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Giant flexibility of crystallized organic-inorganic porous solids : facts, reasons, effects and applications.

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Dedicated to my friend François Fajula for his achievements, on the occasion of his retirement.

This *critical review* focuses on a strange behaviour of the crystallized solid matter : its reversible swelling with large magnitude under the action of various stimulii (T, P, light ...). This review looks first at the structural origin and the limitations of this flexibility before examining the various properties associated to this phenomenon, and which make them both academic tools for the explanation or physical phenomena at the molecular scale and interesting multimaterials finding potential or real applications related to sensors, energy, energy savings, sustainable development and health.

1. The era of pioneers : three laboratory curiosities.

Whereas amorphous polymers or biologic matter sometimes exhibit noticeable flexibility, at least in the dynamics of the chain fragment, inorganic crystallized solids are usually considered as rigid if one excepts the thermal vibrations of its atoms which generally induce to small movements (< 1Å). The discovery of hybrid organic-inorganic porous solids [1,2], a new and rich class of solids in between inorganic and organic polymers, provided some nuances in this preconceived idea. These compounds result from the strong association between inorganic moieties (isolated polyhedra, clusters, chains or even layers) with organic ligands, the most frequently used being carboxylates, phosphonates, sulfonates or nitrogen-based ones (cyano-groups or azolates) [3-6]. They represent a new class of coordination polymers called either porous coordination polymers (labelled as PCPs) or Metal-organic Frameworks (MOFs) which represent a subclass of the former. It resulted in several thousands of new structures, which make now this domain one of the currently most topical areas in chemistry.

Among these numerous new structures, a new phenomenon, predicted by S. Kitagawa[7] in 1998, concerned the six possibilities for some structures to become flexible under the inclusion/evacuation of guests within the coordination polymer network, depending of the dimensionality of the latter (Fig.1).

Fig.1. – *The six possibilities of flexibility of networks as a function of their dimensionality*.

The same year, and independently, Alberti[8] and Clearfield[9], working on pillared Zr diphosphonates, usually rigid, showed that it was possible to generate flexibility after a partial exchange in air (with a relative humidity of 100%) between the diphosphonates with variable long linear carbon chains (4 < n <16) of the structure and short mono-phosphonates.The resulting cavities were initially filled by water molecules. During dehydration, the structure shrinks due to the deformability of the alkane chains which therefore act as springs. This leads to an important decrease of the z parameter from 19.2 Å to 11.2 Å, whereas the framework remains preserved during all the dehydration process. Rehydratation restaures the initial structure (Fig.2).

Fig.2. *(a) Polyhedral projection of the structure of γ-ZrP along [010] and (b) along [001] ; (c) and (d) [010] projections of the completely pillared Zr 1,4- and 1,10-alkane diphosphonates, (e) a schematic view of the fully hydrated phosphate/diphosphonate and (f) of the corresponding dehydrated sample showing the contraction of the carbon chain. Zr octahedra are in pale blue, phosphate groups in yellow, water molecules in dark blue, OH groups in red and white and the carbons in black.*

The third curiosity occurred from 2002 in my group [10-13]. It concerned this time trivalent metal terephtalates $[M^{III}(X)][BDC]$, H_2O (M = Al^{12}, V^{10}, Cr^{11}, Fe^{13}, Ga^{14} ; X = OH, F), hydrothermally synthesized at 180°C under autogenous pressure. They are now known as the MIL-53 topology (MIL stands for Material of Institut Lavoisier). Over the years, this topology has become one of the texbook examples of large reversible flexibility, with thousands of citations [15,16 and refs therein].

As synthesized, their structure consists in a three-dimensional network composed of corner-shared trans chains of metallic octahedra (the OH groups being the shared species) linked in the two other directions by terephtalate ions. This determines large unidimensional lozenge-based tunnels within which water molecules are inserted (Fig.3). In terms of nets, the topology of MIL-53 corresponds to a 4^4 lattice.

Fig. 3. - *Structures of the closed (left) and open (right) forms of the MIL-53 topology. The insert shows the trans chains of corner sharing octahedra (through OH groups).*

With Al and Cr, the cell volume of their hydrated form is close to 1,000 $Å^3$. During their dehydration, it suddenly drastically increase in one step of the latter up to ca. 1,500 $Å^3$, while keeping the same topology. With Fe, the contrary occurs, in two steps : the cell volume of the anhydrous cell decreases down to 900$Å^3$ (Fig.4). All these changes are reversible.

Fig. 4.- *The inverse evolution of anhydrous forms of MIL-53(Fe) and MIL-53(Al,Cr), with their changes of space group when the amount of guests progressively increases in the tunnels (acronyms : vnp for very narrow pores, int for intermediary phase, np for narrow pores anf lp for large pores).*

The case of vanadium is rather different because, during the dehydration, V^{3+} ions are oxidized into V^{4+} ions, which imply that the primitive OH groups are replaced by oxide ions within the chains for satisfying the electro-neutrality of the structure. This oxidation creates irreversibility for rehydration ; indeed, after opening of the tunnels during dehydration, the tunnels curiously remain in their large pores (LP) configuration during rehydration. Beyond the fact that, within a same structure type, flexibility depends on the nature of the metallic ion, the vanadium solid (labelled MIL-47) provides an interesting feature. With it, researchers have indeed at their disposal both the flexible and the rigid forms of the same topology. This will be very important when studying on a physical chemistry point of view the roles of host-guest interactions on the flexibility.

