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Journal of Fluorine Chemistry 128 (2007) 413–422

JOURNAL OF FLUORINE CHEMISTRY

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Review

Crystalline oxyfluorinated open-framework compounds: Silicates, metal phosphates, metal fluorides and metal-organic frameworks (MOF)

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Received 11 September 2006; accepted 14 September 2006

Abstract

This contribution is dedicated to a short overview on the utilization of fluorine for the preparation of crystalline microporous frameworks including different families of solids: zeolites, metal phosphates and metal-organic frameworks (MOF-type). Beside the silicates compounds, this presentation is focused on the different types of fluorinated aluminum or gallium phosphates hydrothermally obtained in the presence of organic structure-directing agent or templates. The structural features of aluminum fluorides synthesized with amines are also detailed as well as the influence of fluorine in the synthesis of the metal-organic frameworks involving trivalent metals. The role of fluorine is described for the hydrothermal synthesis of the different classes of materials. Fluorine is known for playing the role of mineralizing agent and favors the formation of well crystalline phases. The use of HF modifies the pH of the reaction, which allows for the insertion of additional metallic cations on the mineral network. From the structural point of view, fluoride anions can be located within small cavities of the 3D framework and interactions with metals T (T = Si, Al, Ga, . . .) are often observed, resulting in the coordination change (from tetrahedral unit TO_4 to trigonal bipyramid TO_4F or octahedron TO_4F_2). Several configurations are found for fluorine and it seems to favor the stabilization of the specific cubane-like building unit (D4R), in which it is trapped, or participates to the coordination sphere of the metal atoms with bridging or terminal bondings. In general, new three-dimensional topologies with extra-large pores are obtained. The synthesis of purely aluminum fluorides with structure-directing agent is considered but only molecular or low-dimensional structures (chain-like or layered) compounds have been described. Fluorine is also used as a mineralizing agent for the preparation of well crystalline porous aluminum or chromium carboxylates and it was observed to partly substitute the aquo ligands in the giant pore of the compound MIL-100.

Keywords: Microporous compounds; Fluorine; Zeolites; Aluminum phosphates; Gallium phosphates; Metal-organic frameworks

Contents

1. Introduction

The microporous materials are still intensively studied because of the industrial impact in the field of catalysis, gas selective adsorption, molecular sieving and ion-exchangers [1–3]. The most known family of porous solids is zeolites, which are crystalline hydrated aluminosilicates inserting alkaline or earth alkaline cations (discovery of the natural mineral stilbite by Cronstedt in 1756). These compounds exhibit three-dimensional structures based on the connection of channels and cavities with well-defined sizes similar to small

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doi:10.1016/j.jfluchem.2006.09.009

organic molecules (<15 Å). From the structural point of view [4], the inorganic network is built up from the assembly of corner-shared tetrahedral units TO_4 (T = Si or Al), which generates open-frameworks with defined windows bounded by 8, 10, 12, 14 T atoms (or 18, 20, 24 for other families such as metal phosphates). These solids are denoted with a three capital letters code assigned by the *International Zeolite Association* [4]. They are typically obtained from hydrothermal reactions under mild conditions (autogenous pressure, $T < 250\ ^{\circ}C$) in basic medium, which is required for the reactivity of silica in aqueous systems. The zeolites are considered as thermodynamically metastable forms compared to the dense quartz-like variety of silica, but the thermal stability may reach 1000 °C. The combination of the different chemical and physical properties (porosity, thermal stability, wide chemical modification with elements substitution) is of great interest for the industrial processes.

The search of new porous architectures is a continuous quest and new chemical systems are still explored [5]. For the last 50 years, successive breakthroughs occurred [6]. The alkaline cations coming from the inorganic base (NaOH, KOH, etc.) were commonly used by chemists at the beginning of 20th century for the hydrothermal reaction in order to reproduce the different varieties of zeolites observed in nature and they were then progressively replaced by basic organic molecules such as quaternary ammonium salts or amines [7,8]. The latter plays the role of structure-direction or *template* (called SDA for Structure-Directing Agent), allowing the organization of porous three-dimensional networks. This substitution led to the formation of new open-frameworks depending on the various geometrical configurations of the organic species (linear, spherical, branched molecules) and also the decrease of Al/Si ratio of the aluminosilicate networks and purely microporous silica could be obtained (e.g. silicalite-1 [9] corresponds to the pure silica form of the zeolite ZSM-5). In the 1980s, Flanigen and co-workers then successfully discovered a new series of microporous compounds, the aluminophosphates [10] ($AlPO_4$-n, n refers to a structural type), from the observation of the structural analogy between the dense polymorphs of silica (quartz) and aluminum phosphate (berlinite). By varying the nature or geometry of the organic species and the synthesis conditions, some new three-dimensional networks have been reported, some of them are identical to those of the aluminosilicates zeolites, e.g. $AlPO_4$-37 is the analogue of faujasite (FAU), $AlPO_4$-34 is the analogue of chabazite (CHA). Typically, the structures of these solids which have Al/P ratios of 1, are based on the strict alternation of PO_4 and AlO_4 tetrahedral units. Since then, much interest has been concentrated on the preparation of open-framework metal phosphates with new zeolite-like architectures. These studies were then extended to the use of the other elements of the periodic table such as the metals of the column IIIA (Ga, In) and IVA (Ge, Sn), the transition metals (mainly 3d) [5]. More recently, a new class of porous solids involving hybrid organic–inorganic frameworks based on metal carboxylates (MOF or metal-organic framework [11]) was revealed to be very promising for small molecules storage.

