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Un-Assemblable Layered Aluminophosphates from Self-Assembling Structure-Directing Agents: Effect of Fluorine

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ABSTRACT. A new strategy for the synthesis of three new un-assemblable metastable AlPO-based layered framework materials is reported. By using organic molecules with aromatic rings that tend to self-assemble in water solution by establishing π - π type interactions, three new AlPO layered frameworks have been produced with benzylpyrrolidine and its meta- and para-fluorinated derivatives. These new layered materials occlude an extremely large amount of organic material. Interestingly, UV-Visible fluorescence results show that the molecules occluded within the frameworks form supramolecular aggregates, and consequently the crystallization of these structures is strongly dependent on the self-assembly ability of the organic

molecules in water. As a consequence, the ortho-fluorinated derivative, which shows the lowest trend to aggregate in water, is not able to produce a stable self-assembled AIPO framework.

The self-assembly of the organic molecules within the frameworks driven by relatively weak π - π type interactions between the aromatic rings combined with a poor H-bond interaction of the heterocyclic tertiary N with terminal PO groups enable a simple un-assembly (delamination) process of the structures by treating the samples in water.

KEYWORDS: aluminophosphate; supramolecular; self-assembly; fluorine; fluorescence.

Introduction

Nanoporous crystalline aluminophosphates (AIPO), where Si^{4+} and Al^{3+} ions in zeolites are replaced by strictly-alternating Al^{3+} and P^{5+} , were first discovered by Wilson et al. in 1982 [1], and these new materials have yielded a diversity of structural types comparable to that of the previously known aluminosilicate-based zeolites [2]. Usual AIPO frameworks that were initially discovered followed similar bond patterns as those previously observed in zeolites, giving place to neutral three-dimensional frameworks similar to those found in zeolites, but also to other structures found for the first time. The intense research effort applied on the synthesis of these AIPO materials, especially the application of alternative synthetic techniques, such as the solvothermal [3] or ionothermal [4] synthetic routes, and the rich coordination versatility characteristic of Al and P, have yielded a large series of new AIPO-based compounds with original and sometimes striking compositional and structural diversities. To date,

more than 200 structure-types of open-framework aluminophosphates have been discovered [5], including not only three-dimensional zeolite-like nanoporous frameworks, but also anionic AlPO frameworks [6]. Anionic AlPOs comprise three-dimensional frameworks and also frameworks with lower (2D, layered-like, or 1D, chain-like) dimensions, which are built up of alternate Al polyhedra with different coordinations (AlO_4 , AlO_5 , AlO_6) and P tetrahedra $\text{P}(\text{O}_b)_n(\text{O}_t)_{4-n}$ (b: bridging, t: terminal, $n = 1,2,3,4$). The wide versatility of Al and P coordination environments in AlPO frameworks results in a wide diversity of compositional stoichiometries potentially possible; however, some specific compositions are most common, including $\text{AlPO}_4(\text{OH})^-$, $\text{AlP}_4\text{O}_{16}^{9-}$, $\text{AlP}_2\text{O}_8^{3-}$, $\text{Al}_2\text{P}_3\text{O}_{12}^{3-}$, $\text{Al}_3\text{P}_4\text{O}_{16}^{3-}$, $\text{Al}_3\text{P}_5\text{O}_{20}^{6-}$, $\text{Al}_4\text{P}_5\text{O}_{20}^{3-}$, $\text{Al}_5\text{P}_6\text{O}_{24}^{3-}$, $\text{Al}_{11}\text{P}_{12}\text{O}_{48}^{3-}$, $\text{Al}_{12}\text{P}_{13}\text{O}_{52}^{3-}$, $\text{Al}_{13}\text{P}_{18}\text{O}_{72}^{15-}$ [7] or more recently $\text{Al}_6\text{P}_7\text{O}_{27}\text{OH}^{2-}$ [8]. Therefore, AlPO networks provide a wide range of topological frameworks with different dimensionalities and with very different compositions, resulting in very interesting materials, sometimes with unusual large-pores [9].