2. Structural reasons of the flexibility (or rigidity).

2.1. - General remarks

For the above examples, flexibility can therefore be defined as a reversible phase transition occurring in two or more steps, induced by an external stimulus (T, P, chemicals, light…). It leads, for porous solids, either to an expansion or a contraction of the unit cells of large magnitude, depending on the relative strengths of the various types of interactions which occur within the cavities (Fig.5).

Beside the textbook examples provided by the above results, it worthy to note that the ca. 50% variation of the cell volumes does not represent an extremum. Indeed, another chromium dicarboxylate (the chromium diphenyl-dicarboxlate, labelled MIL-88[17]) exhibits a reversible cell volume variation of more than 300% during the hydration-dehydration process without any decrease of the crystallinity of the corresponding solid. In terms of atomic movements, this represents close to 10Å displacements without any amorphization during the transition…

Fig. 5.- *Scheme of the occurrence of flexibility under the action of an external stimulus.*

During some years, only the Kitagawa's group in Kyoto and mine were interested by this new phenomenon but with time, it began to interest the community and has become now a new field of research worldwide. However, in science, it is not enough to multiply the examples. It is necessary to understand and explain the different reasons of such a phenomenon for, eventually, provide later its applications. The present paper looks at this aspect.

The different degrees of freedom which allow flexibility in the structure appear on Fig.6. As detailed below, they concern :
- both the inorganic and organic parts of the framework,
- the guests within the pores and the different interactions (guest-guest and host-guest) they induce in the structures.

Fig. 6.- *The various degrees of freedom in an open structure allowing its flexibility*.

2.2. - Concerning the ligands

The ligands can be either rigid (based on phenyl rings or multiple bonds) or flexible when the carbon chain is aliphatic. Moreover, the functions that they bear can be different : carboxylates (the most commonly used), phosphonates, sulfonates, cyano groups, azolates… Depending on the experimental conditions, the grafting of the functions cited above on the metal of the inorganic block presents several situations, depicted in Fig. 7, and which have different effects on the flexibility through the possible rotations of different parts of the ligand. In particular, as it will be shown below, the rotation of the central part of the ligand is, for steric reasons, very influenced by the functionalization of this part.

Fig. 7.- *The various degrees of freedom of the carboxylate (a,b), phosphonate or sulfonate (c,d,e) and azo-based (e) ligands of an open structure for allowing its flexibility, which depends on their dentation with the metal M. The decrease of the dentation gives more degrees of freedom of the ligand around the inorganic moiety (mainly rotations, indicated by arrows or oriented spheres when the rotation occurs in three directions. The blue arrows concern the rotation of the central part of the ligands vs. the orientation of the function). [Color Codes : Carbon :black ; metal : purple ; nitrogen : blue ; oxygen : red].*

Two examples (Fig.8) illustrate the importance of these rotations/shifts. Fig.8a, devoted to the MIL-53 topology, shows that, depending on the functionalization or not by methyl groups on the phenyl ring, the structure exhibits either its open or closed form, due to the steric hindrance of CH_3 groups which induce a rotation by ca. 90° of the phenyl ring. The magnitude of this rotation is strongly dependent on the nature of the substituent on this phenyl ring[18]. Fig. 8b concerns the solid $[Zn_2(1,4\text{-BDC})_2(DABCO)]$, (also called 'jungle gym') and the effect of progressive introduction of propane-2,ol (IPA) in the cages of the structure[18-23] which is based on Zn_2 dimers which, by linkage with four 1,4-BDC molecules, provide 2D square grids. The pillaring of the latter by the nitrogens of DABCO ensures the 3D structure. By a rotation of the COO groups during the introduction, an intermediate structure is observed, which can be described as a shift between layers.

Fig. 8.- *Two examples of flexibility due to the influence of diverse types of rotation of the ligands : (a) Pristine MIL-53, H_2O and its grafted homologue with 4 methyl groups on the phenyl ring ; (b) the evolution of the structure of $[Zn_2(1,4\text{-BDC})_2(DABCO)]$ during the progressive filling of the cages by propane-2, ol. In the intermediate phase, a shift between two layers is observed due to the rotation of the carboxylate groups of 1,4-BDC (case (a) of Fig.7).*

2.3. - Concerning the inorganic moiety and its junction with the ligand.

In the following, this moiety will be called either '*brick*' or '*building block*'.

It is the most variable part of the framework. It drastically depends on the conditions of synthesis, in particular on two factors : temperature and pH. As illustrated by the example[24-27] of cobalt(II) succinates, the increase of the first favors the increases both the nuclearity of the brick (the number of constituting polyhedra) and the dimensionality of the inorganic subnetwork, all the other synthesis conditions remaining identical. Starting from a single Co octahedron at 60°C, it becomes a trimer at 100°C, resulting into 1D structures. Above this temperature, the building block progressively becomes a tetramer, then a pentamer, before exhibiting hexamers at 250°C in a 3D structure. On the other side, pH will play an important role in the coordinence of the cation involved in the brick. For instance, Al^{3+} cations present a tetrahedral coordination at high pH, and an octahedral one at low pH through a pentagonal one for its intermediary value.

