Fe(II) with CO, already observed by IR. For MIL-100(Fe) activated at  $250^{\circ}$ C, sorption uptakes of CO are higher than those of CO<sub>2</sub> within 6.5 kPa. These results suggest that MIL-100(Fe) with CUS Fe(II) could be used for the removal of CO from CO<sub>2</sub>-rich mixtures issued from, for example, the production of hydrogen from biomass or the removal of CO impurity to protect the deactivation of Pt electrodes in low temperature fuel cells.

The use of mixed-valent MIL-100(Fe) may also be considered for further applications to selective separation or purification of olefins and acetylenes from hydrocarbon mixtures. Indeed, energy-efficient adsorptive separation and purification of these molecules are necessary in petrochemical industry. We focused on the adsorption and separation properties of the propane/propylene system.

<u>Figure II.2.39</u> shows the adsorption isotherms and isosteric heats of adsorption of propane and propylene at 25°C up to 6.5 kPa over MIL-100(Fe) activated at 250°C in He.



**Fig. II.2.39.** – (a) Enthalpies of adsorption (dark points) and amounts (open marks) of adsorbed propylene and propane) in MIL-00(Fe) activated at 250°C for 12h under high vacuum; (b) Sorption profiles of propylene over CUS Fe(III) and CUS Fe(III) measured by operando IR analysis at  $25^{\circ}C$ 

Propane uptakes linearly increase with the sorption pressure, but they are noticeably lower than those for propylene. The sorption affinity to propylene over propane remarkably increases at low pressure. Microcalorimetry confirmed this fact. In the presence of only pure Fe(III) sites (activated at 100°C under vacuum), similar values of the isosteric heats of adsorption (close to -30 kJ/mol) are observed for propane and propylene. In mixed-valent MIL-100(Fe) (250°C under vacuum), the introduction of Fe(II) sites dramatically changes the situation. The heat of

adsorption of propylene rises up to -70 kJ/mol at low coverage while that of propane remains the same. From these results, sorption profiles of propylene after activation at 250°C directly correspond to the sorption in CUS Fe(II) at lower partial pressure (< 0.25 kP) and CUS Fe(III) at higher partial pressure (> 1.25 kPa). These preferential interactions of iron(II) sited with propylene were confirmed by IR.

To evaluate the separation efficiency for propane/propylene mixtures, breakthrough tests of the binary mixtures have been performed using a fixed-bed column packed with pellets of MIL-100(Fe), activated in a He

flux at 150°C for 3 h and 250°C for 12 h. In the breakthrough curves at 40°C and 0.25 kPa of  $C_3$  hydrocarbons, the sample activated at 250°C fully adsorbs two hydrocarbon molecules until 7 min and then it does not adsorb propane any more in the continuous flow of the mixture. Propylene uptakes greatly increase with increasing the temperature to 250°C, i.e. 0.087 mmol/g at 150°C and 0.318 mmol/g at 250°C. This clearly indicates that separation of C3 hydrocarbons at low pressure strongly increases with the presence of CUS Fe(II).

From the curves, the separation factors (a) for propylene over propane are estimated to 28.9 for the sample activated at  $250^{\circ}$ C and 5.1 for the sample at  $150^{\circ}$ C. Moreover, the separation factor at 5 kPa (5.1) is at least 3 times higher than that in HKUST-1 (Cu<sub>3</sub>(BTC<sub>2</sub>). This means that CUS Fe(III) is also effective to adsorption of propylene although the sorption affinity to propylene is weaker than those of CUS Fe(II). Finally, TPD (temperature-programmed desorption) profiles of propane and propylene in MIL-100(Fe) after breakthrough runs at 40°C point out that only propylene remains in the pores above  $40^{\circ}$ C , confirming the high affinity of CUS Fe(II) to propylene, in excellent agreement with the above-mentioned *operando* IR results. The present results obviously demonstrate that

CUS Fe(II) in MIL-100(Fe) leads to a dramatic separation and selective capture of propylene from the gas mixture with low concentrations.

Recyclability and regenerability of MIL-100(Fe) activated at 250°C were also tested. No loss in capacity or separation efficiency is observed after multiple cycles of adsorption-desorption, confirming the regenerability of MIL-100(Fe) even after reduction with 10%  $H_2$  at 120°C for 3 h or in the presence of 10%  $H_2$  in the gas mixture.

From all these results, we can conclude that MIL-100(Fe), with its unsaturated iron sites which strongly increase the strength of interaction with gas molecules with double or triple bonds, such as propylene, methyl acetylene and CO, leads to a dramatic improvement of not only preferential gas sorption but also its separation performance. As it is hydrothermally stable, non-toxic and robust, it paves a powerful way for the design and use of environmentally friendly gas adsorbents with preferential gas sorption properties.

• CUS and the unprecedented  $N_2/CH_4$  and  $N_2/O_2$  separation at room temperature <sup>588</sup>.

The above beneficial separative role played by the unsaturated metal centers (CUS) present in activated MIL-100 structure incited us to look at their efficiency when other gas mixtures are concerned. It is in particular the case for the  $N_2/CH_4$  and  $N_2/O_2$  separations.

The removal of nitrogen from methane is currently achieved by cryogenic distillation, despite the complexity, the high cost (far more expensive than the amine capture of  $CO_2$ ) and the high energy consumption of this technology. Although adsorption-based processes are promising for methane upgrading, the N<sub>2</sub>/CH<sub>4</sub> separation is still far to be optimal. At equilibrium, all the existing adsorbents prefer CH<sub>4</sub> to N<sub>2</sub>, even in the case of the 3D-channel like titanium silicate ETS-4' one of the rare porous materials that allows an effective kinetic separation of nitrogen over methane owing to the small size difference between the two molecules (3.8 Å (CH<sub>4</sub>) vs. 3.64 Å (N<sub>2</sub>)). This adsorbent is highly selective (N<sub>2</sub>/CH<sub>4</sub> selectivity  $\approx$  205 at 283 K).

MIL-100(Cr) was chosen for two reasons: (i) activated at 523K, it shows at 1 bar the highest N<sub>2</sub> uptake (1.64 mmol g<sup>-1</sup>), outperforming its Fe- and Al-analogues (0.25 and 0.43 mmol g<sup>-1</sup>, respectively) but also ETS-4 (0.41 mmol g<sup>-1</sup> at 295 K) under the same operating conditions; (ii) it presents the largest amount of CUS (3.55 mmol/g) compared to the above MIL-100(Fe) (2.53mmol/g). Moreover, at variance to the Al and Fe-analogues which adsorb more CH<sub>4</sub> than N<sub>2</sub> in the whole range of pressure, MIL-100(Cr) adsorbs much less CH<sub>4</sub> than N<sub>2</sub> (lower isosteric heat of adsorption (-27 kJ/mol for CH<sub>4</sub>; -39 kJ/mol for N<sub>2</sub>).

The characteristics of the separation power were determined by the conjugation of IR spectroscopy and of various theoretical calculations (DFT, DOS, GCMC...) related to the nature of  $N_2/CH_4$ -CUS binding.

Operando IR spectroscopy under  $N_2$  flow at 283 K and 1 bar confirmed the high affinity of MIL-100(Cr) for  $N_2$ , whereas, for  $CH_4$ , the absence of significant interactions with the MOF was noted.

Density functional theory (DFT) calculations of the binding energies ( $E_b$ ) of both molecules on the Cr(III) sites ( $E_b = -48.7 \text{ kJ ml}^{-1}$  for N<sub>2</sub>;  $E_b = -35.7 \text{ kJ mol}^{-1}$  for CH<sub>4</sub>) agree with the sequence of the isosteric heats. N<sub>2</sub> adopts an end-on coordination geometry towards the d<sup>3</sup> Cr(III) metal ion with a Cr-N<sub>2</sub> distance of 2.25 Å, significantly shorter than that predicted for CH<sub>4</sub> (2.65 Å). The atomic projected density of states (PDOS) and the molecular orbitals of the cluster models show an unoccupied N<sub>2</sub>-PDOS and Cr(III)-PDOS overlap (in relation with the back bonding interaction between N<sub>2</sub> and the Cr (III) sites). The HOMO d<sub>xz</sub> of Cr(III) shows a bonding state with the originally unoccupied  $\pi^*$  orbital of N<sub>2</sub>. Such a bonding character of molecular orbitals is not found for CH<sub>4</sub> adsorbed on Cr(III). The so-evidenced back-bonding interaction between N<sub>2</sub> and Cr(III), combined with the relatively strong Lewis acid strength of these metal sites evidenced by IR, are at the origin of the high N<sub>2</sub>-affinity of MIL-100(Cr).

Grand canonical Monte Carlo (GCMC) simulations based on the use of the newly DFT-derived guest/Cr(III) force fields, fairly reproduce both the adsorption isotherms and enthalpies for  $N_2$  and  $CH_4$ . MIL-100(Cr) was predicted to be thermodynamically  $N_2$ -selective over  $CH_4$  up to 1 bar for a molar mixture composition  $N_2/CH_4$ : 20/80 with selectivity values comprised between 3 and 4 within the 0-1 bar range. The same trend, even more pronounced, is obtained with the ideal adsorbed solution theory (IAST) applied to the experimental single component adsorption isotherms (~8 at 283 K and 1 bar).

MIL-100(Cr) is therefore the first-ever adsorbent able to thermodynamically capture  $N_2$  over CH<sub>4</sub>.  $N_2$  preferentially forms single quasi-linear N-N<sup> $\sim$ </sup>Cr(III) adducts in both small and large cages while CH<sub>4</sub> is mainly confined at the center of the small cages, interacting weakly with the pore wall.

Breakthrough experiments, carried out at 283 K and 1 bar on two  $N_2/CH_4$  mixtures (20/80 and 10/90) show that methane is first eluted after 2 min, whereas the adsorbent retains nitrogen. After 6 min, the outlet gas contains methane almost 100% pure, demonstrating the production of high purity methane (>99.9%). The resulting  $N_2/CH_4$  selectivity varies between 3.2 and 4.6 depending on the mixture composition. Switching the gas flow into He at 283 K for 10 minutes, easily regenerates the starting material.



