EXECUTIVE SUMMARY

Gérard Férey is a Member of the French Academy of Sciences and of other prestigious foreign Academies. Awarded by the Gold Medal 2010 of CNRS, his achievements concern several domains of the chemistry of Materials Science, including inorganic fluorine chemistry, magnetically frustrated transition metal fluorides, but the part of his activity for which he has an international recognition is devoted to porous solids, inorganic and hybrid (MOFs) as well. In this last domain, he has received numerous prestigious international awards.

Compared to the other pioneers of the theme, mainly interested by synthesis, structure and adsorption properties, his integrated approach is unique. It ranges from genesis to properties and applications of this new class of solids through their mechanisms of formation and the structural prediction of these solids. This strategy first includes the creation of a large number (>150) of new structural types of crystallized porous solids (this excludes the amorphous mesoporous inorganic materials), fully characterized structurally, and internationally known as ULMs (ULM stands for University Le Mans) for the inorganic materials, and MILs (Materials of Institut Lavoisier) for hybrid organic-inorganic porous solids (MOFs). In the recent years, these solids have become strategic materials from the economical and societal points of view.

This first aspect illustrates his exceptional chemical originality and creativity, conjugated with the constant need he has to elucidate by various *in situ* methods (diffraction, NMR, EXAFS, IR) and to explain *at the molecular scale* both the different steps of the formation of these solids and the new properties interesting the different domains of applications of these solids, with a special emphasis on those useful for the society (energy, energy savings, environment and health).

The second step of his strategy was to go far beyond the usual habits of the community by looking, in a chemical physics approach, at the mechanisms of formation of these phases during their hydrothermal synthesis (200°C, 30 bars). The numerous *in situ* studies in real time (NMR *in-* and *ex-situ*, EXAFS, IR, synchrotron diffraction) that he developped provided the explanation of what happened within the autoclaves during the reaction. The formation mainly depends on the structure of the inorganic brick in the precursor. Either it is kept during the reaction (simple case) or is the object of structural modifications (general case) which were identified during the reaction, Whatever the situation, it was proved that the final oligomeric brick in the solution, just before precipitation of the solid, is identical to the brick observed in the resultant solid and can therefore be considered as the last efficient 'reactive' species leading to the solid. This important result is essential for reaching, in a rational way, the possibility of discovering 'tailor made' porous solids based on these bricks as soon as their connection with the chosen organic linkers (mainly polycarboxylates) is known (*Chem. Mater.* to appear in February 2014). These organic linkers and their lengths also allow to tune the dimensions of the pores.

Beside this fundamental conclusion, *in situ* methods provided an interesting result. They indeed allow to determine the *real* pH and evolution of the concentrations during the reaction at 200°C and 30 bars. Completely different from the usual room temperature conditions (for pure water : pH=5 at 25°C and 5 at 200°C), this result implies that the reactivity conditions are specific, and not an extrapolation of what happens at 25°C.

The third stage of his integrated approach concerns the prediction of the possible structures. For that, knowing the geometry of the chosen 'brick', he successfully created a computer simulation programme (AASBU or Automated Assembly of Secondary Building Units) able to identify all the possibilities of 3D connection between the inorganic brick and the chosen linker, and to give the crystallographic characteristics of each possible structure. Once classified by decreasing lattice energies, the programme provides only a few (3-4) 'reasonable' structures within which the experimental solution is always found. This method therefore allows the structural prediction of new porous solids, and simultaneously restricts the structural study, before refinement, to just a comparison between theoretical and experimental X-Ray powder patterns.

From this academic approach, Férey may be considered as the architect and the designer of the porous matter. He has opened the '*black box*' and paved the way for a rational prediction and discovery of new porous solids. Two examples illustrate the success of this strategy :

- the prediction and then the discovery of the two first crystallized mesoporous hybrid solids MIL-100 and -101with huge cells (380,000 and ca. 700,000 Å^3 respectively, which present cages with accessible diameters of 25 and 29Å for the first and 29 and 34Å for the second through large windows (up to 16Å)). Without the combined approach, it would not have been possible to reach the structures in the observed absence of single crystals.

- The discovery of the phenomenon of 'breathing' porous matter (simultaneously with S. Kitagawa in 2002). After, he was alone to deliver the molecular explanation of this strange behaviour and establish the structural rules for possible swelling. The latter can reversibly reach, for example, a 300% volume increase under the effect of an external stimulus (MIL-88). Initially considered as a laboratory curiosity, this concept has become recently a new topic in itself owing to the applications (see below) it implies in several fields.