The traditional synthesis of nanoporous materials is based on hydrothermal methods [10-12]; the inclusion of organic molecules is generally required to direct the crystallization of a certain nanoporous structure, and so they are called structure directing agents (SDAs). In a search for very large pore frameworks, which are desired for applications dealing with processing of large molecules, increasingly larger and more complex SDAs have been used, leading to the discovery of a number of new zeolitic topologies [13,14]. However, this increase in molecular size and complexity is limited by the chemical requirements that SDAs must fulfill, especially regarding hydrophobicity and hydrothermal stability [15]. Despite the large number of SDAs of very different sizes and shapes used up to date, their choice as structure directing agents has almost invariably considered the features of single molecular units;

supramolecular chemistry concepts have rarely been mentioned when studying structure direction of nanoporous frameworks by organic molecules. In this context, a new concept in structure direction of nanoporous materials was proposed by us [16-21] and by Corma *et al.* [22], consisting in the use of supramolecular self-assembled molecules as SDAs. This can be achieved by using molecules containing aromatic rings that tend to self-assemble in water solution with their aromatic rings interacting through π - π type interactions; this synthetic strategy would lead to supramolecular large aggregates composed of several individual molecules that could potentially structure-direct the synthesis of very large-pore framework materials. Besides, the self-assembly of the organic molecules occluded within the frameworks would in principle enable an easy un-assembly of the molecules since the aggregation process is driven by relatively weak intermolecular interactions; this could be useful when considering the removal of the organic molecules within the framework for catalytic applications, or even for un-assembly of entire frameworks and consequent production of AlPO precursors with preorganized inorganic species that could enhance their contact surface with potential reactants, or could be used in the quest of new framework materials such as pillared layered materials.

On the other hand, we have been recently studying the effect of the presence of fluorine atoms in the SDA molecules in an attempt to modify the chemical nature of the host-guest interactions between SDAs and the nanoporous frameworks they direct [23-27]. Several effects of F atoms on the structure-directing efficiency of the SDA molecules have been observed, among which we remark that their presence can influence the ability to form supramolecular aggregates, thus developing a rich supramolecular chemistry.

In this work, we extend the study of benzylpyrrolidine (BP) and its mono-fluorinated derivatives in ortho-, meta- and para-positions of the aromatic ring, as SDAs for the synthesis of AlPO frameworks. In this case, we use a high concentration of the SDA molecules ($2R:1Al_2O_3:1P_2O_5:40H_2O$, where R stands for the SDA) in an attempt to enhance their aggregation trend. We use a combination of physico-chemical techniques to characterize the obtained solids, including UV-Visible fluorescence spectroscopy to study the aggregation behavior of these SDAs both in solution and within the AlPO structures, in an attempt to unravel the effect of the presence of fluorine on supramolecular chemistry.

Experimental details

Details of the synthesis and characterization of the organic molecules employed in this study, benzylpyrrolidine (BP) and its fluorinated derivatives in ortho (oFBP), meta (mFBP) and para (pFBP) positions have been reported previously [24]. Aqueous solutions of the SDA molecules were prepared by adding equimolar amounts of the corresponding organic amine and HCl. In this way, 0.01, 0.1, 0.5 and 1 M aqueous solutions of benzylpyrrolidinium chloride and its fluorinated derivatives were obtained and studied by UV-Visible fluorescence spectroscopy.

AlPO frameworks were prepared from gels with a molar composition of $2 R : 1 Al_2O_3 : 1 P_2O_5 : 40 H_2O$, where R stands for the organic molecule. The gels were introduced into 60 ml teflon lined stainless steel autoclaves and heated statically at 125 °C for periods of time ranging from 3 to 192 h. The resulting solids were separated by filtration and dried at 60 °C overnight.