**Fig. II.2.39 bis.** Adsorptive separation for a binary  $N_2/CH_4$  mixture: *a*, IAST-predicted  $N_2/CH_4$  selectivities of MIL-100(Cr) for a molar  $N_2/CH_4$  (20/80) mixture at two temperatures (283 K and 293 K). *b*, Experimental (filled symbols) and simulated (blank symbols) breakthrough curves of a  $N_2/CH_4$  mixture (molar composition 20/80) flowing through a bed of MIL-100(Cr) (0.75 g) at 283 K with a total gas flow of 5 cm<sup>3</sup> min<sup>-1</sup> at atmospheric pressure. *c*, Local views of the snapshots extracted from GCMC simulations performed for  $N_2/CH_4$  mixture at 283 K in MIL-100(Cr): 0.1 bar (left) and 1 bar (right). The interacting distances are reported in Å and the framework atoms and molecules are represented as follows: Cr, Silver; C, grey; O, red; H, white; CH<sub>4</sub>, green and  $N_2$ , blue.

GCMC simulations based on the newly DFT-derived  $O_2/Cr(III)$  and  $N_2/Cr(III)$  force fields, further predict that MIL-100(Cr) is also highly  $N_2$ -selective from a  $N_2/O_2$  mixture corresponding to dry air (79/21). The  $N_2/O_2$  selectivity ranges from 9 to 12 at 293 K in the pressure range 0-1 bar. This is confirmed by the IAST predictions ( $S(N_2/O_2) = 8.6$  at 293 K and 1 bar (Fig. 4a) and in line with the breakthrough experiments ( $S(N_2/O_2) = 6.8$  at 298 K and 1 bar (Fig. 4b). These outstanding performances surpass that of zeolite LiX commercially used for this application. GCMC simulations evidenced that this separation is also driven by the larger affinity of  $N_2$  strongly bound to the Cr(III) while only a small fraction of  $O_2$  interacts with Cr(III), in agreement with a higher adsorption enthalpy for  $N_2$  compared to  $O_2$ . This demonstrates the unique ability of MIL-100(Cr) to efficiently capture  $N_2$  from diverse  $N_2$ -containing gas mixtures. Noteworthy, its performances are maintained after ten consecutive adsorption/regeneration cycles of breakthrough experiments at 298 K, indicating the easy regeneration and durability of the material.

Inspired by the biomimetic and metal-dinitrogen chemistry concepts, this reveals that designing MOFs with unsaturated metal sites into their cages offers a unique opportunity to achieve unprecedented highly-efficient  $N_2$  capture. MIL-100(Cr), with its unsaturated Cr(III) sites, is the first-ever adsorbent able to thermodynamically capture nitrogen over methane and oxygen at room temperature with large  $N_2$  uptake and easy regeneration.

### solids. 447,462,490,503 5.b.3. – Heterogeneous catalysis and hybrid porous

Whereas catalysis is since a long time one of the main applications of zeolithic solids, it is an emerging field for hybrid materials. Even if, due to a long cooperation with my former postdoctoral student Dr. J.-S. Chang from KRICT (South Korea), I had a first experience of this domain with my nickel phosphates VSB-n<sup>289,295,419</sup>, I am clearly not an expert in this field. Some years ago, I tried to convince experts at least to perform some catalytic tests on my MILs. All of them were reluctant, arguing that our solids were not sufficiently stable at high temperatures for being performant. As I was convinced of the potential of MILs in this domain, I contacted once more Dr. Chang for looking at them, at a time when some scarce papers began to appear.

The ongoing success of our MIL-100 and -101 incited him to look preferentially at them as potential catalysts. MIL-100(Fe) was the first choice.

The use of heterogeneous catalysts in liquid phase Friedel-Crafts type reactions is highly desirable because the conventional homogeneous catalysts for these reactions pose several problems, such as difficulty in separation and recovery, disposal of spent catalyst, and corrosion. In the light of the importance of heterogenous catalyst, we have performed Friedel-Crafts alkylation to confirm the availability of iron-containing MIL-100 as a new porous catalyst. The conversion of benzyl chloride (BZC) (in the liquid phase benzylation of benzene by benzyl chloride) to diphenylmethane (DPM) at 70°C was studied over MIL-100(Fe), MIL-100(Cr) and zeolite catalysts for comparison. MIL-100(Fe) gives high activity and selectivity, showing that 100% BZC conversion, with nearly 100% DPM selectivity, was guickly attained after a short induction period (5 min), far better than the others. The observed high benzylation activity of MIL-100(Fe) might be attributed to the redox property of trivalent iron species (Fe<sup>3+</sup> + e<sup>-</sup>  $\leftrightarrow$  Fe<sup>2+</sup>) to play a significant role in activating both the reactants.

The second test concerned MIL-101. The existence of CUS as Lewis acid sites could be used to induce regioselectivity and shape- or size-selectivity towards guest molecules or reaction intermediates, after a chemical functionalization for, as suggested by Kitagawa, decorating channel surfaces of coordination polymers. However, his strategy included only the functionalization of ligand.

For the selective functionalization of CUS, we chose first an effective grafting reagent with multifunctional chelating groups, i.e. ethylene diamine (ED). As illustrated in Fig. II.2.40d, if one amine group of ED is linked to CUS Cr(III) of MIL-101 by direct ligation, the other amine group can play the role of immobilized base catalyst.

Clearly, this concept does not apply to the surface functionalization of mesoporous silicas because of their lack of the unsaturated surface sites in general.



Fig.II.2.40. - Site-selective functionalization of MIL-101 with unsaturated metal sites: (a) perspective view of the mesoporous cage of MIL-101 with hexagonal windows; (b-c) evolution of coordinatively unsaturated sites from chromium trimers in mesoporous cages of MIL-101 after vacuum treatment at 423 K for 12 h; (d) surface functionalization of the dehydrated MIL-101 through selective grafting of amine molecules (i.e. ethylene diamine) onto coordinatively unsaturated sites; (e) selective encapsulation of noble metals in the amine-grafted MIL-101 via a three-step process (see text). Chromium atoms (or octahedra) are in yellow, carbon in pale gray and the pure oxygen atoms in red.

The synthesis of the ED-grafted MIL-101 (ED-MIL-101) by coordination of ED to the dehydrated MIL-101 framework was performed in toluene under reflux condition. The almost unchanged X-ray diffraction patterns (XRDP) show that the ED grafting occurs with no apparent loss of crystallinity with, however, some slight variations of the Bragg intensities. IR spectra confirmed the full grafting of ED on the CUS of  $Cr^{3+}$ . The N<sub>2</sub> adsorption isotherms showed a decrease of the N<sub>2</sub> adsorbed amount and of the specific surface.

The catalytic performances of dehydrated ED-MIL-101 in base catalysis were measured using the Knoevenagel condensation as a base-catalyzed model reaction and its activities compared to those of the APS-grafted mesoporous silica SBA-15 (APS-SBA-15). [*APS is the acronym of 3-AminoPropyltrialkoxySilane*].

Looking at the condensation of benzaldehyde with cyanoethyl acetate over various amine-grafted molecular sieves at 353 K, the dehydrated mesoporous silica SBA-15 has only negligible activity, whereas the dehydrated MIL-101 revealed low but distinctive catalytic activity (31.5% conversion at 19 h). Interestingly, for a small amount of catalyst (20 mg or 1.12 M), catalytic activities of ED-MIL-101 are noticeably better than those of APS-SBA-15 even though the content of free amine groups in ED-MIL-101 (1.04 mmol/g) is significantly lower than that of APS-SBA-15 (2.89 mmol/g). For the condensation of benzaldehyde into trans-ethyl cyanocinna-mate, the conversion for ED-MIL-101 is 97.1% with high selectivity (99.1%). By contrast, the APS-SBA-15 exhibits only 73.8% conversion with 93.5% selectivity. Moreover, in terms of turnover frequency (TOF), ED-MIL-101 shows a remarkably superior activity (10 times higher than that of APS-SBA-15). In this case, TOF values of the grafted MIL-101 were calculated after subtracting the catalytic activity of MIL-101 from those of the grafted MIL-101. The higher activity of ED-MIL-101 might be mainly attributed both to the easily accessible amine functional groups and to its high surface area. The lower activity of APS-SBA-15 can be ascribed to the actual loss of catalytically active sites by the formation of Hbondings between functional groups. The DETA- and APS- grafted MIL-101 (DETA-MIL-101 and APS-MIL-101) show also much higher activities than APS-SBA-15. The recyclability test of ED-MIL-101 clearly supports that it is easily isolated from the reaction suspension by filtration and can be reused without significant loss of activity in the third run.

ED-MIL-101 exhibits high catalytic activities for various substrates in the Knoevenagel condensation. Dimethyl ketone, benzaldehyde, and methylbutyl ketone are found to be collected as good substrates producing more than 90% conversion to adducts in the condensation with ethylcyanoacetate or malonitrile. Remarkably, ED-MIL-101 reveals the size dependence on catalytic activities due to the change of the substituent groups of carbonyl compounds in the Knoevenagel condensation. For example, with benzophenone, the condensation reaction with malonitrile is hard to realize because the formation of the quite large product, diphenyl methylene malononitrile might be occluded in the pores, indicating the transition state or product shape-selectivity already known in microporous zeolites. The size-selective reactivity in ED-MIL-101 points out that the reaction essentially takes place in the amine-grafted pores taking into consideration the guest-selective properties of a 3D porous coordination polymer with amide groups in the base-catalyzed Knoevenagel condensation. This currently leads us to tune the pore size of MIL-101 by the type and shape of grafting agents leading to the pore modification.

The current successful concept of amine-grafting on CUS has a very important consequence: the encapsulation of metals for which only few attempts have been made until now but with no sufficient proofs attesting that the metals are well within the pores. Therefore, inclusion of metallic nanoparticles in MOFs remained a challenge. We then proposed another important way for the encapsulation of noble metals such as Pd, Pt and Au over the amine-grafted MIL-101 according to the procedure depicted in Fig. II.2.40e. The encapsulation procedure comprises the neutralization of the surface amine groups with an aqueous HCl solution, ionic reactions of the positively charged surface ammonium groups with anionic noble metal salts :  $PdCl_4^{2-}$ ,  $PtCl_4^{2-}$  and AuCl<sup>-</sup> by anionic exchange of chloride anions, followed by the gentle reduction of noble metals with NaBH<sub>4</sub> at low temperature.