Beside his chemical creativity (more than 150 new structural types discovered up to now), Férey initiated new properties for these solids, beside the classical ones like adsorption. For that, he played simultaneouly or independently on the three characteristics of the porous solids : (i) the skeleton which contains the metallic species, (ii) the internal specific surface and (iii) the pores. Moreover, in his strategy, he also took into account a selection of criteria aiming at ***useful*** materials, which means the search of :

- very large, tunable and accessible pores (for storing large amounts of guests) coupled with high specific surfaces (for catalysis),
- thermally and environmently stable solids, non toxic and biodegradable,
- easy preparation in large amounts (scale-up and industrial production),
- facile shaping (bulk, pills, thin films, nanoparticles) adapted to the desired application,
- cheap precursors for low-cost industrial production.

In terms of new properties, he pioneered several breakthroughs. Playing on the **skeleton** (by the introduction of 3d and 4f transition metals), he was the first to discover magnetic porous solids (even ferromagnetic), to generate both electronic and ionic conduction in the usually insulating MILs (for use as electrode materials), and to show that 4f-doped MILs exhibit high luminescence effects and, for the first time, '*antenna*' effects between the ligand and the rare-earth, a property useful for UV sensors.

Playing on the **specific surface** (which can reach in his case close to 6,000 m^2/g) and its engineering, he showed that his MILs can be useful for energy savings since they act as good catalysts, their performances being enhanced by confinement effects, but also as efficient separating agents (CO_2/CH_4; propane/propylene at 25°C…) by creating unsaturated metal centers or mixed-valency on the inorganic parts of the internal surface.

Finally, playing on the **pores** and the tunability of their dimensions, he used both his mesoporous MIL-100 and 101 with huge pores and the flexible solids MIL-53 and MIL-88 for introducing many kinds of species in the pores.

When gases are concerned, he showed that activated MIL-101 is one of the few materials able to store at 77K large amounts of hydrogen (6.1 wght%) for energy purposes and, by far, the best for storing CO_2 at room temperature (390 vol/vol). Moreover, in terms of efficient separation of gas mixtures *at room temperature* (propane/propene, but also CH_4/N_2, O_2/N_2, for which, at variance to other adsorbents, pure N_2 remains trapped in the pores), he pioneered and explained the use of cationic unsaturated sites (CUS) on the metal sites of the framework.

It is also by using the flexible MIL-53 (now produced at the industrial scale) and its extraordinary sensitivity to external stimulii that he is the first to have explained and quantified the atomic reasons of the physisorption of CO_2 and CH_4 by hybrid porous solids (including its dynamic aspects) by the recourse to several complementary *in situ* techniques and to molecular dynamics.

For catalytic applications, he also succeeded both to introduce molecular species like polyoxometalates and to generate *in situ* nanometric metallic aggregates of noble metals by reduction of adsorbed precursors within the pores. These species and confinement effects strongly enhance the catalytic properties.

The use of the pores as nanovectors for drug storage and delivery is his last breakthrough. It is promised to tremendous developments since it concerns health, and because the drugs chosen by Férey are important antitumoral and anti-retroviral ones, active against leukemia (busulfan), breast and kidney cancer (Doxorubicin) and HIV (AZT-TP). Indeed, if compared to the currently used nanovectors (liposomes, which store small amounts of drugs (1-5g of drug /100 gr of liposome, delivered in one day), non-toxic Fe-based MILs, in a nanoparticule form, not only store much larger amounts of these drugs (20-40g of drug /100 gr of MIL) but deliver them in 5-14 days, depending on the drug. Moreover, their non-toxicity has been proved by *in vitro* and *in vivo* tests, and the choice of iron makes that these solids are active in magnetic resonance imaging. The combination of all these features (large storage, long-time delivery, imaging activity) currently opens the way to a new branch of molecular medecine « ***theragnostics*** », which combines in the same nanovector diagnostic and therapy, paving the way for a personal treatment of patients.

The final step of the achievements of Férey concerns the industrial relations he initiated. The high reproducibility of his rational syntheses, the stability, the easy scaling-up and the exceptional performances of his solids have attracted the interest of several companies, particularly BASF which, in collaboration with Férey, is now able to produce daily several tons of some of his products. Moreover, very recently, in 2013, they launched the first car feeded with natural gas, which is stored inside one of the aluminum-based MILs. Its autonomy is above 400km.

His achievements have led to ca. 600 papers highly cited in the best journals (h :94, > 44,000 citations), 14 patents and many plenary lectures in the international symposia. Beside, he has received numerous famous international awards emanating from most of the scientifically developped countries (see CV).

Finally, even if it is not purely scientific, the action of Férey toward the information of young people and adults about chemistry (close to 300 meetings in three years) must be noted. He is conscious of the importance of convincing the public of the key role of chemistry for the future and has begun a crusade in France on this point, with now the help of all the components of the French community of chemists (industrial and academics) that he gathered by creating the association « Ambition Chimie », in order to change the bad image that chemistry has currently in France.