Typically, the microporous materials are based on an oxide matrix (SiO_2, $AlPO_4$, etc.) and the utilization of fluorine for their preparation is quite recent. Pure silica zeolites are generally synthesized at high pH in the presence of hydroxide ions but also at lower pH in the presence of fluoride anions. The latter method was pioneered by Flanigen and Patton [12] in 1978 with a publication of a patent describing the hydrothermal formation of zeolite silicalite-1 (MFI) in a nearly neutral pH medium with fluorine. The aim was to study the possibility of introducing mineralizing anions such as fluoride species, substituting hydroxide anions coming from the inorganic or organic base in order to decrease the reaction pH. Since then, the so-called fluoride route [13,14] was developed by different research groups for the synthesis modification of zeolite-like materials under hydrothermal conditions and was one of the most productive methods for the elaboration of compounds with novel three-dimensional architectures, some of them incorporating the element fluorine.

2. Silicates and related compounds

The use of fluorides anions was extended to the hydrothermal synthesis of different types of zeolites in the eighties by Guth and Kessler [15,16] at the University of Mulhouse (France) who brought a significant contribution in this field. They assigned specific roles for fluorine: first of all, it is a remarkable mineralizing agent and contributes to the formation of homogenous and well crystalline phases. It seems that the nucleation rates and the crystal growth kinetics are slower favouring fewer crystal defects and improving the crystallization processes. In some cases, single crystals of zeolites with very large sizes are observed with dimensions in the range 0.4–5 mm, involving non-aqueous solvents (pyridine//HF mixture) [17,18]. However, the addition of fluorine in hydrothermal medium drastically modifies the reaction pH, which can be neutral or slightly acid. In these pH conditions, the solubility of silica and alumina is very low, but Guth and Kessler suggested the formation of soluble fluorinated complexes (e.g. $[SiF_6]^{2-}$) preventing the precipitation of the starting oxides reactants and allowing the crystallization of zeolites at lower pH (5–9). Moreover, the relative instability of silicon fluorides species favours its incorporation into the inorganic network and led to rich silicon phases. The fluoride method was also used for the insertion of other metals (B, Fe, Ga, Ge, Ti, etc.), which are able to form low soluble species (rapid formation of hydroxides) or does not react at high pH.

The fluoride ions are also incorporated into the microporous aluminosilicates structures and the syntheses of high-silica zeolites obtained in fluorine medium were thoroughly investigated. For example, in silicalite-1 (MFI) [19], the fluorides anions were located with accuracy within the pore system of the inorganic network (Fig. 1). It was found that fluorine resides in unusual positions, within small cavities including 4-ring units (ring containing four silicon atoms) and preferentially interacts with some silicon atoms. This induces the distortion of the tetrahedral coordination (SiO_4) and trigonal bipyramid surroundings (SiO_4F) have been reported.

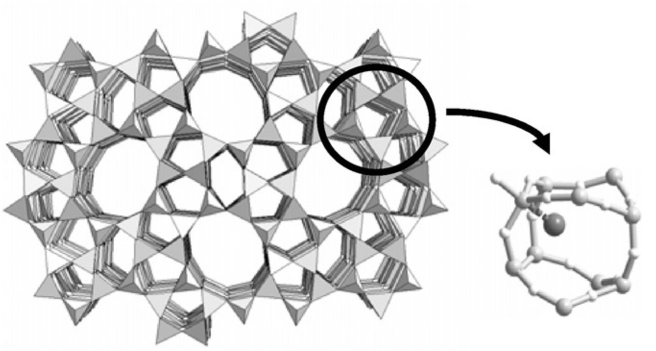

Fig. 1. Polyhedral view of the zeolite silicalite-1 (silica form of ZSM-5, type MFI) with the detail of the position of the fluoride anion trapped in the small cavities [$4^15^26^2$] delimited by the 5-ring windows. Fluorine preferentially interacts with one silicon atom ($d_{Si–F}$ = 1.915(3) Å) inducing the modification of the coordination (trigonal bipyramid SiO_4F instead of tetrahedral SiO_4).