After the reaction, X-Ray powder diffraction shows that there is no apparent loss of crystallinity, and no supplementary Bragg peaks. However, the Bragg intensities change specifically to each metal, confirming their introduction within the pores. TEM images of 1 wt% noble metal-containing MIL-101 materials (0.93 - 0.96 wt% based on ICP analysis) also support the successful encapsulation. The images show fine nanoparticles in the range of 2 - 4 nm, in agreement with the cage diameters, although some larger nanoparticles still remain outside the pores.





#### Fig.II.2.41. – Evolution with time of the yield of the Knoevenagel condensation with various substituents R1 and R2.

Moreover, Pd-loaded APS-MIL-101 and ED-MIL-101 exhibit obviously high activities during the Heck reaction at 393 K which is the most powerful method to couple alkenes with organic moieties. The recyclability test of Pd-loaded MIL-101 confirms that the reaction takes place mainly in a heterogeneous manner. The current attempts to extend the present strategy will open up the development of versatile hybrid materials with new functions.

Our third experience is recent and concerned the use of MIL-103, a rigid rare-earth carboxylate with large pores as a Ziegler-Natta catalyst for the selective polymerization of isoprene with the formation of a MIL elastomer composite<sup>503</sup>.

### **2** 5.c. Properties close to those of dense phases, sometimes related to the domain of ENERGY.

For this domain, hydrogen storage for fuel cells has already been presented.

Before tackling the domain of porous solids, I was used, as a solid state scientist, to look at the physical properties of dense oxides and fluorides (conductivity, magnetism and optics). I was surprised to see that this concern was not shared enough by my new colleagues, more interested by the usual applications of these zeolitic compounds (catalysis, storage, fine chemicals...). It therefore became one of the axes of my integrated strategy to open some new windows for this new domain, first for the development of academic knowledge.

It began with the discovery of the first magnetic inorganic porous solids (ULM-3, ULM-12), already detailed in the first part of this manuscript. I extended this orientation to hybrids.

Indeed, my chemical strategy had allowed the evidence of the importance of temperature for the syntheses. In particular, its increase provoked the evolution from 0D to 3D systems for the inorganic part of the structures. As dimensionality is in close relation with the physical properties of the solid, attention had to be paid on the latter as a function of the various dimensionalities encountered during the creation of our solids. Among these properties, electric conductivity is probably the most important for energy applications : supraconductors for energy transport, semi-conductors for photovoltaïcs are good exemples of this importance. Was it possible for hybrids ?

# 5.c.1. Electronic and ionic conductivity in MILs.<sup>444,482,498,523,527,536,562.</sup>

Electronic conductivity requires at least two conditions : (i) 1D structures, necessary for establishing long range interactions for the electrons and (ii) the existence of mixed valences for the cations in the inorganic framework.

If the first condition is easy to fulfill with our solids, it is not the case for the second. Indeed, a first look at all the compositions described in the literature shows that, except for the couple Cu<sup>+</sup>/Cu<sup>2+</sup> for which a very small number of examples exist, there was no mention of mixed-valence solids in metal-organic frameworks, at variance to dense oxides where this characteristic is common. Despite numerous trials in various conditions, we never succeeded to overcome this limitation, and as-synthesized MOF compounds are insulators, precluding their applicability for electrochemical intercalation.

So, if the mixed valence is not 'natural', we had to create it by indirect methods. Temperature of activation can be a way, as seen with MIL-101 for the propane-propene separation (see above). Another possible way to bypass this limitation was to use MOFs based on earlier (3d) transition metals to take advantage of the lower occupation of 3d-electron orbitals (higher oxidation states) and therefore higher M-O bond stability with respect to charge variations, and to bring about some long-range electron delocalization through the stabilization of class II or III mixed-valence states associated with a double-exchange mechanism.

The MIL-53 family could potentially serve as a test for this purpose. It exists with many 3d-transiton metal trivalent cations ( $V^{III}$ ,  $Cr^{III}$ ,  $Fe^{III}$ ). With  $V^{III}$ , through the oxidative removal of a template, we formed MIL-47 [ $V^{IV}O(bdc)$ ], thus providing the first evidence of chemically induced redox reactions within this system. Jacobson *et al.* further synthesized [ $Fe^{III}(OH)(bdc)(py)_{0.85}$ ] and [ $Fe^{III}(bdc)(py)_{0.42}(dmf)_{0.25}$ ] (*py=pyridine, dmf=dimethylformamide*), which contain  $Fe^{III}$  instead of  $Fe^{III}$ , thus providing the first example of a M<sup>II</sup> analogue with the bridging species along the chains being neutral. This example provided the possibility of inducing mixed-valence states within the same structure type, inciting us to use electrochemical methods and insertion of lithium for this purpose. As it was the first case of such a method, a complete physical study was undertaken.

MIL-53(Fe)·H<sub>2</sub>O [Fe<sup>III</sup>(OH)<sub>0.8</sub>F<sub>0.2</sub>(btc)]·H<sub>2</sub>O] was chosen as the most suitable candidate for our investigation, the insertion of metallic Li provoking the reduction of the same amount of Fe into the divalent state (work done in collaboration with Pr. J.-M. Tarascon). Owing to the high reactivity of Li with moisture, electrochemical cells (Swagelok cells) were assembled in an argon-filled dry box, after evacuating water for 1h at 120°C in the antechamber of the box. Fig. II.2.42 shows a typical voltage-composition trace (cycled between 1.5 and 3.5 V) for an electrochemical cell (Swagelok cell) that has the water-free phase mixed with 15 wt % carbon (a conducting additive) as the positive electrode and Li as the negative electrode. During the first discharge, the potential rapidly reaches 2.9 V, drops smoothly with a small knee until x = 0.35, and then sharply falls down until x = 0.6 prior to the onset of another voltage pseudo-plateau near 1.5 V. Upon recharge, most of the 0.6 uptake lithium ions can be removed (e.g. 70 mA h g<sup>-1</sup> of MIL-53(Fe)).



**Fig.II.2.42.** – Left : Evolution of the nature of cations within the chains with the insertion of lithium (yellow :  $Fe^{3+}$ , green :  $Fe^{2+}$ , blue : lithium) ; Middle : evolution of the magnetic character with insertion ; Right : (C) Voltage profile for a Li/MIL-53(Fe) half cell cycled between 1.5 and 3.5 V at a C/40 rate (one equivalent of Li in 40 h) using 10 mg of active powder spread over a 1 cm<sup>2</sup> surface ; the insets display the capacity retention and the power rate (as determined on charge by using the signature protocol) ; <sup>57</sup>Fe Mössbauer spectra recorded at 77 K for a fully lithiated (x = 0.6) electrode recovered from a Li/MIL-53(Fe) cell that was partially discharged or charged, evidencing the mixed valence character of the solid.

Nevertheless, a striking feature is the instantaneous 1.3 V increase in the cell potential once the cell is switched from the intercalation to the deintercalation mode, indicative of a hysteretic Li reaction. The subsequent charge/discharge curves neatly superimpose, leading to a spectacular steady capacity retention, indicative of a

highly reversible process involving an uptake/ removal of  $\text{Li}^{\dagger}$  ions concomitant with the reversible reduction of  $\text{Fe}^{III}$  into  $\text{Fe}^{III}$ . Furthermore, such cells could sustain respectable rate capabilities since about 80 % of the total electrode initial capacity can be delivered in one hour. Finally, attempts at inserting more than 0.6 Li atoms per unit formula by lowering the cell discharge voltage down to 0.5V lead to an irreversible decomposition, as deduced from both X-ray and high-resolution transmission electron microscopy data.

Galvanostatic (GITT) and potentiostatic (PITT) intermittent titration techniques were performed to further approach the thermodynamic/kinetic characteristics of this interaction electrode. The measurements realized in a GITT mode using charge/discharge current steps of one hour at C/10 (i.e., one equivalent of Li in 10h) rate separated by relaxation times necessary to reach equilibrium potentials that change by less than 0.1 mV per hour, served to accurately determine the open-circuit voltage (OCV) values. The voltage knee near x = 0.35 is well-resolved with OCV values that progressively decay to 2.65 V at x = 0.35 and then remain constant up to x=0.6. Interestingly, the charge OCV profile nicely traces the discharge OCV up to x=0.35, but deviates rapidly in a continuous manner as x increases up to x = 0.6. In this composition range, the OCV remains flat, leading to deviations from the voltage curve as large as 1.2 V at x = 0.6. Such large voltage deviations, not infrequent for insertion materials, can result from kinetically limited reactions associated with crystallographic and/or electronic changes.

The kinetics of the two reversible (0 < x < 0.35 and 0.35 < x < 0.6) redox processes were thus studied by PITT. The chronoamperometric response clearly indicates two different domains. For low x values (0 < x < 0.35) the current curves follow a Cottrel-type law indicative of a solid-solution insertion process that is kinetically limited by Li<sup>+</sup> diffusion, while, for high x values, they show a more limited diffusion step that can be linked to a two-phase transition. This latter result is even more evident during the early recharge that displays a bell-shaped variation, reminiscent of a biphasic process that is kinetically limited by the two-phase interfacial migration. These results, together with the striking differences between the discharge and charge profiles, suggested redox processes with complex lithium-driven electrode structural and/or electronic modifications.