The crystallization of the AlPO framework structures was studied by X-Ray Diffraction (Seifert XRD 3000P diffractometer, CuK_{α} radiation). The organic content

of the samples was determined by chemical CHN analysis (Perkin-Elmer 2400 CHN analyzer) and thermogravimetric analysis (TGA) (Perkin-Elmer TGA7 instrument). Elemental analyses for Al and P were performed by inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin-Elmer 3300DV instrument) after sample dissolution by alkaline fusion. Scanning electron microscopy (SEM) was performed using a JEOL JSM 6400 Philips XL30 operating at 20kV and a Hitachi TM-1000 Table Microscope operating at 15 kV. Solid State MAS NMR spectra were recorded at room temperature using a Bruker AV-400-WB spectrometer with a 4 mm probe spinning at 10 kHz. ^1H to ^{13}C cross polarization (CP) spectra were recorded using $\pi/2$ rad pulses of 3 μs for ^1H , a contact time of 3.5 ms and a recycle delay of 4 s. The ^{27}Al spectra were measured using a $\pi/4$ pulse of 3 μs , contact time of 3 ms and recycle delay of 2 s operating at 40 MHz. For ^{31}P , a $\pi/6$ pulse of 2 μs , contact time of 3 ms and recycle delay of 20 s were used. These spectra were recorded while spinning the samples at 162 MHz.

The aggregation state of the molecules in solution and in the solid samples was studied by fluorescence spectroscopy. Liquid and solid state UV-Visible fluorescence excitation and emission spectra were recorded in a RF-5300 Shimadzu fluorimeter . The fluorescence spectra were registered in the front-face configuration by a solid sample holder in which the samples were oriented 30 and 60° with respect to the excitation and emission beams, respectively. Liquid solutions of the SDAs samples were placed in 0.1 mm pathway quartz cells whereas the fluorescence spectra of the solid aluminophosphate samples were recorded by means of thin films supported on glass slides elaborated by solvent evaporation from a dichloromethane suspension of the solid samples.

The process of un-assembly of the AlPO frameworks was studied by putting the as-prepared samples in contact with water or ethanol (ratio of 1g of solid per 100 ml of liquid) at room temperature under continuous magnetic agitation for selected periods of times (0.5, 3 and 24 h). The resulting materials were studied by XRD, TGA and SEM.

Results

A) Aggregation behavior of BP as a function of the presence of fluorine.

We first studied by fluorescence spectroscopy the effect of the presence of fluorine atoms in the different positions of the aromatic ring on the aggregation behavior of protonated BP chlorides in water solution at increasing concentrations (Figure 1). Two fluorescence bands can be clearly observed in all cases, one centered at around 282 nm, and another broader band around 318 nm. The increase of the intensity of the latter upon increase of the concentration indicates that the former corresponds to the emission of the molecules as monomers, and the latter to the emission of aggregated molecules.

Results show that BP has a high trend to self-aggregate in water solution. Interestingly, fluorine in ortho-position dramatically reduces such aggregation behavior, and even at the highest concentration of 1 M, most of the molecules still arrange as monomers. Fluorine in meta-position reduces slightly the aggregation of the SDAs in water, but the aggregated species predominate at 1 M concentration. Similarly, fluorine in para-position also reduces slightly the aggregation trend, although to a lower extent than in meta position. In sum, it becomes clear that fluorine plays an important role on the aggregation behavior; it reduces the trend to self-aggregate, but differently depending on the position. The aggregation-trend of protonated BP chlorides as a function of fluorine follows the decreasing order BP >

pFBP > mFBP >>> oFBP. Similar results were previously observed for the fluorinated derivatives of (S)-(-)-N-benzylpyrrolidine-2-methanol [28].

B) Crystallization of AlPO frameworks.