Therefore, once the synthesis conditions fixed, the structure of the precipitated hybrid porous solid results from the linkage between the brick and the function of the ligand, often from its exchange with those surrounding the cation in the solution before the precipitation. For ensuring the three-dimensional character of the framework, the ligand, in most of the cases, is a ditopic polycarboxylate, whereas tri- or tetratopic ones lead to rigid frameworks. and it is the type of association brick-ligand which, in this case, determines or not the flexibility.

The latter implies coordinated movements between the different parts of the framework. It is for one part the symmetry of the brick which will mechanically create the possibility for the framework to be flexible (the other being, as seen below, the relative strength of the interactions existing within the structure). Whatever the nuclearity of the brick, it must possess a plane of symmetry for allowing such cooperative movements. For instance (Fig.9), both the bricks of 'jungle gym' [Zn_2(1,4-BDC)$_2$(DABCO)], built up of Zn dimers, and MIL-88 (Fe(III)O,*ligand*) whose building block is a trimer of octahedra, allow these cooperative movements of the carboxylates up and down their plane of symmetry. On the contrary MOF-5[28], based on a tetramer of Zn tetrahedra, does not permit these symmetrical displacements and is therefore rigid.

Fig. 9.- *Three examples of bricks allowing or not the possible flexibility of the framework. In the 'jungle gym' [Zn_2(1,4-BDC)$_2$(DABCO)], based on dimers (a) and in MIL-88 based on a trimer of corner-sharing octahedra linked through a μ_3-O oxygen (b), the existence of a plane of symmetry in the inorganic brick allows cooperative and symmetrical movements of the ligands attached to the brick (indicated by green arrows). They are not possible for MOF-5 (c), the tetrameric brick of which having no mirror plane.*

The type of junction brick-ligand determines the topology of the whole framework which will depend both on the chemical nature and nuclearity of the inorganic brick and also on the number of ligands attached to it, for which their length and steric hindrance can play a role on the flexibility. This number of ligands around the brick is also called the *connectivity* of the network. It is extremely variable as a function of the nuclearity of the inorganic brick and can reach more than 20. Fig.10 present some of the most frequently arrangements with their corresponding connectivity.

Fig. 10.- *Connectivity of some of the most encountered inorganic bricks : four (a), six trigonal pyramid (b), six octahedral c), nine (d,e) and twelve (f). White arrows indicate the different directions toward which the nearest inorganic bricks are found.*

Finally, speaking in terms of flexible topology, there is one characteristic for which flexibility is immediately forbidden. It is the case when the topology exhibits odd cycles of inorganic bricks. This was particularly evidenced with the 3D vanado-terephtalate MIL-68[29] , a polymorph of MIL-53 which exhibits this time triangular and hexagonal tunnels (6.3.6.3 net) instead of the lozenge ones . The extreme rigidity of the triangles rules out any flexibility of the framework. It was also proven with the crystallized mesoporous solids MIL-100[30] and MIL-101[31] , which both exhibit pentagonal windows for their cages.

2.4. - Influence of the various interactions on the flexible character.

When considering that the pores are occupied by guests, they are of three types :
- the host-host interactions,
- the guest-guest ones
- the host-guest ones

and their relative strengths will play a major role on the flexible character. This will be shown in detail by using mainly the MIL-53 topology as support.

2.4.1. The host-host interactions.

They are the less encountered. This point was already mentioned with the case of MIL-47, becoming rigid during the oxidation of V(III) into V(IV) with a correlative change of the OH groups into oxide ones, thus preventing the existence of hydrogen bonds between the framework and the guests. Another example of this type of interaction is provided by the aluminum 2,6-naphtalene dicarboxylate MIL-69 (Al(OH), *ndc*)[32]. At variance to its terephtalate homologue MIL-53(Al) which opens during dehydration[33], MIL-69 remains in its narrow pore (NP) form when dehydrated. This is explained by the predominance of the strong $\pi-\pi$ intermolecular interactions between two adjacent naphtalene double rings. By far energetically stronger than others, due to the short distance between them, they block the topology in its NP configuration (Fig.11).

When they are weak enough for allowing flexibility in the absence of guests, these latter interactions depend on temperature through a second order phase transition between the LP and the NP forms. By using neutron thermo-diffraction, Brown *et al* [34] showed that MIL-53(Al),*bdc*, once dehydrated, (Fig.11 left) remains open under N_2 at 300K but, by cooling, it undergoes from 200K a reversible transformation into the NP form. The rehydratation of the empty LP form in air at 300K regenerates the initial hydrated NP form. This was confirmed by an independent ^{129}Xe NMR study of its adsorption isotherms in the range 77-300K[35,36]. The enthalpy of transformation, measured[37] by mercury porosimetry, is close to 5 kJ.mole^{-1}. Very recently, a thorough structural study using X-ray diffraction described in detail the evolution of the MIL-53(Al) structure, which is now perfectly known[38] .