In situ X-Ray powder diffraction performed in real time during charge and discharge proved that the initial anhydrous solid which adopted the NP form of MIL-53 transforms into the LP form during insertion. The process is fully reversible during the cycle without any loss of crystallinity. An in situ EXAFs study completed the structural information<sup>498</sup>. Moreover, the Mössbauer spectra recorded at both 300 and 77 K for the fresh electrode and for Liinserted MIL- 53(Fe) samples recovered from partially discharged (x = 0.3 and x = 0.6) and fully recharged (x = 0) electrochemical cells exhibit a set of quadrupolar components with narrow Lorentzian lines. The hyperfine structure changes progressively from a pure high-spin (HS) state  $Fe^{III}$  paramagnetic quadrupolar doublet (IS<sub>77K</sub> = 0.50(2) mm.s<sup>-</sup> <sup>1</sup>) into a quadrupolar structure which consists of both HS Fe<sup>III</sup> and HS Fe<sup>III</sup> paramagnetic species (IS<sub>77K</sub> = 0.50(2) mm.s<sup>-1</sup> and 1.30(2) mm.s<sup>-1</sup>, respectively). Their proportions are very similar at 77 K and 300 K, suggesting that the f-factor values are rather temperature-independent. The percentage of the Fe<sup>II</sup> component of the Mössbauer signal increases from 0 to 0.45(2) % as the Li-inserted sample content is increased from x = 0 to 0.5, and returns to close to zero as the sample is fully recharged. This observation provides an unambiguous proof of the reversible appearance/disappearance of a mixed-valence state in this Fe-based MOF upon Li insertion/ deinsertion. It induces a change in the magnetic character of the resulting phase. Pure MIL-53(Fe) which was a pure antiferromagnet below 8K, as expected for a solid with a structure containing 1D chains, becomes ferrimagnetic at 6K for x = 0.6 due to a Fe<sup>III</sup>/Fe<sup>II</sup> structural ordering to some extent. The small size of Li<sup>+</sup> residing in the tunnels implies also an ionic conductivity simultaneously with a 1D electronic conductivity.

# This experiment provided a spectacular example of the capacity for a hybrid porous solid to be a multifunctional material, simultaneously being an adsorber, an electronic and ionic conductor and a magnet, even if their performances are not outstanding. At least, for academic knowledge, new windows were opened.

Finally, for being complete, first-principles electronic band structure calculations were investigated to seek for an explanation for the rapid decay of the potential that was observed near x = 0.6 during the Li insertion process. As expected from the structure, the Fe<sup>III</sup> metallic bands around the Fermi level not only exhibit a quasi-one-dimensional character along the chain direction, but are also doubly degenerate, thus indicating that the two Fe<sup>III</sup> chains of pure MIL-53(Fe) act as electronically independent systems. The local distortion and packing of the {Fe<sup>III</sup>(OH)O<sub>5</sub>} octahedra along the chains are consistent with very weak (oxygen-mediated) superexchange interactions, in agreement with the small bandwidth observed in the chain direction. Very close energies for both the antiferromagnetic and the ferrimagnetic structure are thus expected down to very low temperature, in perfect agreement with the paramagnetic behavior observed in preliminary magnetic measurements. Spin-polarized calculations confirm the high-spin state of Fe<sup>III</sup> in the nonlithiated compound, and the insulating Mott–Hubbard ground state expected for such one-dimensional half-filled systems. Upon Li insertion, the doping of the empty narrow band lying just above the Fermi level is unlikely to induce significant electron delocalization along the chain. A class I or class II mixed-valence state, consistent with the Mössbauer results, is therefore expected. While two electrons can be formally

added to the two electronically independent chains, that is, one Li atom per Fe atom, our inability to go beyond x = 0.6 is indicative of an electronically driven phase transition directly linked to the Fe<sup>III</sup>/Fe<sup>II</sup> charge ordering along the chains. This limitation is confirmed by full structural relaxations that were performed on the lithiated species Li<sub>0.5</sub>-MIL-53(Fe) and show a distorted to regular octahedral distortion for every other iron ion along each chain, fully consistent with the stabilization of a localized Fe<sup>III</sup>/Fe<sup>II</sup> mixed-valence state associated with two different crystallographic sites and with a gap opening in the electronic structure. Magnetic, electric, and structural temperature-dependent measurements are presently being conducted to test the above hypothesis. Besides providing the first hint of evidence for such transitions, they have already confirmed the appearance of Fe<sup>III</sup> high spin upon Li insertion.

Without regard to the physics underlying the maximum uptake of lithium prior to collapse of the structure, this study provides unambiguous evidence that it is possible to achieve mixed-valence states in Li-based MOF materials. Moreover, such materials reveal an aptitude to absorb electrolyte molecules within their channels, therefore offering great advantages in terms of ionic conductivity. The realization concept of hybrid materials, in which conducting organic polymers are interleaved between the layers of an inorganic oxide lattice, was introduced about ten years ago by L. Nazar as the ideal electrode for high kinetics (e.g. high-power-rate electrodes). Nevertheless, such a concept never truly materialized. Could such a situation be realized with the MOFs that combine a microporous framework host with pores evenly distributed at the nanometer scale that is capable of incorporating electrolyte solvent molecules? We realized that<sup>444</sup> with many other electrolytes ((EC, DMC, propylene carbonate (PC), diethyl carbonate (DEC), THF).

The door we had opened needed to go further. To push back these limits, we decided to increase the capacity through the adsorption of an electro-active molecule, i.e., 1,4-benzoquinone, which can theoretically accept two electrons per molecule but can also play a role as a redox mediator enhancing the electronic transfer in the MIL-53(Fe) structure.

Quinone was introduced<sup>482</sup> in the tunnels of MIL-53(Fe) by simply-hand milling of the solids during a few minutes in the course of a solid-solid reaction at 25°C under argon. We first characterized the new composite structure formed following sorption of quinone molecules in the pores of the pristine MIL-53(Fe). We then evaluated its electrochemical properties in a classical lithium cell. A mechanism for taking into account the electrochemical properties was put forward on the basis of the information obtained from in situ X-ray diffraction and <sup>7</sup>Li and <sup>13</sup>C NMR spectroscopy.



**Fig. II.2.42.** – Left : Structural evolution of the MIL-53(Fe)-1,4-benzoquinone with temperature. top : the anhydrous MIL-53(Fe) structure (NP); middle : structure at  $25^{\circ}$ C; down left : phase transition at  $120^{\circ}$ C affecting only the positions of quinone ; down right : the structure after the loss of 0.5 quinone at  $120^{\circ}$ C. Right : Voltage composition profiles are shown in (a) for Li/MIL-53(Fe), (b) Li/quinone, and (c) Li/MIL-53(Fe), quinone1 in Swagelok cells cycled in the range 1.8-3.5 V at a C/10 rate, respectively. Electrodes contained from 5 to 8 mg of active material per cm<sup>2</sup>.

At room temperature, MIL-53(Fe). quinone<sub>RT</sub> contains guest molecules lying inside the channels that are nearly

parallel to half of the four organic walls (Figure II.2.42a). Double chains of quinone molecules are aligned along the metal oxide chains. The quinone molecules are not hydrogen-bonded to the hydrophilic part of the octahedral chain but interact through  $\pi$ - $\pi$  interactions between both equivalent neighboring quinone molecules of two adjacent chains and quinone molecules and the benzyl units of the dicarboxylate linkers.

At 120°C, a phase transition appears, which only concerns the position of the guests. Within the same tunnel, the double chain is still nearly parallel to half of the four organic walls, whereas the double chain is tilted in order to be nearly parallel to the second half of the four organic walls in the nearest neighboring tunnels. This phenomenon can be described as a "flip flop effect". At 160°C, this structure losses one-half of its guests keeping their respective positions within adjacent tunnels. This new solid (MIL-53(Fe). Quinone<sub>0.5</sub>) which remains stable after cooling down at 25°C, now allows both (i)  $\pi$ - $\pi$  interactions between quinone molecules and the benzyl units of the dicarboxylate linkers and (ii) hydrogen bonds to the hydrophilic part of the octahedral chain. It is interesting to note that one oxygen in the quinone molecule is now hydrogen bonded to the OH group of the chains of corner-shared octahedra.

From the electrochemical point of view, MIL-53(Fe). quinone<sub>RT</sub> contain two redox centers : the couple Fe<sup>II</sup>/ Fe<sup>III</sup> and the quinone molecules, which are both active separately toward Li insertion, with different voltage profiles (Fig.II.2.42 right). Their combinaison within the same solid gives a surprising result. During the first discharge, the first 0.2 lithium moles (x = 0.2) are inserted through a constantly dropping voltage (indicative of a solid solution process) until the potential reaches a plateau, indicative of a two-phase process, at 2.72 V. This plateau, which extends for 0.4 Li moles and ends at x = 0.6, is followed by a smooth drop in potential until x = 1.05 and a faster decay until x = 1.2. The overall amount of lithium that can be intercalated into MIL-53(Fe). quinone<sub>RT</sub> equals 1.2, which represents a gravimetric capacity of 93 mA h g-1. The subsequent charge presents three main distinctive features with (i) a plateau, located near 2.72 V, similar to that observed in pure MIL-53(Fe) and accounting for almost 0.4 lithium ions, which is followed by (ii) a sloping voltage domain between x = 0.7 and x = 0.4, around 3 V, and finally (iii) ends in a high-voltage (near 3.3 V) deintercalation process. The most important difference between quinone-free and quinone-containing electrodes lies in the discharge plateau near 2.7 V seen solely in the latter. Thus, we directly ascribe this plateau to the reduction of the inserted quinone molecules.

An overall benefit of the quinone uptake is an increase in the electrode capacity from 65 to 93 mA h g<sup>-1</sup>. However, this value is not maintained for too long as the capacity of the MIL-53(Fe). quinone<sub>RT</sub> rapidly decays to reach that of a quinone-free MIL-53(Fe) electrode after only five cycles. Such an observation is suggestive of a progressive release upon cycling of the quinone molecules from the MIL-53(Fe) host. To test this hypothesis, we checked the effect of resting the battery prior to the cell discharge on its first discharge capacity. The lowest discharge capacity was observed for the battery left for the longest resting period (48 h), confirming our hypothesis. Thus, an electrolytedriven leaching of the quinone molecules present in our host MIL-53(Fe). quinone<sub>RT</sub> precursor phase appears to be occurring. When the cell is discharged, the quinone molecules present in the lattice are reduced to quinolate species, which are no longer soluble in the electrolyte. Maintaining the electrode in its discharge state should not therefore affect the electrode capacity. This prediction was experimentally confirmed by the full reversibility displayed by a cell that was discharged, left 24 h on rest, and relaxed 48 h prior to its full recharge. However, once the recharge is performed, the recovered quinone molecules are again prone to dissolution. Hence, after a few cycles, none of the quinone molecules in the MIL-53(Fe) precursor are left to be reduced, leading to the merging of the capacity retention curves after 6-8 cycles. NMR studies confirm all these results.