By using the four SDA molecules at high concentrations (2R:1Al₂O₃:1P₂O₅:40H₂O) and a low crystallization temperature (125 °C), four unknown phases have been obtained (Figure 2); an increase of the crystallization temperature to 150 °C leads to the crystallization of AlPO-5. The four phases share a first intense diffraction at around 5.3 2θ, which points to a low-dimensional framework (See Figure 1-Supporting Information for comparison). Evolution of the crystallinity of these phases with time indicates that the materials obtained with BP, mFBP and pFBP are stable with time, at least up to 192 hours, under the synthesis conditions used in this work (Figure 2, 3 and 4-Supporting Information). However, the material obtained with oFBP is not stable, and it rapidly transforms to AlPO-5 (Figure 5-Supporting Information). SEM pictures (Figure 6-Supporting Information) show small plate-like crystals for the phases obtained with BP and mFBP, while the material obtained with pFBP show larger crystals with also a plate-like morphology. In contrast, the AlPO phase obtained with oFBP (after 3 hours of crystallization) does not show a particular crystalline morphology, possibly because of the presence of amorphous material in the solid.

TGA (Figure 3) shows a very intense weight loss between 230 and 260 °C, depending on the sample, in which most of the organic matter (40-50 %) is desorbed. A previous desorption is observed in all samples, but is more intense for the AlPO frameworks obtained with BP and mFBP, which is assigned to physisorbed water. A final desorption in the range between 300 and 800 °C, of around 3-5 %, is ascribed to combustion of remaining organic matter. The integral incorporation of the molecules

was verified by CHN analyses (Table 1), which gave C/N ratios close to the theoretical one (11). The organic content, determined from the C content, was around 45 %, slightly higher for the sample obtained with pFBP, in agreement with TGA results. The extremely high organic content of these materials suggests that they might be low-dimensional (1D- or 2D-) AlPO frameworks in order to accommodate such organic content. Hereafter, only the stable materials obtained with BP, mFBP and pFBP will be studied.

The integrity of the molecules occluded within the AlPO frameworks was confirmed by ^{13}C NMR (Figure 4-see bands assignment); all the resonances corresponding to the different C atoms were observed in the three samples. Additionally, splitting of the resonances of aromatic C atoms and the appearance of a new signal at 160 ppm (C-F) evidences the incorporation of the organic F atoms within the frameworks obtained with mFBP and pFBP. It is interesting to note that the resonance corresponding to the C atoms bonded to fluorine in the material obtained with mFBP is splitted into two well-differentiated signals at 161.6 and 162.6 ppm, what might be a consequence of a different intermolecular chemical environment (F interacting through non-bonded interactions with different species); this could be due to different conformations or aggregation states of mFBP molecules within the AlPO framework.

^{27}Al and ^{31}P MAS NMR was used in order to analyze the chemical environments of the framework atoms within the different phases. ^{27}Al NMR spectra of the three phases (Figure 5) show intense resonances around 43 ppm, which are typical of Al in tetrahedral coordination in AlPO frameworks. However, two differentiated resonances composing this broad band seems to be present in all cases, although some differences in their relative intensities are observed among the three materials. In addition, a broad signal around 8 ppm is observed in the three samples; the chemical shift position and

the wide nature of the band suggests that it might be due to the presence of unreacted pseudoboehmite [29-31].

The ^{31}P MAS-NMR spectra of the three phases are represented in Figure 6. All the materials display resonances around -20 ppm, which is commonly assigned either to $\text{P}(\text{Q}_4)$ or $\text{P}(\text{Q}_3)$ species [32]. As for Al species, this complex band seems to be composed of at least three different components, with subtle differences in relative intensities found among the three phases. In the case of the material obtained with mFBP, a very low-intense resonance at around -30 ppm is observed, which could be due to the presence of traces of AlPO-5 that crystallize together with the unknown phase [24] (this phase might not be detected by XRD due to overlapping of the diffraction peaks; however, additional evidence for its presence is given below). In sum, both ^{27}Al and ^{31}P NMR spectra show that the materials are composed of tetrahedral Al and $\text{P}(\text{Q}_4)$ or more probably $\text{P}(\text{Q}_3)$, and suggest a certain degree of complexity of the AlPO network due to the presence of different environments. Elemental ICP analyses (Table 1) show that the three materials possess an Al/P ratio around 0.9; however, this should be taken with care since other material that accompany the AlPO phases (as unreacted pseudoboehmite observed by ^{27}Al NMR) can mislead the interpretation of data.