Fig. 11.- *Influence of the $\pi-\pi$ interactions between the ligands on the reversible opening (MIL-53, **bdc**) or not (MIL-53, **ndc**) of the MIL-53 type (**btc** for 1,4-benzene dicarboxylate ; **ndc** for 2,6-naphtalene dicarboxylate).*

2.4.2. The guest-guest and host-guest interactions.

They are strongly correlated and occur within the pores. The guest-guest interactions, in the center of the tunnels, serve as a backbone for the other interactions. They can be dipolar, quadrupolar (in the case of CO_2), or of the Van der Waals type, depending on the chemical nature of the guests (which are often the molecules of solvent trapped in the cavities of the porous structure). The host-guest interactions on their part are essentially related to hydrogen bonding (mainly O…H or N…H), and the evaluation of the corresponding distances provides a first information of their strengths before using microcalorimetry for quantifying them, but such measurements are rather rare.

On the other side, the extreme sensitivity of flexible solids to these interactions render them a powerful tool for the qualitative comparison of their strengths, just by looking at the evolution of the cell volumes of the filled cavities. The use of the MIL-53 topology was extremely fruitful to demonstrate that, starting from MIL-53(Fe), H_2O, whose cell volume of the NP form is *ca*. 1,000 Å^3.

When we put this solid in another solvent, the exchange between water and the new guest was total and immediate. It provided the LP form at a more or less extent, depending on the nature of the guest. In order to verify that and to evaluate if there were a progressive change of the cell parameters when adding drop by drop increasing amounts of the new solvent, we performed an *in situ* X-Ray diffraction study using the synchrotron radiation at Daresbury at 300K[39]. Surprisingly, even for very minute amounts of the new solvent, the opening is complete with no intermediary displacements of the Bragg peaks. We called '*the forceps effect'* this phenomenon.As soon as the first molecules of the new solvent arrive in contact with the solid, they immediately induce the change of it cell volume by a destruction of the initial interactions.

The use of many other solvents in this experiment allowed us to describe the evolution of the cell volumes for each of them, and therefore to compare the strengths of the different host-guest interactions within the same topology. The larger the cell volume, the weaker the host-guest and guest-guest interactions. Note that this evolution, which occurs in the range 1,000 - 1,500 Å^3, is not related to the size of the guest molecules. Only the energies of interaction are concerned. In the whole series, even if the space groups of the structures change, due to small reorientations of the octahedral chains, the topology is preserved. Moreover (Fig. 12), the different cell vollumes fit with the theoretical curve representing d/D = f(V$_{cell}$), d and D being the small and long diagonals of the lozenge section of the MIL-53 structure. The third parameter, corresponding to the axis of the chains, remains constant along the evolution.

Fig. 12.- *Left : the effect of an exchange of solvents on the swelling of the MIL-53 topology ; (right) : the evolution of the d/D ratio (see text) vs. cell volume for some solvents trapped in the tunnels. The black line corresponds the theoretical evolution of d/D with the volume of the cell. The change of the space groups is also mentioned.*

The length of the small diagonal is also an indicator of the extent of swelling, function of the relative strengths of the guest-guest (I$_{G-G}$) and the host-guest (I$_{H-G}$) interactions. It allows a beginning of classification of the various openings of the MIL-53 topology (Fig. 13) . When I$_{G-G}$ and I$_{H-G}$ are strong and of the same order of magnitude, the structure is shrinked (Fig. 13 left) . It corresponds to the left part of the curve of Fig. 12. If I$_{G-G}$ > I$_{H-G}$ (Fig. 13 top right), the strong backbone is preserved but the weakening of the host-guest interactions lead to an opening of the tunnels (medium part of the curve Fig.12). Finally, when I$_{G-G}$ < I$_{H-G}$, the host-guest interactions, despite weak, predominate at such a point that the ordering of the guests in the tunnels disappears. The cell volume becomes maximum (ca. 1,500 Å^3) and leads to very large pores.

Fig. 13.- *Degrees of opening as a function of the competition between the energies of guest-guest (I$_{G-G}$) and host-guest (I$_{H-G}$) interactions.*

The swelling/shrinkage of the framework has also another advantage : to establish the optimum contact (depending of the host-guest energies) between it and the species inserted within the pores. This can lead to confinement effects (equivalent to an internal pressure) which can modify the structural arrangement of guests inside the tunnels. A good example is provided by the comparison of pyridine and lutidine guests within the tunnels of MIL-53 (Fe) (Fig. 14). With lutidine, due to the steric hindrance of the two methyl groups which weakens the O-H…N host-guest interactions, the $\pi-\pi$ guest-guest interactions between the phenyl rings are favoured and therefore, the ordering of the molecules in the tunnels is similar to that existing in pure solid lutidine with, in both cases, a stacking of the molecules in the LP structure. It is not the case for the inserted pyridine which establishes dominant host-guest interactions in the rather closed form. They oblige the phenyl rings to align, like in lutidine, but this time, the organization of the pyridines is completely different from what happens in the solid pure pyridine, governed by N…H bonds. In other words, the flexibility of MIL-53 induces in this case a phase transition for pyridine, that one can consider as a high pressure form of this solid,due to confinement effects.

Fig. 14.- *Illustration of the confinement effects induced by the flexible MIL-53 structure for pyridine,by comparison to the case of lutidine (see text).*

MIL-53,H_2O illustrates well all these interactions (Fig.15). They are of three types, demonstrated from *in situ* Al, C and H NMR experiments[33] : (i) the guest-guest H-O…H-O interactions at the center of the tunnel (green) which serve as the backbone and the two kinds of symmetrical host-guest ones : the $H_{H2O}…O_{carboxylate}$ (blue) and the $O_{H2O}…H_{hydroxyl}$ (purple). Their symmetrical positions around the backbone, joined to the O-O kneecap role played by the carboxylate connected to the chains, explain the shrinkage of the structure when hydrated.