• The flexible MIL-53(Fe) was proved to be an interesting host for electrochemical reactions but it must be recalled that, depending on the conditions of synthesis, it has a rigid polymorph : MIL-68 with the same inorganic SBU but with triangular and hexagonal pores. The redox activity of the MIL-68(Fe) was thus investigated<sup>527</sup> using it as a positive electrode material in a classical two-electrode Swagelok-type cell using LiPF<sub>6</sub>-containing ethylene carbonate/dimethyl carbonate (EC/DMC) electrolyte in which metallic lithium foil was used as the negative and reference electrode. At a regime of *C/10* in galvanostatic mode, around 0.35 Li per Fe atom can be inserted into the MIL-68(Fe) structure, which is slightly lower than the corresponding value for MIL-53(Fe). This corresponds to 30 mA h g<sup>-1</sup>. Note that this capacity can be increased to 40 mA h g<sup>-1</sup> if the current density is decreased to *C/50*. It is difficult to explain these differences between MIL-53(Fe) and MIL68-(Fe). The main difference between these two structures is based on the presence of triangular-shaped pores. It is probable that no electrolyte can enter these pores unlike the hexagonal pores of MIL-68(Fe) or the uniform porous structure of MIL-53(Fe). This difference could limit the diffusion of lithium into the structure and may be the cause of the lower capacity observed with MIL-68(Fe). These lower performances made that the study was not continued.

• Finally, after our experience with benzoquinone, we tested another possibility for electro-active organic molecules, but this time serving as linker in the hybrid framework. A good example was the tetrathiafulvalene tetracarboxylate

which inserts divalent metals in the skeleton (M = Ni, Co). TetraThiaFulvalene (TTF), a sulfur rich conjugated core, is known to present two reversible and easily accessible oxidation states, and when crystallized in a mixed-valence state, able to give rise to conductive or superconductive organic molecular solids. We therefore characterized several TTF-based new hybrids using either alkaline (K, Rb, Cs) or 3d transition metals (M = Ni, Co). The first<sup>523</sup> are 3D and act as rather efficient positive electrodes for lithium ion batteries. The latter (MIL-136) exhibit a 2D network.



**Fig.II.2.43.** - Solid-state cyclic voltammetry between the voltage range of 2 and 4 V versus  $Li/Li^{\dagger}$  at 0.1 mV s<sup>-1</sup> sweep rate for (a) *MIL*-136(*Ni*) and (b) *MIL*-136(*Co*).

The magnetic and redox properties of these complexes were also investigated<sup>536</sup>. Temperature and field dependent magnetic measurements first indicate that the divalent cations are pseudo-isolated, as almost no intra or intermolecular magnetic coupling was detected. Solid state electrochemistry shows that, contrary to the solids based on the same linker but alkaline ions, the  $\{[M(H_2O)_4]_2(TTF-TC)\}_3 4 H_2O$  (M = Ni, Co) MIL-136 complexes are not suitable candidates for use as positive electrodes for Li batteries, but exhibit an unexpected, fully reversible two electron oxidation process for the TTF core (Fig.II.2,43). These observations are tentatively related to the strength of the metal-carboxylate bond.

• All the above results used microporous solids as hosts. A question arose : what about the behaviour of *mesoporous* solids ? In our research team, the representative example is MIL-100(Cr), used several times above. We dedicated it to the study of cathode composite for Li-S batteries<sup>562</sup>.

Li-S rechargeable batteries are attractive for electric transportation because of their low cost, environmentally friendliness, and superior energy density. However, the Li-S system has yet to conquer the market place, owing to its drawbacks, namely, soluble polysulfide formation. To tackle this issue, we present here a strategy based on the use of a mesoporous chromium trimesate metal-organic framework (MOF) named MIL-100(Cr) as host material for sulfur impregnation. Electrodes containing sulfur impregnated within the pores of the MOF were found to show a marked increase in the capacity retention of Li-S cathodes. Complementary transmission electron microscopy and XPS (X-ray photoelectron spectroscopy) measurements demonstrated the reversible capture and release of the polysulfides by the pores of MIL-100 during cycling and evidenced a weak binding between the polysulphides and the oxygenated framework. Such an approach was generalized to other mesoporous oxide structures, such as mesoporous silica, for instance SBA-15, having the same positive effect as MIL-100 on the capacity retention of Li-S cells. Besides pore sizes, the surface activity of the mesoporous additives, as observed for the MIL-100, appears to also have a pronounced effect on enhancing the cycle performance by confinement effects. Increased knowledge about the interface between polysulfide species and oxide surfaces is on the way and could lead to novel approaches in the design and fabrication of cyclic long-life S electrodes.

These pioneering electrochemical studies illustrate one of the most unexpected properties of MOFs concerning the domain of energy with the use of the MILs – after improvement - as possible positive electrodes in fuel cells and Liion batteries. Some applications are arising and studies on this point are currently in progress.

### 5.c.2. Magnetism in MILs

This property has less to see with energy. This aspect, even disappointing in view of applications, was rather neglected by the MOFs community. As we did for inorganic porous solids, we however looked at this property on our MILs for increasing the global academic knowledge of this family of solids.

We never expected outstanding properties from these studies for two reasons : (i) the majority of our phases contain inorganic clusters. Even if they are linked by the conjugated bonds of the linkers, the long-range interactions between these clusters are very weak and lead to low magnetic ordering temperatures, in the vicinity of 10K; (ii) when the framework of solids exhibit higher dimensionalities for the inorganic part of the structure (*a priori* more favourable for the onset of magnetic properties), they unfortunately exhibit a network of edge-sharing octahedra; this corresponds to 90° M-O-M superexchange interactions which are known since the Kanamori-Goodenough rules to be weak.

Despite these two disadvantages, many MILs were characterized <sup>216,237,243,263,275,276,287,308,318,322,335,343,344,349,358, 362,363,380</sup>. Based on V, Cr, Fe, Ni Co, Cu cations, most of them are classical antiferromagnets in the range 4-20K and do not need here any special development. One could except however for some of them a non-antiferromagnetic character. We just mention them. It is the case of a pure Co ferromagnet<sup>216</sup>, the antiferromagnet MIL-62(Fe) corresponding to the AF coupling of ferromagnetic chains<sup>335</sup>, and the two Ni carboxylates ferrimagnets

### 5.c.3. Luminescence in MILs and the 'antenna effect'.

This property is usually created using rare-earth-based compounds and a lot of Ln-based MILs were synthesized and structurally characterized in the group<sup>215,248,371,376,378,394,407,416,423,437</sup>. We reserved our luminescence studies to solids in which the coordination polyhedron of the rare-earth does not contain water molecules which are well known for quenching the luminescence. Attention was paid to the various Ln-2% doped yttrium trimesate MIL-78..



**Fig.II.2.44.** Top row : crystal structure of MIL-78, a  $Eu^{3+}$ -2% doped yttrium trimesate and the strong enhanced induced coloration under UV irradiation. Second row : schematic explanation of the orbital origin of the so-called antenna effect with the total emission spectrum of MIL-78 and the detail of the transition at 6129Å.

Under UV irradiation (excitation at 252 nm), MIL-78, doped with different rare-earth cations, shows a drastic enhancement of its luminescence. Five transitions are observed on the luminescence spectrum of Eu<sup>3+</sup> in  $(Y,Eu)((C_6H_3)-CO_2)_3)$  and  $Eu((C_6H_3)-CO_2)_3)$ . These transitions can be well interpreted on the basis of electronic transitions from the  ${}^5D_0(Eu^{3+})$  emitting state to the  ${}^7F_1$  (J=0 to 4) multiplets. Two lines recorded at 579.1 and 579.7 nm corresponding to the  ${}^5D_0 \rightarrow {}^7F_0$  transition spectral range, reveals that two optical sites are occupied by Eu<sup>3+</sup> in that structure. However, the intensity of the spectrum which  ${}^5D_0 \rightarrow {}^7F_0$  is observed at 579.1 nm is very weak. From laser site selective excitation, this minor site can be ascribed to Eu<sup>3+</sup> ions in a parasitic phase in very low concentration or in the lattice nearby an impurity or a distortion due to local strain which will play the role of trap for the energy migration.

The excitation spectrum monitoring the hypersensitive  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition exhibits a very intense band located in the UV range (200-340 nm), the transitions from the Eu<sup>3+</sup> ground state  ${}^{7}F_{0}$  to the  ${}^{5}L_{6}$  and  ${}^{5}D_{2}$  states being very weak. To determine the energy of the lowest ligand triplet state, the emission spectra and decay time measurements for the Gd<sup>3+</sup> doped material were performed. Since, the  ${}^{6}P_{7/2}$  emitting level of Gd<sup>3+</sup> is located at high energy, it allows the identification of the lowest triplet state when situated at lower energy. The UV excitation of  $Y((C_{6}H_{3})-CO_{2})_{3})$ :Gd<sup>3+</sup> (2%) gives rise to two structured emission bands located at 480 and 576 nm respectively at room temperature. These emissions which cannot be ascribed to electronic transitions within the 4f<sup>7</sup> (Gd<sup>3+</sup>) configuration are ascribed to emission from the ligand triplet states  ${}^{3}T_{1}$  to the ground state  ${}^{1}S_{0}$ . The absence of Gd<sup>3+</sup> emission means that the triplet states lie at lower energy than the lowest excited state of Gd<sup>3+</sup> ions precluding any energy transfer from the triplet states of the ligand to Gd<sup>3+</sup> ions. These two emission bands are excited in the UV range from 320 to 260 nm. The  $Y((C_{6}H_{3})-CO_{2})_{3}$ ): Gd<sup>3+</sup> optical properties allows a complete determination of the ligand energy level scheme. The triplet state excitation spectrum is quite similar to that of the  ${}^{5}D_{0}$  (Eu<sup>3+</sup>) level in the UV range. The triplet state emission is completely quenched in the 0.2 at% Eu doped compound, the ratio of the UV band intensity to the  ${}^{7}F_{0} \rightarrow {}^{5}L_{6}$  and  ${}^{5}D_{2}$  excitation lines is 100 and 200 respectively. This result allows deducing for an efficient energy transfer from the ligand triplet state to the Eu<sup>3+</sup> states when excited in UV.