This structural feature is observed by X-ray diffraction [20] with a Si–F distance of 1.915(3) Å and NMR experiment [21], which indicated a slightly longer bond (2.07(3) Å). Similar situations are encountered in many aluminosilicates such as ferrierite (FER), chabazite (CHA) [22], with Si–F distances in the range 1.7–2.1 Å. This unique configuration of fluorine induces NMR specific signatures with chemical shifts ranging from −150 to −140 ppm for ^{29}Si and −78 to −56 ppm for ^{19}F. Moreover, fluorine is also observed to orientate the formation of specific networks of zeolites such as ITQ-4 [23], ITQ-3 (ITE) [24], SSZ-42 (IFR) [25] or SSZ-55 [26] prepared by Corma (Valencia, Spain) or Zones (Chevron-Texaco, USA). In other topologies (octadecasil-type AST [27], ITQ-12 (Fig. 2) [28], ITQ-13 [29], etc.), fluorine is encapsulated within small cubic D4R cages (double 4-ring containing eight silicon atoms at the corner of a cube T_8O_{20}). It is characterized by chemical shift values close to −38 ppm (^{19}F). In absence of fluorine, these solids are not obtained. Fluorine exhibits a stabilizing role for the construction of some frameworks and would also play the role of structure-directing agent or *template*, similar to the amine molecules. In contrast to the zeolites prepared in basic medium with OH^- ions as mineralizing species, the high-silica phases made in the presence of fluoride anions exhibit crystallites with much fewer lattice defects. This phenomenon would be due to the encapsulation of fluorides species in the mineral framework, which compensate the positive charges of the organic *template*. This has a direct effect on the decrease of the Si–O– species concentration in the crystal bulk which avoids the stabilisation of Si–OH type defaults and prevents from the formation of $Si–O^- \cdots OH–Si$ bonding [30].

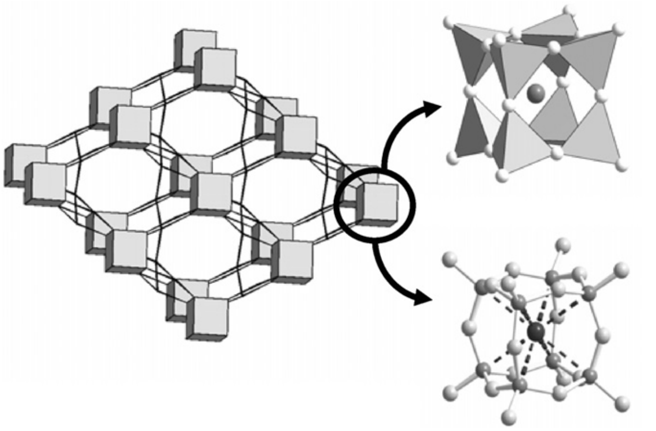

Fig. 2. view of the zeolithe ITQ-12 (ITW) showing the arrangement of the cubic building units of D4R type [46] encapsulating a fluorine atom.

The occurrence of the cubane-like D4R building unit stabilized by fluoride anions is also a structural feature found in the series of mixed silicon–germanium compounds. Corma (Valencia, Spain) and Patarin (Mulhouse, France) described new architectures with systems of inter-crossing channels bound by 10, 12 or 14 TO_4 units (ITQ-n materials [28,31–33], IM-10 [34], IM-12 [35]). It seems that the addition of germanium together with fluorine favours the formation of new open-frameworks based on the D4R units (^{19}F NMR signature at ≈−10 ppm), whilst the pure silica analogues do not exist for some of them.

3. Fluorinated aluminum or gallium phosphates

Following the discovery of the synthesis of microporous crystalline aluminophosphates, $AlPO_4$-n, by Flanigen and coworkers [10], Kessler (Mulhouse, France) applied and developed the fluorine route to the preparation of metal phosphates with new zeolite-like architectures in the presence of organic *template* [36,37]. His work was focused on the synthesis of aluminum or gallium-based open-framework solids and this was then investigated by other groups (Cheetham [38,39], Santa Barbara, USA; Morris [40–42], St. Andrews, UK; Nenoff [43–45], Albuquerque, USA; Férey [46,47], Versailles, France).

The first attempts were focused on the formation of the aluminum phosphates and the syntheses of known structural types have been reproduced. However, aluminum offers three types of coordination polyhedra (tetrahedron, trigonal bipyramid and octahedron) in contrast to silicon with only the tetrahedral surrounding SiO_4 found in zeolites. Fluorine usually belongs to the mineral framework and it induces a structural behavior with aluminum similar to the silicon with a surrounding change. It is observed a five- or six-fold coordination with AlO_4F and AlO_4F_2 environments. This is the case of the aluminophosphate SSZ-51 (SFO) [48] with trigonal bipyramid AlO_4F units with a Al–F–Al corner-link. The situation is also encountered in the $AlPO_4$ forms of chabazite (CHA) [37,49,50] and gismondine (GIS) [51], where it exists a building unit with two aluminum centers in octahedral coordination (instead of the tetrahedral one in the aluminosilicate forms). The bi-octahedral motif has a common edge of fluorine ($Al_2O_8F_2$). As reported in silicates, fluoride anions can be encapsulated within small cavities of the $AlPO_4$ network and stabilize specific configuration such as the cubic-like D4R cage. Fluorine would play the role of co-structuring agent besides the organic template and interacts weakly with the cations of the 3D framework. Two examples are the $AlPO_4$-