Fig. 15.- *Evidence of the three types of interactions governing the shrinkage of hydrated MIL-53 structure type (guest-guest H-O…H-O (green) at the center of the tunnel ; $H_{H2O}…O_{carboxylate}$ (blue) and the $O_{H2O}…H_{hydroxyl}$ (purple) host-guest ones.*

3. Some properties of flexible solids.

Hybrid porous solids (MOFs and PCPs), as other classes of the solid state, exhibit physical properties which could lead in the near future to possible real applications related to the domains of energy, energy savings, environment and health as soon as they evidence both sufficient stabilities toward temperature and humidity, and easy scaling-ups and shapings. For carboxylates, the above stabilities mainly depend on the the nature of the metals and on their oxidation number ; they generally increase from II to V. Moreover, the extent of these physical properties depends also on the cleverness of chemists who, by pertinent cationic substitutions, can generate properties which did not exist in the as-synthesized solids. The main physical properties of this new class of solids will be briefly recalled in $3.2.

However, within this family, specific behaviours appear, which are related to the flexible character.

3.1 - Properties intrinsic to flexible solids.

Their specificity comes from their extreme sensitivity to external stimulii and from the fact that the atoms of the internal surface of their frameworks adapt their proximity often as a function of both the steric hindrance of the guests and of the strength of their specific interactions with the surface. This continuous structural adaptation, inherent to flexible solids, induces original behaviours, pioneered in my group, which mainly interest the domain of adsorption/capture/delivery.

The first striking example of these phenomena concerns the adsorption of CO_2 and CH_4 by the flexible MIL-53(Cr & Al) and its comparison with the isotypic non-hydroxylated MIL-47(V) at room temperature[39,40]. For MIL-53 type, whereas the CH_4 isotherm exhibits a typical one step type I behaviour, the CO_2 one presents an unexpected hysteretic two-steps shape, hitherto unknown before our experiments (Fig.16a). For CO_2, the adsorption enthalpy, measured by microcalorimetry, is very exothermic, and lies in the range -45 - -30 kJ.mol.$^{-1}$, depending on the adsorbed amount[39]. An original continuous *in situ* powder X-Ray diffraction as a function of the applied pressure[41,42] proved first that, under vacuum, the structure is in its large pores (LP) form. As soon as two CO_2 molecules per tunnel are inserted, the structure suddenly shrinks into its narrow pores (NP) which remains up to ca. 6bars. This corresponds to the plateau in the isotherm. At higher pressures, the structure reopens and one observes an order-disorder transition for the CO_2 arrangement. During desorption, the LP form persists down to 2 bars, where NP pores intermediary appear, before reopening under vacuum.

The above structural study also allowed the localization of the CO_2 molecules in the tunnel (Fig.16b). Their backbone effect along the tunnels is evidenced through the short distances between them. The

short distances between the oxygen atoms of CO_2 and the hydroxyl groups of the skeleton (< 2Å) indicate that adsorption, in this case, is a physisorption driven by the strong interactions between the quadrupolar CO_2 molecules and the dipolar OH groups. Moreover, a careful IR study[43,44] showed first that the OH groups do not present a significant acid character and that, during adsorption, carbonatation of CO_2 does not occur.

Fig. 16.- *(a) adsorption isotherms of CO_2 and CH_4 in MIL-53 with, for CO_2 (left), the structural information vs. pressure. For methane, the structure remains in its LP form whatever pressure ; (b) localization of the CO_2 molecules (C: yellow ; O: pink) within the tunnels of the MIL-53 structure. The octahedral chains are in green and the interaction between quadrupolar CO_2 and the OH groups (O : red ; H : white) is visible.*

Such a two-steps phenomenon does not exist with the rigid MIL-47(V), which does not possess OH groups and, consequently, cannot give interactions with CO_2. The isotherm exhibits the type I shape. The enthalpy of adsorption (-25 - -20 kJ.mol.$^{-1}$) is by far lower than before. The structure remains in its LP form in the whole range of pressure, with disordered CO_2 molecules which progressively fill the tunnels, as evidenced both by the 2D energy maps extracted from Quasi-Elastic Neutron Scattering (QENS) and computer simulations performed by G. Maurin *et al.*[45-50].

The same disorder is observed at 300K when CH_4 is inserted in the pores of MIL-53 as well as for MIL-47. Compared to CO_2, methane is a spherical apolar molecule which of course cannot give the same type of interactions with the framework. Indeed, these interactions are not sufficient for generating the flexibility observed with CO_2. Whatever the amount of methane introduced, MIL-53 remains in its large pore form. This striking difference of behaviour was questionable. Microcalorimetry measurements applied to methane (non flexible) and its superior alkanes (flexible in two-steps) provided an explanation. They indeed show[51,52] that the enthalpy of adsorption of these species in MIL-53 and MIL-47 is a linear function of the number *n* of carbons of the alkanes with equations of variation of 7.016 + 9.274*n* for MIL-53 and 5.197 + 9.270*n* for MIL-47. This implies that the MIL-53 structure can become flexible only if the enthalpy of adsorption is > ca. 20 kJ.mol.$^{-1}$) which is in agreement with the experimental value observed for CH_4 (-17 kJ.mol.$^{-1}$).