Selective excitation into the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  lines at 579.1 and 579.7 nm was performed at low temperature (T=10K) and a complex emission spectrum which contains the contribution of both  $Eu^{3+}$  types is recorded. No simplification of the spectrum can be observed. This result compared to the  ${}^{5}D_{0}$  decay profile recorded in the full concentrated sample as a function of the temperature suggests that energy migration is occuring.

The  ${}^{5}D_{0}$  fluorescence transient recorded as a function of temperature in the diluted sample exhibits an exponential function with time whatever the temperature. The decay time, varying from 3.51 ms to 3.24 ms from 10K to room temperature, reflects a very low non radiative contribution by multiphonon relaxation. On the opposite, above 50K, the  ${}^{5}D_{0}$  fluorescence transient in the full concentrated sample exhibits a non exponential behaviour with time, the discrepancy to an exponential law increases with temperature. This temperature dependence can be explained by assuming a temperature dependence of the migration probability.



**Fig.II.2.45.** <sup>5</sup>*D*<sub>0</sub> fluorescent transient as a function of temperature

The non exponential behaviour of the intensity with time ascribed a migration process within Eu<sup>3+</sup> ions. Taking into account for the structural data, especially the distances between RE ions in adjacent sites within a chain (0.392 nm) and those between adjacent chains (0.544 and 0.926 nm), three dimensional interactions seem unlikely. The decay profiles as a function of time and temperature were fit using the model of Balagurov

and Vaks (BV) assuming a 1D migration with randomly distributed traps. This model assumes that impurities are randomly distributed along the chain. The asymptotic form of the decay is expressed as:

$$I(t) = I_0 \frac{16}{\pi} \left(\frac{k_1 t}{3\pi}\right)^{1/2} \exp\left[-W_r t - 3\left(\frac{k_1 t}{4}\right)^{1/3}\right]$$
(1)

where  $W_r$  is the radiative rate for the isolated centre,  $k_1$  stands for the trapping rate parameter. In Eq. (1) the term in the exponential that reflects one-dimensional trapping depends on t<sup>1/3</sup>. Using Eq. (1) and  $W_r(T)$  values deduced from the diluted sample, the  $k_1$  constant was determined and its temperature dependence has been derived. Several mechanisms were considered to explain the temperature behaviour of the diffusion constant. Fitting  $k_1$ =f(T) curve allows to exclude Raman and one-phonon processes as well the lowest Stark component of the <sup>7</sup>F<sub>1</sub> state (278 cm<sup>-1</sup>). Further experiments are underway to understand the role of the electronic structure of the ligand in the UV excitation process and of the exchange interaction between Eu<sup>3+</sup> which should operate. Excitation spectra demonstrate an efficient energy ligand – rare earth energy transfer process, usually called as an **'antenna effect'** by physicists. This is a rare phenomenon, and it occurs for the first time in hybrid porous solids. This, joined with the thermal stability of MIL-78, allows to imagine rapid applications of this solid as sensor of events in the ultra-violet region.

# **5.d.** Properties related to the domain of HEALTH <sup>427,428,463,508,526,528,544,556</sup>.

This probably represents the most promising development for our MILs. We were at the origin of its discovery in the international community of MOFs. It concerns the storage and the delivery of drugs.

Great effort is currently being devoted to the development of methods to control drug release to satisfy the evergrowing demand for prolonged and better control of drug administration using various **nano-carriers**. Before our discovery, two routes had been set up: the "organic route", which uses either biocompatible dendritic macromolecules or polymers and the "inorganic route", in which the hosts are inorganic porous solids, such as zeolites or mesoporous silicate materials. In the first case, a wide range of drugs can be encapsulated but a controlled release is difficult to achieve in the absence of a well-defined porosity. In the second case, this release is performed by grafting organic molecules on the pore walls but implies a decrease in the drug-loading capacity. Currently, the best nano-carriers used in the hospitals are phospholipidic liposomes. Despite their relative fragility in the body and their small pores sizes which allow to carry only 5 wt% of drug, they are currently the selected materials for storage and delivery of drugs.

We thought that the combination of high and regular porosity with the presence of organic groups within the framework might cumulate the advantages to achieve both a high drug loading and a controlled release. Our hybrid inorganic–organic solids with large pores exhibit such characteristics and could represent a valuable alternative in such purposes. **We introduced a third way: the "hybrid route"** that we tested first on our mesoporous solids MIL-100 and MIL-101. Due to its importance in the future, this discovery deserves a rather long explanation.

### 5.d.1. Validation of the method

We first studied the adsorption and delivery by MIL-100 and MIL-101 of Ibuprofen, a model analgesic and antiinflammatory drug <sup>427</sup>. Although the toxicity of chromium compounds is well known, they served as initial hosts for their remarkable stability and for their excellent crystallinity which allows a better structural control of the insertion, thus illustrating their use as delivery systems. Once validated, the method used after the iron(III) homologues, with close stability and whose non-toxicity is well established.

Ibuprofen was adsorbed by the dehydrated powdered materials from a solution in hexane, and the adsorbed amount was determined by thermogravimetric analysis, UV/Vis spectroscopy, elemental analysis, and X-ray fluorescence ; the presence of Ibuprofen was also confirmed by IR spectroscopy. The influence of material dehydration, of Ibuprofen/material ratio, immersion time, and the number of consecutive impregnations on the amount of adsorbed drug was studied.

X-Ray powder diffraction performed on both treated materials proved an invariance of their structures. Moreover,  $N_2$  adsorption after the incorporation indicated almost no residual porosity. This means that either the drug completely fills the pores or/and blocks the windows of the cages, thus leaving approximately no accessible pore volume for nitrogen. <sup>1</sup>H NMR experiments show that ibuprofene is diprotonated in the cages, and <sup>13</sup>C NMR indicates some conformational distribution, at variance with the well-defined crystalline order observed in its pure ibuprofene crystal. As Ibuprofen is being inserted as an anion, several situations may occur to justify the observed changes: (i) the proton may be fixed on the terminal water molecules of the chromium trimeric units and ensure the interaction with anionic Ibuprofen; (ii) the latter could to some extent form a complex with the chromium center, thus replacing the bound terminal water molecules as a result of the Lewis acidic character of these sites or (iii) be strongly located close to a proton in the framework.

The MIL-100 and MIL-101 materials showed remarkable Ibuprofen adsorption, variable with their distribution of pore sizes. On one hand, MIL-101, with its larger cage sizes [( $\phi$ : 29 and 34 Å), windows apertures ( $\phi$ : 12 and 16 Å), and pore volumes (12,700 and 20,600Å<sup>3</sup>)], shows an unprecedented amount of adsorbed drug, larger than the initial matrix weight ( $\approx$ 1.4 grams of Ibuprofen/gram of dehydrated MIL-101). These findings are very important as only very small amounts of nanocarrier are required for the optimal administration of high dosages. On the other hand, for MIL-100, the dimensions of the two types of spherical cages are smaller [( $\phi$ : 25 and 29 Å), windows apertures ( $\phi$ :

4.8 and 5.8 Å), and pore volumes (8,200 and 12,700Å<sup>3</sup>). This limits the adsorption to 0.35 g of Ibuprofen/gram of dehydrated MIL-100.

The drastic difference in adsorption between MIL-100 and MIL-101 can be explained by a selective occupation of only the larger cages in MIL-100, whereas all the cages are occupied in MIL-101. According to the weight increase, one can estimate that each "small" cage of MIL-101 hosts approximately 48 Ibuprofen molecules and the large cage approximately 96 molecules. This behavior illustrates three facts: (i) the ever-growing need for very large pores, that I previously claimed;<sup>222</sup> (ii) the hierarchy of mesopores when tunable can act as an internal molecular sieve for a given guest of important dimensions with a selective occupation of the cages (the empty cages remain able to host a different species); and (iii) such matrices may provide tools for the study of nanoassemblies of organic compounds and help the development of nano-organic chemistry.



**Fig.II.2.46.** View of the larger cage of MIL-101 and the molecules of ibuprofen (IBU) in it. Top right: percentage of IBU delivery with time by MIL-100 and MIL-101. Down right: Amount of IBU (in  $g.g^{-1}$ ) delivered by MIL-100 and MIL-101; in green, and for sake of comparison, the capacity of delivery by the amorphous mesoporous MCM-41<sup>428</sup>.

It took 6 days to the complete drug release with MIL-101. The kinetics of Ibuprofen delivery to simulated body fluid (SBF) was displayed at 37°C and with continuous stirring. The delivered Ibuprofen concentration was determined by HPLC. In the Ibuprofen delivery from MIL-100 and MIL-101, three stages related to the drug location within the cages can be distinguished. For each type of cage, two situations occur for the guests: when they are close to the walls, the host–guest interaction is governed both by anion–cation electrostatic interactions and  $\pi$ - $\pi$  interactions between the aromatic rings of Ibuprofen and the organic part of the skeleton, and are therefore dependent on the size of the cage. Once these interactions are fulfilled, the additional Ibuprofen molecules occupy the leaving space of the cavity, with just Ibuprofen–Ibuprofen concerns only the weakly bonded molecules. The kinetics of Ibuprofen delivery for MIL-100 in the first 2 hours are empirically adjusted with regression factors of > 0.99 to zero-order kinetics, drug-concentration independent, and characteristic of pharmaceutical forms that do not disaggregate. The complete release of Ibuprofen is achieved only after 3 days of assays in vitro, thus illustrating the difference in strength of the two types of interactions.

Ibuprofen delivery for MIL-101 in the first stage (8 h) is mainly governed by a diffusion process, which can be predicted by the Higuchi model ([IBU] = K t  $^{1/2}$ ). Considering that the external diffusion process is avoided by constant agitation during the assays, the diffusion process is only due to the drug movements through the windows of the cages; thus, the delivery rate is limited by the dissolution and diffusion process.