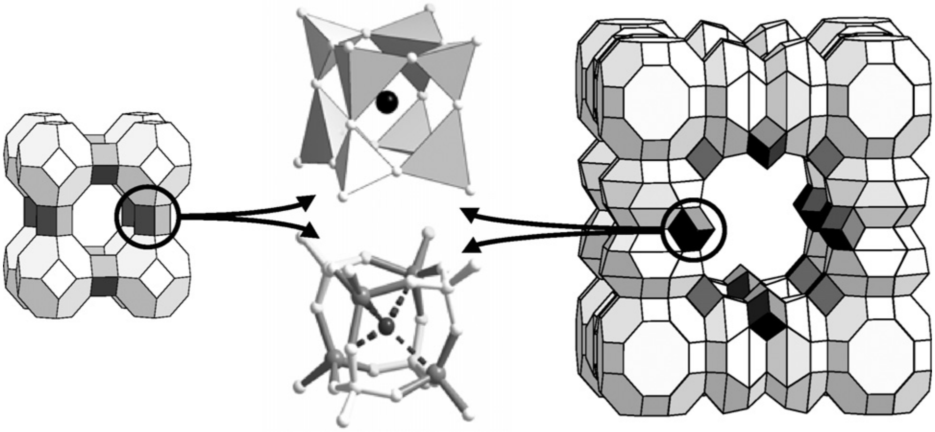

Fig. 3. Polyhedral views of the structures of the gallium phosphates GaPO-LTA (left) and cloverite (right) showing the cubic cage (D4R) inserting the fluoride anions. These two topologies are described from the D4R unit containing four PO_4 and GaO_4 groups in a strict alternation.

16 (AST type) [52] or LTA-type $AlPO_4$ [53], constructed from D4R units trapping fluoride species.

However, more attention has been paid on the study of the amine–gallium–phosphate system in the presence of fluorine and a large number of new network topologies has been reported. Gallium exhibits crystal chemistry features similar to aluminum with a flexible coordination ranging from four to five or six. It results in the formation of complicated structures, which drastically differ from the aluminosilicate structures for some of them. The origin of this work is the discovery by Kessler in 1991, of the fluorinated gallophosphate cloverite (–CLO) [54], which has one of the largest 3D pore system with channels delimited by 20 TO_4 units (Fig. 3). Its structure is built up from the assembly of D4R blocks trapping fluoride anions. These blocks are arranged in the manner to form three-dimensional inter-crossing channels with clover shape of 13.2 Å diameter. The LTA-type $GaPO_4$ [55] (Fig. 3) or the gallium phosphates Mu-1 [56], Mu-2 [57], Mu-3 [58], Mu-5 [59] and Mu-15 [60] were obtained by the group of Mulhouse (Patarin) and all these frameworks include the D4R units hosting a fluoride atom. Such a cubic building block was also described in other $GaPO_4$ solids reported by Morris [61] and Hong [62]. It was suggested that fluorine plays a templating role for the stabilization of the specific cubane-like D4R cage in these compounds. Fluorine is easily observable by ^{19}F NMR spectroscopy with a chemical shift value close to -70 ppm (-90 ppm in the $AlPO_4$ series). A thorough analysis of the unusual configuration of fluorine within the D4R cavity has indicated that this atom is often off-centered and preferentially interacts with one, two or three gallium atoms, inducing geometrical distortions of the gallium coordination polyhedra (the environment becomes a trigonal bipyramid instead of a tetrahedron). In the gallium phosphate ULM-18, detailed NMR experiment [63] has also shown the occurrence of an isolated ‘‘HF’’ molecule inserted in the D4R instead of the expected fluoride anions F^-. This unique configuration was investigated by means of DFT calculations, which confirm the existence of the H–F molecule within the D4R [64].

On the other hand, fluorine can belong directly to the coordination sphere of gallium with coordination changes similar to aluminum: GaO_4F (trigonal bipyramid) or GaO_4F_2 (octahedron) instead of GaO_4 (tetrahedron). This was well illustrated in the series of ULM-n (University Le Mans) and MIL-n (Materials Institute Lavoisier) or Mu-n (Mulhouse) compounds obtained in the chemical system Ga_2O_3–H_3PO_4–HF–amine–H_2O, reported by the Férey's and Patarin's groups. The structures of these phases can be described from distinct building units containing four (tetramer: Ga_2P_2), six (hexamer: Ga_3P_3) or eight metallic centres (Ga_4P_4 or D4R). It was shown that fluorine has the role of ligand with the formation of μ_2-F bridges between gallium atoms with five- or six-fold coordination. A statistical disorder OH/F is observed for some cases. Fluorine was found to direct the formation of a specific secondary building unit (SBU), $Ga_3(PO_4)_3F_2$, containing one octahedral unit GaO_4F_2, two trigonal bipyramids GaO_4F and three phosphate groups PO_4 (Fig. 4). Within the building cluster, two fluorine atoms bridge the three gallium atoms. This Ga_3P_3 motif can be used as a Lego® brick for the construction of open-framework solids. Depending on its connection mode and orientation or connection with additional building units (e.g. D4R), several inorganic networks are generated. Some of them exhibit three-dimensional structures based on 10-(ULM-3 [65] and ULM-4 [66]) 12- (TREN-GaPO [38,67]), 16- (ULM-5 [68] and ULM-16 [69]) or 18-ring channels (MIL-31 [70], MIL-46 [71] and MIL-50 [72]). A structural correlation of the SBU type could be made as a function of the pK_a values of the different diamines [46]. Fluorine may be also involved in a terminal bond with shorter Ga–F distances as found in $GaPO_4$-CJ2 [73] (1.903 Å), TMP-GaPO [74] (1.79 Å), Mu-3 [58] (1.824–1.862 Å), Mu-15 [60] (1.86 Å) Mu-23 [75] (1.854–1.885 Å) and Mu-28 [76] (1.80–1.86 Å). Due to its higher electronegativity, it preferentially interacts *via* strong hydrogen bonds with the ammonium groups of the amine molecules. It acts as an anchoring point of the inorganic framework for the structure-directing molecule. It results in longer Ga–F distances compared to the Ga–O ones (Ga–F $\approx$ 2.0 Å and Ga–O $\approx$ 1.90 Å). In general, the negative charge of fluorine, which is incorporated into the inorganic framework, is compensated by the positive charge of the amine, usually present under its protonated form in the cavities.