This thorough study, completed by the NMR study of the adsorption of xenon on MIL-53(Al) [35,36], further allowed numerous computer simulations in front of experimental data (Figs. 17-18). They concerned first the simulation by Maurin *et al.* of the shape of the curve (Fig.17a) and the hysteretic structural modifications (Figs.17b,c) as a function of temperature and pressure [53,54 and refs therein], a study which also predicted the temporal variations of the MIL-53 cell volume as a function of the number of CO_2 molecules introduced in the tunnels (Fig. 17d,e). The latter results show that the adsorption, in all the cases, is extremely fast (< 350 ps).

Fig. 17.- *(a) Current simulation (red) vs. experience (black) of the two-steps behavior; (b) Simulation of the second order hysteretic LP-NP phase transition vs. temperature ; (c) Simulation of the second order hysteretic LP-NP phase transition vs. pressure; (d,e) variation with time of the MIL-53 cell volume as a function of the number of CO_2 molecules introduced in the tunnel.*

On the other side, developing a new approach by DFT calculations, Boutin, Coudert and Fuchs [55-57] were able to establish the T,P phase diagram of MIL-53 when CO_2, CH_4 or Xe fill the tunnels (Fig.18).

Fig. 18.- *The (T,P) phase diagram of the LP-NP transition for three types of molecules inserted : CO_2, CH_4 and Xenon (with courtesy of F.X. Coudert, A. Boutin and A. Fuchs).*

From 2008, MIL-53 and MIL-47 were often used as model structures for studying the dynamics of some guests within their tunnels as a function of the presence of OH groups (MIL-53) or not (MIL-47) in the framework. For that, experimental data coming from Quasi-Elastic Neutron Scaterring (QENS)

were combined with molecular dynamics simulations. The gases involved were CO_2[58,59] and CH_4[60], alone or in mixture[61], alkanes[51,62-65], aromatics[66-70], water[71-73] and H_2[74-76].

For the two first gases, it was shown that their transport diffusivities are larger than those of zeolites. In the case of MIL-53 filled with CO_2[58], an increase from the NP to LP is observed, while keeping a 1D microscopic diffusion mechanism, evidenced from 2D free energy maps. For methane in MIL-53[60], despite a similar but less pronounced 1D diffusion mechanism, the diffusion process is slower than in MIL-47 with respective times of residence of 5.4 and 3.3 ps.

When light alkanes (ethane to butane) in LP MIL-47 are concerned[62], the rotation of ethane is isotropic whereas that of butane is better reproduced as an uniaxial rotational model. The situation is intermediate with propane. These alkanes do not exhibit any strong interaction with the μ_2-O of the skeleton. The 2D free energy maps indicate a 1D microscopic diffusion mechanism. Surprisingly, the self-diffusion coefficients decrease from ethane to butane. This experimental trend evokes a « blowgun » effect, n-butane behaving like a dart flying in a tube. For higher alkanes (C9-C16)[63], the experimental diffusivities are about one order of magnitude higher than in the zeolite silicalite. The lower activation energies for diffusion indicate less conformational changes in this 1D-channel type MOF, compared to zeolite. When MIL53 is the host[64], the shape of the isotherms depends on the number of carbons in the alkane. For C3 and C4, which exhibit a two-steps behaviour, modelization of the isotherm requires the analytical 'phase mixture' procedure[65] for predicting the fractions of both NP and LP forms in the transition zone.

The adsorption of some aromatics (benzene, xylene) in these two solids was also studied. Benzene molecules inserted in MIL-47 move in a corkscrew motion[68], as already observed with bacteria and during RNA polymerase translocation. Also, the insertion of xylene in MIL-53 at different loadings, followed by H2 NMR, has a controlled influence on the rotation dynamics of the phenylene rings of the terephtalate[69]. This dynamics is very sensitive to the loading of xylen guests and the MIL-53 structural state. The rotation rate is higher and the activation barrier lower for the LP state for the poorly loaded material. The two latter have inverse variations at high loadings. When the rigid MIL-47 is used[70], experience and simulations agree for all the xylene isomers to show an unusual non-monotonous evolution of self-diffusivity coefficient with temperature. At low temperature, the xylene molecules are close to the internal surface, with a high activation energy barrier. In the high temperature regime, the xylenes are located at the center of the tunnels and the activation energy for the diffusion lower.

The simulation of the historical case of water in MIL-53 is recent[71-73] and used different approaches. Salles *et al.*[71] were the first to look at this aspect. They considered the water molecule as a rigid body, and used Newtonian dynamics of the water and the framework. Later, Paesani[72] took into account quantum dynamical effects. In 2013, Coudert and Boutin[73] refined the results by means of DFT-based molecular dynamics simulations. They all agree to explain the hydrophilic character of the NP form and the midly hydrophobic one for the LP structure. From QENS experiments and 2D free energy maps, it appears that, in NP, the 1D diffusion mechanism for water is strongly confined in the milddle of the pores and that the diffusion is continue along the direction of the tunnels, whereas a jump sequence is preferred for LP, the μ_2-OH groups acting as steric barriers. Moreover, Coudert and Boutin[73] paid attention to the behavior of the OH groups and to the water molecules bound to μ_2-OH and their dynamics.