This spectacular result incited us to look at the behaviour of flexible MILs as nano-carriers <sup>463</sup>. MIL-53(Cr) and MIL-

53(Fe) were chosen. If, due to the smaller size of the tunnels, the adsorbed amount of ibuprofen is lower, the most strking feature concerned the time of delivery of the drug. If it took 6 days with the rigid MIL-101, it reaches almost three weeks for both MIL-53 for the complete delivry in the SBF fluid.



**Fig.II.2.47.** - Left: percentage of IBU delivery with time by MIL-53(Fe) and MIL-53(Cr). On the right, the performances of MIL-53 are compared to those of MIL-101, already depicted in Fig.II.2.46.

The filled solid was characterized by X-Ray diffraction, IR and NMR and modelized using DFT calculations. Several features are of interest : (i) Once filled, MIL-53 exists in its LP form. NMR shows that Ibuprofen is adsorbed in MIL-53 solids after 3 days this time as a neutral molecule which has a small mobility within the pores; (ii) once Ibuprofen is inserted, its COOH groups and the OH groups of the framework strongly interact, as characterized simultaneously by the high temperature (260°C) at which Ibuprofen leaves the pores and by FTIR and DFT observations; (iii) the nature of the metal can have some influence on the first steps of the delivery; and finally (iv) unusually long times for delivery are observed with a quasi zero-order kinetics. Compared to zeolites with similar sizes of micropores (Ø 7.4 Å), which afford similar capacities (15-20 wt %), their corresponding release times (7 days) are much shorter than those in MIL-53. The same observation is made with mesoporous solids, pure or functionalized (2-7 days). This clearly shows an influence of the flexibility of MIL-53 on the time of release, without neglecting the presence of OH groups in the structure which create strong interactions with the COO functions of Ibuprofen as modelized by DFT calculations (Fig.II.2.48).



**Fig.II.2.48.** – Optimized arrangement of the Ibuprofen molecule in the MIL\_53(Fe) material obtained from our DFT calculations. The distances are reported in Å (iron in blue, oxygen in red, carbon in gray, hydrogen in white).

From all these results, one could expect very long therapies using MOF solids for drug delivery. Also, the administration could be provided. This would lead to a stable blood concentration, a minimization of the toxicity effects, as well as a decrease in patient discomfort. Moreover, the slow release will protect the drug from degradation processes by increasing its plasmatic half-life and bioavailability, and therefore its efficiency. This had to be verified on molecules important for health, especially on antitumoral and anti-retroviral drugs.

### 5.d.1. Application to the storage and delivery of antitumoral and anti-retroviral drugs.

Our strategy concerned (i) the choice of various non-toxic hosts (ii) a selection of important drugs against AIDS and various types of cancer, (iii) evaluation of the toxicity of nano-carriers and (iv) the evaluation of their performances doing *in vivo* and *in vitro tests* on mouse macrophages and (v) the study of the potential of these nanoMOFs as contrast agents.

### O choice of the materials ;

We have synthesized, in biologically and environmentally favourable aqueous or ethanolic medium, some non-toxic iron(III) carboxylate MOFs (flexible MIL-53, MIL-88A, MIL-88B, MIL-89, and rigid MIL-100 and MIL-101-NH<sub>2</sub>) and have adapted the synthesis conditions to obtain these materials as nanoparticles which were characterized in terms of biocompatibility, degradability and imaging properties (Fig.II.2.49). These materials were also chosen for the various hydrophilic/hydrophobic character of the linker of the framework : hydrophilic aliphatic with fumarate (MIL-88A), hydrophilic aromatic linker for trimesate (MIL-100), or hydrophobic aromatic linker, tetramethylterephthalate (MIL-88 Bt). For biological applications, the nanoMOF surfaces were engineered by coating with several relevant polymers (pegylation). This treatment prevented aggregation of the nanoparticles but did not improve the results.



**Fig.II.2.49.** – Scheme of the engineered MILs for the delivery and imaging of the chosen drugs. Down row : images of the nanoparticles of various MILs used for the study.

### O selection of drugs

The efficiency of these materials as drug carriers was tested with four challenging anticancer or antiviral drugs (busulfan (Bu), azidothymidine triphosphate (AZT-TP), cidofovir (CDV) and doxorubicin (doxo)), which, except the latter, could not be successfully entrapped using existing nanocarriers. Some cosmetic molecules, such as caffeine (liporeductor), urea (hydrating agent), benzophenone 3 and benzophenone 4 (UVA and UVB filters) were also tested.
## O cytotoxicity and biodegradability of the pure nanocarriers

Their *in vitro* degradation under physiological conditions shows that, in the case of MIL-88A (fumarate) and MIL-100 (trimesate), a major degradation occurred after seven days of incubation at 37° C. The nanoparticles lose their crystallinity and release large quantities of their ligands (72 and 58wt% of the fumaric and trimesic acids, respectively), indicating a reasonable *in vitro* degradability of the MOF nanoparticles. Interestingly, in the case of MIL-88A, the degradation products (iron and fumaric acid) are endogenous, and show low toxicity values (LD<sub>50</sub> (Fe) = 30 g.kg<sup>-1</sup>, LD<sub>50</sub> (fumaric acid) = 10.7 g.kg<sup>-1</sup>; LD<sub>50</sub> (trimesic acid) = 8.4 g.kg<sup>-1</sup> and LD<sub>50</sub> (terephthalic acid) > 6.4 g.kg<sup>-1</sup>.

The nanoMOF cytotoxicity, studied *in vitro* (MTT assay) on mouse macrophages, was low (57  $\pm$  11 µg.ml<sup>-1</sup> for MIL-88A) and comparable with that of the currently available nanoparticulate systems. Acute *in vivo* toxicity experiments were then carried out after intravenous administration of nanoMOFs in Wistar female rats.

Three different loaded porous iron(III) carboxylate nanoparticles were used for their various hydrophilic/ hydrophobic character already mentioned : MIL-88A, MIL-100 and , MIL-88Bt. Doses up to the highest possible injectable amounts were administrated (220 mg.kg<sup>-1</sup> for MIL-88A and MIL-100, and 110 mg.kg<sup>-1</sup> for MIL-88Bt). Different indicators (the animal behaviour, body and organ weights and serum parameters) were evaluated up to three months after injection. Their comparison with control groups did not show significant differences between them, except a slight increase in the spleen and liver weights, attributed to the fast sequestration by the reticuloendothelial organs of the nanoMOFs not protected by a PEG (polyethylene glycol) coating. As all the body organ weights were back to normality one to three months after injection, the phenomenon was fully reversible. The absence of immune or inflammatory reactions after nanoparticle administration supports their lack of toxicity. Moreover, the absence of activation of cytochrome P-450 suggests a direct excretion of the polyacids, in agreement with their high polarity. Finally, *in vivo* subacute toxicity assays were carried out by injecting up to 150mg of MIL-88A.kg<sup>-1</sup>.day<sup>-1</sup> during four consecutive days. No significant toxic effects were observed up to ten days after administration.





## O The efficiency of iron(III)-based nanocarriers.

The non-toxicity of the iron nanoMOFs, proved above, led us to investigate their ability to entrap anticancer and antiviral drugs. Chemotherapy indeed plays a key role in the treatment of cancer in children. Thanks to its efficiency, three out of four children can now be cured. Nevertheless, 25% of paediatric cancer patients go uncured, and chemotherapy-induced long-term side effects justify the continued development of new strategies to fight childhood cancer. Research in paediatric oncology is now encouraged and supported by European legislation.

In this context, the amphiphilic antitumoral drug busulfan (Bu) is widely used in combination with highdose chemotherapy regimes for leukaemias, especially in paediatrics, because it represents a good alternative to totalbody irradiation. However, Bu possesses a poor stability in aqueous solution and an important hepatic toxicity due to its microcrystallization in the hepatic microvenous system (hepatic veno-occlusive diseases). Moreover, the current encapsulation of Bu in known drug nanocarriers, such as liposomes or polymeric nanoparticles, is not satisfactory because loading never exceeds 5–6 wt% rendering our search of efficient nanocarriers an attractive challenge.

Bu was loaded in the preformed nanoMOFs by soaking in saturated drug solutions. The maximum amounts of drug adsorbed in several porous iron carboxylates were outstanding. The Bu loading in the rigid mesoporous MIL-100 may be considered as exceptionally high (25 wt%), which means five times higher than the best system of polymer nanoparticles (5-6wt%) and 60 times higher than with liposomes (0.4wt%). Owing to their lower pore volumes, Bu entrapment in microporous flexible structures (MIL- 88A, MIL-53, MIL-89) is lower than for MIL-100, but significantly larger than for the existing materials. Consequently, the use of porous iron carboxylates as nanocarriers could represent important progress for Bu therapy, especially because smaller amounts of solids would be required to deliver the needed dose of this drug. Indeed, considering the actual intravenous dosage of Bu (Busilvex, Bu solution in N,N'-dimethylacetamide), the total amount of MIL-88A or MIL-100 to be administered would be only around 100 and 20 mg.kg<sup>-1</sup>.day<sup>-1</sup> respectively, for four days. Moreover, Bu-loaded nanoMOFs could avoid the use of toxic organic solvents (N, N' -dimethylacetamide) during administration and reduce the liver toxicity mentioned above owing to the entrapment of Bu in its molecular form within the pores. We have verified on cell culture experiments that the nanoMOFs were able to release Bu in its active form. Studies on human leukaemia and human multiple myeloma cells in culture have shown that Bu has the same activity whether it is in its free form or entrapped in the nanoMOFs. In the same way, we have confirmed the total absence of cytotoxicity of the empty MIL-100 nanoparticles in the same cell lines.

In addition to alkylating agents such as Bu, nucleoside analogues are also of major importance in the treatment of cancer and viral infections. They include the monophosphorylated form of the antiviral phosphonate cidofovir, and the triphosphorylated form of azidothymidine, which are the active forms of these anti-cytomegalovirus and anti-HIV compounds, and doxorubicin, one of the most effective agents in the treatment of breast cancer. However, the clinical use of nucleoside analogues is limited by their poor stability in biological media, often resulting in short half-lives and low bioavailabilities, as well as sometimes partial resistance to the drug. The important hydrophilic character of nucleoside analogues also strongly limits their intracellular penetration owing to their low membrane permeability. Some nanocarriers were previously developed to circumvent these inconveniences, but show poor efficiencies together with 'burst effects'.