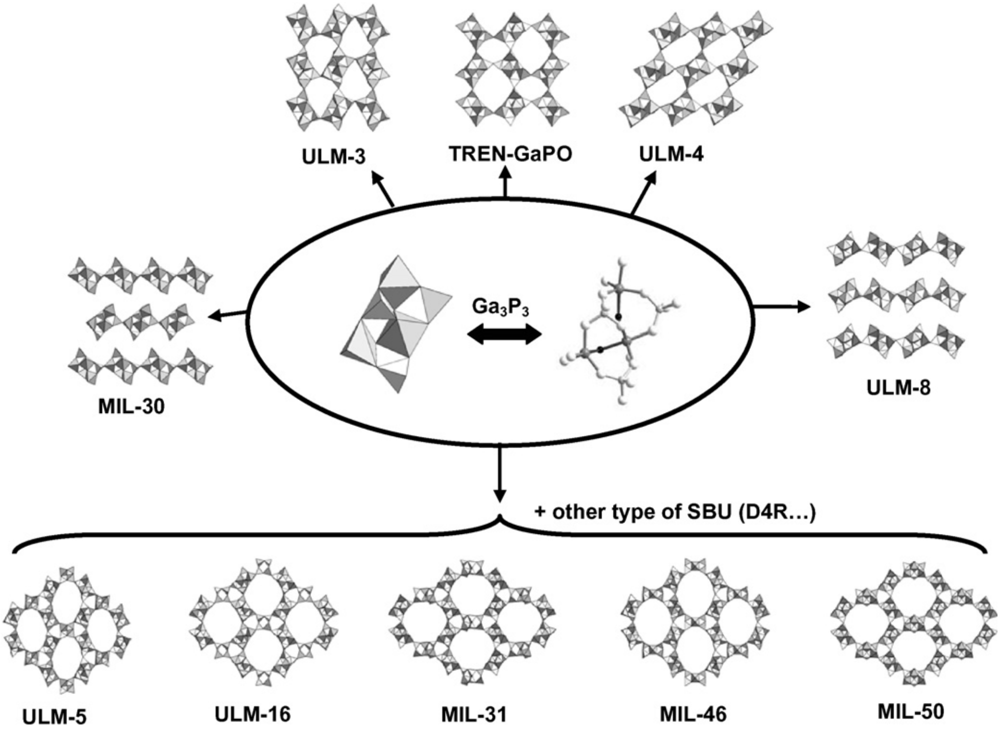

Fig. 4. Polyhedral representation of the series of the fluorinated gallium phosphates open-frameworks built up from the hexameric motifs Ga_3P_3. Fluorine is located in the bridging position between two gallium atoms with coordination V (trigonal bipyramid) and VI (octahedron). ULM-n for University Le Mans; MIL-n for Materials Institut Lavoisier; Mu-n, Mulhouse.

Despite the structural diversity observed in the different fluorinated GaPOs, most of these materials are thermally unstable upon removing the organic template (by heating process at 350–400 °C). Indeed, fluorine seems to direct and stabilize the formation of inorganic frameworks (D4R units, $F\cdots H_3N$–R interactions), but it is a major drawback for the departure of these molecular species since the removal of fluorine induces bond breakings followed by the collapse of the structure. The framework stability of such solids was estimated by means of computational method using lattice energy minimization calculations. These theoretical studies [77] indicated that the structures are not energetically viable and agree with the experimental data showing the decomposition of the solid after removal of the template.

Some recent studies were also focused on the synthesis of aluminum [78,79] or gallium [80,81] phosphonates (corresponding to the R–PO_3 moiety, where R = alkyl, benzene, etc.) giving rise to organic–inorganic hybrid architectures. In most of cases, layered structures with the organic group pointing toward the interlamellar space have been reported except the three-dimensional open-framework compounds AlMepO-α [82] and AlMepO-β [83] obtained with the methylphosphonic acid The use of diphosphontate groups usually lead to the formation pillared layered compounds. The fluorine route was also applied for the hydrothermal preparation of aluminum phosphonates and fluoride ions were found in the aluminum octahedral surrounding with the AlO_4F_2 motifs, resulting in the formation of infinite –Al–F–Al– chains. Zig-zag chains with the –*trans*–*cis*– sequence or straight chains with the –*trans*–*trans*– sequence are thus observed in the different fluorinated layered aluminum phosphonates [84–87]. Similar structural arrangements are encountered in the parent family of gallium phosphonates [84,88,89]. Fluorine was also used for the stabilization of aluminum phosphonate isolated clusters based on tricyclic capped six-ring moieties and the cubic-like D4R unit [90].