For the first, while its oxygen atom is rather constrained and has a low amplitude of movement (0.2Å), the position of the H atom (and therefore the orientation of the μ_2-OH groups) varies more widely around the Cr-O-Cr plane in both the NP and the LP forms. The wagging of μ_2-OH is harmonic. When water molecules are considered in the NP form, they rotate rather freely while keeping intact the hydroxyl-water hydrogen bond. During this rotational diffusion, it appears fromthe calculations that the water's H atom sometimes comes in close vicinity to the oxygen of a carboxylate of the skeleton, even

for short times of residence. This confirms the previous experimental results of our group, extracted from NMR studies [12,33]. The situation is different when water is inserted during high loadings. The molecules are highly disordered, with a large distribution distribution of $O_{\mu 2-OH}$ - O_{water} distances and the organization of water molecules in the LP form is close to the behavior of 'bulk' water with however some differences.

Finally, with H_2, stored in large amounts at 77K (3.7wt.% for MIL-53) with hysteresis[74], a very high H_2 diffusion is observed from QENS experiments [75,76]. At low loadings, the diffusivity of hydrogen is about two orders of magnitude higher than in zeolites. Such a high mobility was never experimentally observed before. Even at high loadings, the fits of QENS spectra show a 1D diffusion model for H_2 in MIL-53 with jumps of ca. 7.5Å (1.0), close to the distance between two consecutive μ_2-OH groups (6.8Å), whereas a 3D behaviour is observed with MIL-47.

All these calculations, applied to various guests, opens a promising direction to improve the selectivity of MOFs by playing both on the sensitivity of flexible MILs to adapt their aperture to various guests and on their selective energies of interaction with the framework.

For example, whereas the adsorption of CO_2 and CH_4 in empty MIL-53 was described in detail (see above), with a preference for CO_2 adsorption when a mixture of the gases is sent on this solid[77], the phenomenon is completely different when taking the NP MIL-53, H_2O instead of MIL-53 as adsorber[78]. Up to ca. 10 bars (Fig.19a), a 'gate effect' is observed with almost no adsorption of these two gases. Above, only CO_2 is adsorbed, whereas CH_4 is always not.

This was also exemplified by De Vos *et al.* who tested the selectivity of MIL-47 toward the different xylene isomers and ethyl-benzene[79]. Their different positions each of them occupy in the tunnels indicate different host-guest interactions (Fig. 19b). Therefore, using MIL-47 as a chromatographic separator, they proved that the separation performed on an equal mixture of them leads to a quantitative separation within 20mn at room temperature.

Fig. 19.- *(a) The drastic difference of behavior between MIL-53 and MIL-53,H_2O used as adsorbers for CO_2 and CH_4.*

The last property that I shall mention illustrates the ability of the flexible solid to establish tight and energetical contacts with the guest. It is particularly true for the storage and delivery of drugs. Initially discovered for rigid MOFs in 2006 in our group[80], this property also applies to flexible solids[81-82]. This makes MOFs the best drug nano-vectors discovered up to now[83], far better than the liposomes currently used. They combine excellent stability in physiological media, storage of important amounts of drugs and long times deliveries. For example, the MIL-53 structures, not only adsorb large quantities of Ibuprofen (1g/g of solid), but deliver the latter quantitatively in a quasi-linear manner (Fig.20). Delivery is complete after the unprecedented time of 3 weeks. Due to their non-toxicity and and their sensitivity in medical imaging, the Fe-based solids are chosen for *in vitro* and *in vivo* characterizations. Beside the test drug Iboprofen, the MIL-53 structure adsorbs and delivers many other drugs with different hydrophilic/hydrophobic characteristics (Busulfan against leukemia, doxorubicin against breast and kidney cancers, AZT-TP against HIV…) and also poisonous gases (CO_2, H_2S) which, at high doses are lethal but, at small doses, are very useful in heart surgery[84]. The time of delivery strongly depends on the nature of the drug.For the flexible Fe-based MOFs, it ocurs inthe range 2-11 days.

Fig. 20.- *Delivery of ibuprofene as a function of time for MIL-53(Cr) and -(Fe) The drastic difference of behavior between MIL-53 and MIL-53,H_2O used as adsorbers for CO_2 and CH_4.*

3.2 - Properties shared between flexible and rigid solids.

For becoming multifunctional materials, MOFs and PCPs must present a large range of properties, far beyond those of adsorption and gas storage, on which a large majority of colleagues focused on. As dense inorganic phases, in the past, obtained a great success in the area of multifunctional materials (superconductors, batteries…), our group decided to look at this aspect for knowing the spectrum of possibilities MOFs and PCP could offer in this area, whatever the flexible or rigid character of these phases. Even if it is at the limit of the scope of the present paper, I just shall recall briefly the major properties discovered in the laboratory :

• magnetism[85-88] : most of the *3d* transition metal-based MOFs are antiferromagnets, at rather low temperatures, except the Ni-based solids whwich exhibit ferromagnetism ;

• conductivity[89-92] : MOFs are usually insulating, but the electrochemical introduction of Li metal renders them conductors, combining electronic and ionic conductivity ;

• strong luminescence[93-95] when *4f* elements are in the framework, with the first evidence of an 'antenna' effect for MOFs ;

• photoluminescence[96] when Ti^{4+}-based MOFs are submitted to UV radiation which provokes a reduction of Ti^{4+} into Ti^{3+}.