The performance of iron carboxylates therefore indicated major promise for the entrapment of all the above important drugs In the case of AZT-TP and CDV, this was achieved by simply soaking the preformed dried nanoMOFs in aqueous solutions of the drugs. Even if the concentration of the drug in the solution was low, the active molecules could be loaded with high efficiency (in most cases, higher than 80%); the nanoMOFs act as remarkable molecular 'sponges'. For instance, MIL-100 nanoparticles load up to 25, 21, 16 and 29 wt% of Bu, AZT-TP, CDV and doxo, respectively. An unprecedented capacity of 42 wt% can be achieved for AZT-TP and CDV with MIL-101.NH<sub>2</sub> nanoparticles, compared with 1 wt% values reported in the literature for these drugs in usual nanocarriers.

A progressive release of the three active molecules (AZT-TP, CDV and doxo) is observed using MIL-100 nanoparticles with no 'burst effect' (immediate delivery). The comparison between kinetics of drug delivery and the degradation profiles suggests that the delivery process is governed mainly by diffusion from the pores and/or drug–matrix interactions and not by the MOF degradation. Indeed, the total delivery of AZT-TP occurred within 3 days, when only approximately 10% of MIL-100 was degraded. Moreover, tests carried out in nanoparticles with smaller pore size than the drug dimensions have shown very low drug capacities and 'burst' release kinetics. This suggests that, in this last case, the drug was adsorbed only onto the external surface and not within the pores.

The promising data obtained with AZT-TP in MIL-100 nanoparticles incited us to evaluate the anti-HIV activity of AZT-TP *in vitro* in human peripheral blood mononuclear cells infected by HIV-1-LAI. A significant anti-HIV activity was observed only for (AZT-TP)-charged nanoparticles (about 90% inhibition of HIV replication) for a concentration of 200 nM in AZT or AZT-TP. In parallel, the empty nanoparticles demonstrated no cytotoxic effects, even at the highest tested dose (10µg.ml<sup>-1</sup> of nanoparticles).

From the above results, it is clear that porous iron(III) carboxylates currently represent the best nanocarriers for the release of important drugs. Their unprecedented encapsulation capacities apply to a large number of challenging drugs, not only hydrophilic (AZT-TP, CDV, urea and benzophenone 4) but also hydrophobic (doxorubicin, ibuprofen and benzophenone 3) and amphiphilic (busulfan and caffeine) molecules. The adaptive internal microenvironment (for example, amphiphilic polar metal and non-polar linker) of the pores of this family of solids could probably explain the exceptional qualities of these porous materials whose time of delivery lies in the range 3-11 days depending on the nature of the drug.

As iron (III) is known for being active in Magnetic Resonance Imaging (MRI), we have finally investigated the potential of the nanoMOFs as contrast agents. We first proved by Mössbauer spectroscopy that the MOFs themselves (and not eventual iron oxide and/or hydroxide degradation products) act as contrast agents. MRI measurements have been made on Wistar female rats 30 min after injection of 220, 44 and 22 mg.kg<sup>-1</sup> suspensions of MIL-88A nanoparticles (Fig.II.2.51). Both gradient echo and spin echo sequences show that the treated organs are darker than the normal ones. The resulting aspects of the liver and the spleen are indeed different between control and treated rats. Also, three months after injection, the liver and spleen returned to a similar appearance to that of the untreated animals. This is in accordance with the temporary accumulation of the nanoparticles in these organs, as discussed previously.



**Fig.II.2.51.** - *Magnetic resonance images.* The images were acquired with gradient echo (a, c, d, f) or spin echo (b, e) sequence of control rats (left; a-c) and rats injected with 220 mg.kg<sup>-1</sup> MIL-88A (right; d-f), in liver (a, b, d, e) and spleen (c, f) regions. 30 min after injection, product effect is observable on the liver and spleen. (dm, dorsal muscle; k. kidney; li, liver; s, spleen; st, stomach).

The favourable *in vivo* detection of the iron carboxylate MOF nanoparticles makes them interesting candidates for contrast agents, and, to the best of our knowledge, this represents the first example for iron-based MOFs, whereas Gd or Mn as potential contrast agents have been recently reported. The efficiency of our iron- based nanoMOFs is directly related to their relaxivity, in other words their capacity to modify the relaxation times of the water protons in the surrounding medium when a magnetic field is applied. The higher the quantity and the mobility of the metal coordinated water in the first and second coordination spheres, the higher the relaxivity. In this sense, our MOF nanoparticles possess not only paramagnetic iron atoms in their matrix, but also an interconnected porous network filled with metal coordinated and/or free water molecules.

In conclusion, our porous iron carboxylate nanoMOFs have many advantages when used as non-toxic and biocompatible drug nanocarriers. In terms of synthesis, they are obtained in aqueous or ethanolic solutions, instead of using organic solvents, and provide an example of what 'green' technology can afford for biomedical applications. In the biomedical sense, they act as molecular sponges, encapsulating drugs with different polarities, sizes and functional groups by immersion in corresponding solutions. This simple entrapment method has been applied to previously challenging antitumoral and antiviral drugs, as well as cosmetic agents. Progressive release was obtained under simulated physiological conditions. Moreover, anti-HIV activity of AZT-TP loaded nanoMOFs has been proven.

These results open new perspectives for improved treatment with anticancer and antiviral drugs and for the development of adapted formulations in paediatrics (using Bu nanoMOFs). Finally, the iron-based cores are endowed with good relaxivities, which makes these nanoparticles good candidates for magnetic resonance imaging (contrast) agents. These complementary properties might open new opportunities to use nanoMOFs for the eventual goal as theranostic agents. Indeed, theragnostics is a new branch of molecular medecine which combines in the same solid the therapy with the drug and the diagnostic with the nanocarrier active in magnetic resonance imaging. According to the doctors interested by our pioneer work in this domain, the porous iron(III) carboxylates seem to be the very first example of efficient nano-carriers in this new field of medecine.

## 6. From interesting to useful porous hybrid solids: scaling-up and shaping.

All the above results were performed at the laboratory scale and were proved to be of interest for a further development, which could participate to the benefit of mankind by using the above properties to transform them into real and/or dedicated applications. This requires two conditions to be fulfilled : (i) an easy scaling-up, which means the passage from the gram-scale to the ton-scale and (ii) the possibility for our solids to become real (multi-functional) materials, which means that, beside the knowledge of their synthesis, structures and properties, a shaping (thin films, nanoparticles...) adapted to a special application is easy to realize. It was the last step of our integrated strategy.

## 6a. Scaling up.

As academic researchers, we are not familiar with this aspect, whereas engineers are used to do that every day in the companies. It is because BASF was interested by our aluminum-based MILs that they contacted me. Their reasons were simple : after a bad experience with a colleague whose recipes were not very much reproducible, they tested my MIL-53(AI) which presented the three qualities necessary for an interesting industrial development : low cost of the precursors, good stability toward humidity and temperature (some of our MILs are stable up to 550°C) and reactions occurring in the very cheap water medium, at variance to organic solvents and their toxicity. Their initial interest concerned hydrogen storage. The cooperation that we established is still active and was recently extended through a Large European Project to which the petroleum company TOTAL is associated for applications in  $CO_2$  capture.

Technically, U. Müller's group in BASF was in charge of the scaling-up following our initial recipes. It occurred first with MIL-53(AI) in several steps at the 10g-, 100g-, 10kg- and 300kg-scale. At every step, the properties (including the almost 100% yield) of our solid were preserved and allow now a 1 ton production/day and is now commercialized under the label Basolite A-100. Other MILs are currently submitted to this scaling-up.



**Fig.II.2.52.** – *Sccaling-up images* : Two views of the hydrothermal reactor images and, on the right, a 50 liters container filled by bulk powdered MIL-53(AI).

We had mentioned at the beginning of this chapter that our MILs could be obtained using microwave synthesis which had the advantage for MILs to be fast (reaction achieved in 40mn) to provide well crystallized solids, even at short time (1 mn) in the form of nanoparticles. This allowed a continuous preparation of the desired material in good conditions. This technique is now at the plant-scale and allows the preparation of large quantities in a single batch.



**FiG.II.2.53.** - A photograph of a transparent PMMA box (70 I) containing the dried MIL-100(Fe) powder obtained from a largescale batch (200 I).

6a. Shaping.

Depending on the desired application, one can need a special shaping of the product adapted to the property to be developped. These shapings are mainly nanoparticles for nanophysics, thin films for sensors, or pills for medicinal applications.



**FiG.II.2.54.** – Examples of shapings realized with MILs. Left : MIL-53(AI) pills produced by BASF for medicinal applications ; Middle : Nanoparticles of MIL-101 issued from microwave synthesis and suitable for veinous injection of drugs ; Right : Thin films of MIL-101 of optical quality and of low rugosity obtained by soft ligand exchange.<sup>501</sup>

We elaborated these different ways of shaping. They are now at the disposal to those who want to develop new applications for them.



The cycle is closed ...

During these twenty years, with my young students, I had the chance after having defined an integrated strategy, to discover a new world with these wonderful solids, to scrutinize the formation of the MILs by opening a 'blackbox', to try to predict their structures from physical chemistry and to evidence for them numerous properties, most of them being unprecedented, and which find some applications *a priori* beneficial for the society through my industrial contacts. I am really convinced that I had a big chance also to go to the end of my dreams. I finish my carreer as a happy old man, proud, through our numerous results, to have educated my young students who are now distinguished scientists, with the same passion for chemistry that I always had. It is their life now, but I am sure that they will continue to explore this fantastic field with new their ideas.

Chemistry is a science ; it is also an art, and through my discoveries, starting from common bricks to build up new fascinating architectures, I had the other chance to find an **unexpected resonance between art and science** : the bricks and the mosaïcs, the cages already drawn by Leonardo some centuries ago or painted more recently by Victor Vasarely. Definitely, artists are always in advance to describe our world....



Many thanks to all of them !...