4. Organically templated aluminum fluorides and derived solids

Beside the intensive investigations for the synthesis of new microporous based on silicates or metal phosphates, the preparation of purely fluorinated inorganic open frameworks in the presence of organic structure directing agent was less studied. In early 1990s, the use of quaternary ammonium cations or amines was reported for the formation of organic fluoroaluminate salts [91,92], which are thermally decomposed into different crystalline metastable polymorphs of AlF_3. For instance, the thermolysis of $[(CH_3)_4N)][AlF_4]\cdot H_2O$ or $[C_5H_5NH][AlF_4]$ under vacuum gave the t-AlF_3 [93] and η-AlF_3 [94] forms, respectively. Depending on the AlF_3 structure, this material may find applications in catalytic processes in fluorochemicals manufacture and offer novel ozone-friendly alternatives to the production of chlorofluorocarbon (CFC) [95,96].

Following the strategy developed for the formation of microporous aluminum or gallium phosphates, the reactivity of a wide variety of amine molecules was tested but it was found that only low-dimensional networks were obtained in the fluoroaluminates family. This would be partly due to the

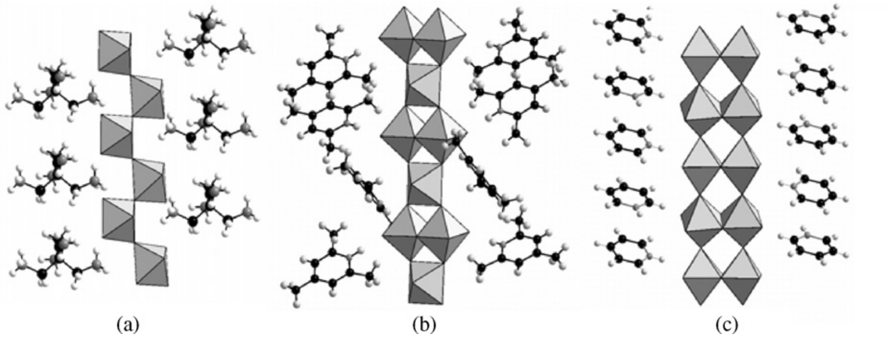

Fig. 5. Examples of chain-like aluminum fluorides (grey octahedra) intercalated by amine molecules with different connection modes: corner-sharing (a) $[AlF5]^{2-}$ with the pentaerythrityl-tetramonium cations [98] and mixed corner and edge-sharing (b) $[Al2F8]^{2-}$ with the 2,4,6-trimethylpyridinium cations [105] (c) $[Al2F8]^{2-}$ with the pyridinium cations [106].

exclusive octahedral surrounding commonly observed for aluminum with fluorine, which seems to limit the size of the network cavities because of the number of linking ligands: a greater number of connections occurs in the octahedral coordination AlF_6 than in the tetrahedral coordination AlO_4 (or SiO_4, PO_4) encountered in zeolite-like materials. Indeed, most of the organically templated aluminum (or gallium) fluorides correspond to the isolated anions $[AlF_6]^{3-}$ [97,98] (or $[GaF_6]^{3-}$ [98,99]) connected to each other through a hydrogen bond network of the counter-cationic amine species. However, recent works from the groups of Zou (Sweden) and Leblanc & Maisonneuve (France) revealed new various isolated clusters such as $[Al_3F_{12}]^{3-}$ [100], $[Al_7F_{30}]^{9-}$ [101] and infinite chains $_\infty[AlF_5]^{2-}$ [102], $_\infty[Al_7F_{29}]^{8-}$ [101] (Fig. 5). In these polyanions, the AlF_6 octahedra are corner-shared to each other as it is usually observed for the crystalchemistry of the aluminum fluorides. Edge-sharing connection mode is scarce and is observed only in a few phases, most of them obtained with pyridine. Five different structural arrangements of edge-sharing octahedral building units are reported in the isolated molecular clusters $[Al_2F_{10}]^{4-}$ [103,104], two types of chain-like moieties $[Al_2F_8]^{2-}$ [105,106] and a layered solid $[Al_3F_{10}]^-$ [107] (Fig. 5). No organically templated aluminum or gallium fluoride arrays with 3D open-frameworks have been described up to now.

Nevertheless, other chemical systems were investigated with elements adopting a tetrahedral surrounding in order to replicate the condensation mode of the SiO_4 or AlO_4 species in zeolites. Only small cations of the first period such as lithium, beryllium or boron are known with a four-fold coordination with fluorine. This idea was particularly exploited by Weller (UK) who reported the formation of different amine-templated lithium beryllofluorides exhibiting three-dimensional open-frameworks [108] or two-dimensional networks [109,110], constructed from the connection of MF_4 (M = Li, Be) tetrahedral units. In contrast, the synthesis of fluorides incorporating larger cations such as uranium [111–117] or thorium [118] were extensively explored in the presence of amine species and chain-like or layered solids were described; one of them consists of U–F sheets with 12-membered rings [117]. Very recently, the scandium–fluorine–amine chemistry system was investigated [119] and a 3D framework similar to that of $Rb_2In_3F_{11}$ was evidenced. With zirconium, an example of 3D structures was also reported in the compound $ZrF_5 \cdot guanidine \cdot H_3O$ [120], containing ZrF_8 polyhedra linked by edges and/or corners.