• catalysts[97-99] (this aspect was mainly developed out of the laboratory[99])

• reversible dehumidificators[100,101].

All these studies (and many others) are just at their very beginning and deserve a deep attention for proving more and more that MOFs and PCPs are among the best multimaterials ever evidenced. For that, clever and creative chemists are necessary, and they exist !... Indeed, always at the laboratory scale, a new and rich tendency is currently exploding: the technological use of these solids in microstructures through a clever miniaturisation of the processes. For these materials, it represents the transition from science to technology. Mainly developped for rigid PCPs, this requires a process optimization (choice of the good material), followed by engineering (a careful control of the geometry of the material and a tuning of th eproperties for the desired application), and finally an integration into a useful platform (which means the connection with other materials and components). Some results are already striking. Most of them are enumerated in a recent remarkable review by Falcao *et al.*[102].

4. The onset of real applications of flexible solids. Perspectives.

Indeed, there is a gap between interesting properties evidenced at the laboratory scale, which could *potentially* find applications in several domains, and real applications at the industrial scale. Indeed, global trends that influence our civilization and economy are essential. A growing world population, an increasing demand on energy and climate protection implies important innovations in the domains of energy, energy savings, environment and health. Due to their properties, detailed above, MOFs and PCPs can, in the future, play a major role in these domains.

To reach such an objective, this implies, before any production, the upstream verification of some criteria on both flexible and rigid solids :
• the non-toxicity of the chosen solids ;
• the reliability and the high yield of their syntheses ;
• the test of their various stabilities (temperature, humidity,chemistry) at the laboratory scale ;
• the low cost of the precursors and solvents employed in the reactions ;
• their ability to scale-up from the gram to 100g at least, through the verification of the invariance of the properties for increasing amounts of solid ;

• their easy shaping (nanoparticles, thin films…) for dedicated applications (health, sensors…).

Among the thousands of hybrid porous solids discovered up to now, only a few satisfy these six conditions. It is the merit of the company BASF to have applied these criteria, far before others, to the development of some MOFs and PCPs through international patents[103-106]. Among the solids they produce under the label BASOLITE (MOF-5, HKUST-1…), and through a nice collaboration between us, a particular attention was paid to our aluminum-based solids.

For economical reasons, they currently represent the best compromise between costs, yields and stability[107 and refs therein]. The flexible MIL-53 was the first to be produced industrially (BASOLITE A100) but, undoubtly, the best material is currently the rigid Al fumarate with the MIL-53 topology. It cumulated a room temperature synthesis in water, using Al sulfate as precursor, interesting surface area (> 1,300 m^2/g), short times of reaction, excellent yields (98%) and an outstanding Space-Time-Yield ratio (> 3,600 kg/m^3/day). It is now commercialized at the industrial scale (BASOLITE A520). Its considerable methane storage capacity at room temperature makes that BASF now produces a system storing natural gas for heavy duty vehicles. A prototype of the latter was launched in February 2013 at Ludwigshaften (Fig.21). If methane is stored at 35 bars, the autonomy of the vehicle is ca. 350 km. This allows to think about the use of A520 for the exploitation and the transport of gas shales.

Fig. 21. – *(a) The launch of the BASF prototype equipped with the system of methane storage for vehicles, (b) The pilot plant for the production of A520 ; (c) bulk A520 ; (d) Pills based on MIL-43 (A100) [b, c & d with courtesy of BASF] ; (e) nanoparticles of MIL-53(Fe)[82] ; (f) thin films of optical quality[109-114].*

However, and for the same reasons, projects are in progress focusing PCPs for purification of air and water[100,103]. BASF develops also now the use of flexible MOFs for adsorption of odors and hazardous volatile products contained in air. Moreover, we have shown that our Al-based products can perfectly reversibly adsorb hydrogen sulfide[77], which could be used for the purification of natural gas from H_2S for a potential substitution to amine treatments.

Finally, all these above properties and applications of flexible solids prove that this class of solids is already very rich, but also consider that flexibility is a bistable system between the NP and the LP forms. However, it was recently shown by J.R. Long and us[115] that the concept of flexibility is much more general than bistability. Indeed, a new cobalt(II) pyrazolate presents five steps in the flexible behavior instead of two. They were structurally characterized ; this opens the way for more sophisticated applications, particularly in separation processes.

Notes added in proof :
1. Among the pioneers of flexibility, but in another way, K. Kaneko and his ELM Frameworks must also be mentioned[116] ;
2. Concerning the extreme sensitivity of flexible solids to a stimulus, the paper of Sheveleva *et al.*[117] is particularly illustrative. The EPR study of the introduction of extremely small amounts of stable radicals (1 in 1,000 cells of MIL-53(Al)) proves that these radicals can act as sensitive nitroxide spin-probes for the tiny modifications of the crystalline state.

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Giant structural flexibility is a characteristic of organic-inorganic frameworks. This perspective describes its history, its behaviours, the analysis of its structural reasons at its consequences in terms of properties and applications.