5. Metal-organic frameworks

The so-called metal-organic frameworks (MOF) materials are an emerging new class of porous solids with promising applications for the small molecules storage (H_2, CH_4, CO_2, etc.) catalysis, separation, molecular recognition, luminescence, magnetism, and conductivity [121,122]. They are characterized by infinite crystalline 1D–3D architectures built up from the assembly of discrete metal (M) centers with functionalized organic ligands containing N- or/and O-donor atoms. Through the formation of M–N–C or M–O–C bondings, it results in extended networks with different degrees of complexity depending on the geometry adopted by the starting organic linker and the coordination type of the metal center. The utilization of rigid multidentate organic linkers (carboxylic acids) derived from the aromatic molecules [11] and metals such as divalent copper, zinc or trivalent chromium led to the production of relatively stable highly porous three-dimensional frameworks with a zeolite type behaviour (BET surface area >4000 m^2/g [123,124]). For example, Yaghi and co-workers recently reported a series of compounds based on zinc benzenedicarboxylates characterized by periodic pores varying from 3.8 to 29 Å [125] and Férey reported two chromium benzenecarboxylate (MIL-100 and MIL-101) with cubic cell parameters of 73–89 Å and giant cavities up to 20,000 Å^3 deriving from the MTN zeolite topology [124,126].

These porous MOF-type compounds are usually prepared by self-assembly processes of predetermined metal-centered building blocks and organic linkers using various synthesis routes such as diffusion or gel crystal growth techniques in organic solvent. The solvothermal method was also developed for the synthesis of organic–inorganic hybrid materials. We recently focused our attention on the hydrothermal synthesis of aromatic poly-carboxylates with different trivalent metals such as rare-earth elements, 3d transition metals (V, Cr, Fe) and p elements (Al, Ga, In). Theses compounds are typically obtained after a hydrothermal treatment of a mixture of metal nitrate, carboxylic acid and water. Different series of solids have been obtained and include, for instance, the MIL-53 [127–129] and MIL-88 [130,131] compounds, exhibiting large swelling effects upon molecules sorption or extra-large pore solids such as the lanthanide carboxylates MIL-103 [132] or the zeotypic MIL-100 [126] and MIL-101 [124]. They are described from infinite *trans*-connected chains of metal octahedra $MO_4(OH)_2$ (M = V, Cr, Al) linked to each other through the carboxylate ligands (MIL-53 [127–129], MIL-61 [133,134], MIL-68 [135], MIL-69 [136]) or μ_3-oxo-bridged trinuclear units composed of octahedra $MO_5(H_2O)$ (M = V, Cr, Fe) isolated to each other *via* the carboxylate linkers (MIL-59 [137], MIL-88 [130,131,138], MIL-100 [126] and MIL-101 [124]). Preliminary adsorption experiments have been reported for the MIL-53 series and they were found to be good candidates for the gas storage of different molecules such as H_2 [139], CH_4 and CO_2 [140].

Problems of samples crystallinity or occurrence of amorphous by-products may be observed after the hydrothermal reactions of some compounds. In this case, the fluoride route was chosen in order to promote the crystal growth of the final products. This technique was particularly applied for the synthesis of MIL-53 with incorporating chromium or aluminum or the chromium carboxylates MIL-100 and MIL-101. For instance, the phase MIL-53 (Al) is synthesized from the mixture of aluminium nitrate, terephthalic acid and water heated at 210 °C for 3 days and a fine white powder is obtained with crystallites of a few micrometres. After adding hydrofluoric acid (with a Al/F = 0.4 ratio), single crystals of 20–30 μm size are observed. Similar behaviour is found for the compound MIL-69 (Al) obtained with the 2,6-naphtalenedicarboxylate ligand; for the aluminum trimesate MIL-96 [141], single-crystal XRD analysis (crystal sizes ≈20–30 μm) was performed from a hydrothermal reaction in fluoride medium. In the structures of MIL-53 and MIL-69, the infinite trans-connected chain of octahedra $MO_4(OH)_2$ are connected *via* the terephthalate (MIL-53) or naphthalate (MIL-69) species, leading to the formation of one-dimensional channel system with free apertures of 8 Å. The hydroxo groups link the metal atoms to each other and the structural characterization revealed that fluorine is not incorporated in the framework by substituting the OH anions.

The situation is slightly different in the giant pore metal-organic framework chromium (III) trimesate MIL-100 (Fig. 6). Firstly, the synthesis of such a solid requires the presence of fluorine as mineralizing agent otherwise poorly crystalline phases are formed. Secondly, fluorine belongs to the inorganic network. The cubic structure of this phase is built up from super-tetrahedral motifs composed of four μ_3-oxo-centered trinuclear units located at the corners of a tetrahedron and linked to each other via the trimesate ligands, being at the faces of the tetrahedron. This is equivalent to the tetrahedral primary building unit MO_4 encountered in the zeolites of $AlPO_4$ compounds and the three-dimensional arrangement of such super-tetrahedral species corresponds to the topology MTN [4] derived from the high silica zeolite ZSM-39. The porous chromium trimesate framework delimits pentagonal and hexagonal windows of 5 and 8.5 Å, respectively, and the internal diameter of the largest cavity is ≈29 Å. The MIL-100 compound has a cationic inorganic network, compensated by a negative default charge, which corresponds to one fluorine atom per three chromium atoms of the trinuclear unit. Fluorine is involved in the terminal bond of the trimeric chromium species and partly substitutes the terminal water molecule attached to chromium. The fluorine amount was estimated from the chemical analysis and quantification of carbon monoxide adsorption experiments [142]. The terminal water species are easily replaced by the CO molecule during the adsorption. The exact F/Cr ratio was measured to be 0.285 (instead of the expected value 0.333) and hydroxo groups are assumed to be present in substitution to fluorine, leading to the chemical formula $Cr_3OF_{0.85}(OH)_{0.15}(H_2O)_2[btc]_2 \cdot 26H_2O$

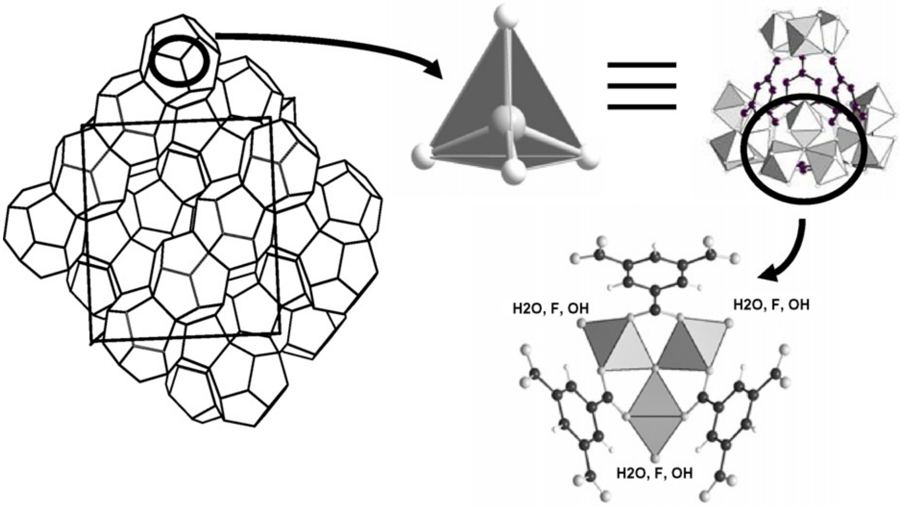

Fig. 6. Structure of MIL-100 (Cr). Representation (on left) of the MTN topology showing the connection of rods composed of dodecahedral cages. Each node of the network corresponds to a tetrahedral unit (SiO_4) in the zeolite ZSM-39 or a super-tetrahedral one in the parent solid MIL-100. The latter consists of four μ_3-oxo-bridged trinuclear motifs located at each corner and trimesate ligand at each face of the tetrahedron. The trimeric unit contains three terminal bondings corresponding to water molecule, hydroxyl or fluorine groups.

(btc = *b*enzene*t*ri*c*arboxylate or trimesate). Moreover, the relative fluorine distribution was determined from the thorough examination of the IR spectra of MIL-100 interacting with CO. The measured intensity of the adsorption triplet bands of ν(CO) at 2207, 2200 and 2193 cm^{-1} indicated the populations of 18, 45 and 37% for 2, 1 or 0 fluorine occurring in the trimer.

In the vanadium terephtalate MIL-71 [143], fluorine was clearly identified and participates to the octahedral coordination sphere of vanadium (III). The structure is built up from corner-sharing $VO_2(OH)_2F_2$ octahedra forming layers (perovskite-type) pillared by the terephtalate ligands. Fluorine/hydroxyl ordering was determined on the basis of the V–F and V–O distances difference.

On the other hand, fluorine may be found attached to the organic part of the carboxylate ligand. A contribution reported such a situation with the use of the molecule 4,4′-(hexafluoroisopropyl idene)-bis(benzoic acid) containing terminal CF_3 groups associated to copper (II) [144]. Although this compound does not exhibit large pores (<5 Å), it is able to adsorb 1%wt of hydrogen under 48 atm at room temperature.

6. Conclusions

Fluorine was typically used as a mineralizing agent in the hydrothermal synthesis for the formation of well crystalline microporous compounds belonging to different families of solids (zeolites, AlPOs, GaPOs and more recently extended to the preparation of MOF-type phases . . .). Fluorine is found to orientate the formation of specific inorganic three-dimensional networks, some of them exhibit extra-large pore systems. This was well illustrated with the series of gallium phosphates cloverite and MIL-50 for example. In some cases, fluoride anions are found to be incorporated into small cubic cavities T_8O_{20} of D4R type (T = Si, Ge, Al, Ga, etc.) or they belong to the coordination sphere of the metal with a modification of its surrounding (from tetrahedron TO_4 to trigonal bipyramid TO_4F or octahedron TO_4F_2). The D4R unit is often observed in novel frameworks, which may offer new potentialities in the area of catalysis (petro-chemistry). Surprisingly, there are very few reports of pure metal fluorides obtained in the presence of organic structure-directing agents. Usually, only low-dimensional networks have been described in the aluminum fluorides compounds. In the case of the new emerging class of metal-organic framework system, fluorine is rarely incorporated into the network although it could be used for the crystallization of product during the hydrothermal treatment.

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