We then studied the aggregation state of the molecules incorporated within the different AlPO frameworks by UV-Visible Fluorescence spectroscopy (Figure 7); emission bands around 282 nm indicate the presence of the molecules arranged as monomers, while bands at higher wavelengths (above 310 nm) are due to the presence of aggregates [19]. Both monomers and aggregated species are clearly observed in the AlPO frameworks containing BP and mFBP; in the former case, several different types of aggregates seem to be present, some of them with very strong π - π interactions

that strongly shift the emission band to 400-500 nm, while the aggregate band of AlPO-mFBP is much narrower. In contrast, the presence of monomers in the framework obtained with pFBP is very minor, and most of the molecules arrange as aggregates within this framework, again evidencing differences among the three materials.

C) Un-assembly of AlPO frameworks.

The observation of self-assembled aggregates within the space between the inorganic network, which are stabilized by relatively weak π - π type interactions, suggests that these materials could in principle be easily un-assembled by simple treatments in which the π - π interactions between the aromatic rings would be broken. Such an un-assembly process is interesting since it could potentially lead to pre-organized AlPO precursors with high surface areas which could be used as single-site catalysts, maximizing the contact with eventual reactants, in a similar fashion as was carried out for MCM-22, for instance [33], or as pillared materials. Indeed, delamination and intercalation of layered AlPO frameworks have been previously studied [34-37]. The un-assembly process of the four AlPO frameworks (after 192 hours of crystallization except for that obtained with oFBP which was crystallized only for 3 hours) was studied in water and ethanol at room temperature by XRD and TGA (Figures 8-10).

XRD results (Figure 8) show that the materials do not resist treatment with water. The lowest stability is found for the material obtained with oFBP, in concordance with previous observations. All the materials start to partially lose their framework organization already after 30 minutes of immersion in water at room temperature (blue lines); such collapse is complete for the oFBP framework at this time, but seems less

intense for the material obtained with mFBP, suggesting a relatively higher stability to hydrolysis. The reduction of the XRD intensities of the initial frameworks is enhanced after 3 hours (red lines), although again such collapse is less intense for the mFBP framework; a new diffraction is observed in the framework obtained with BP at $9.15^\circ 2\theta$ whose origin is not clear at the moment. Finally, all the materials completely lose their structure after 24 hours of treatment in water (only wide diffractions matching those of pseudoboehmite are observed, again confirming the presence of unreacted pseudoboehmite); however, some low-intense diffractions corresponding to the AFI framework are observed in the sample obtained with mFBP; we should note that these diffractions were also present in the initial framework, and hence it is likely that a minor amount of AlPO-5 was initially present, although the intensity of these diffractions seem to have slightly increased upon the AlPO-mFBP framework collapse. It is interesting to remark that in the sample obtained with pFBP, even despite the collapse of the framework after 24 hours, the crystal morphology resembles that of the original sample (see Figure 7-Supporting Information); the same cannot be argued for the other samples, but this might be due to their much smaller crystal size (see Figure 6-Supporting Information). TGA of these treated samples (Figure 9, red lines) indicate that most (if not all) of the organic matter present within the frameworks has been removed upon treatment with water for 24 hours. An intense weight loss around 110°C is observed in all cases, associated to desorption of water molecules probably coordinated to Al in the amorphous (or the alumina) phases; another weight loss of around 10 % between 200°C and 900°C is also appreciated, which might correspond to desorption of rests of remaining organics or to desorption of water after dehydroxylation processes.

XRD patterns of the AlPO frameworks treated with ethanol are displayed in Figure 10; a different behavior than that observed with water is appreciated. In this case, the samples seem to be slightly more resistant to immersion in ethanol than in water. Again, the AlPO-framework obtained with oFBP is the less stable one; an intermediate state after 3 hours of treatment is observed, where some of the diffractions remain and a very wide diffraction at low angles is observed (Figure 10, top-right, red line), but the framework is completely lost after 24 hours. In contrast to the behavior observed in water, the material obtained with BP is rather stable, and even after 24 hours the diffractions remain, although their intensity is sensibly reduced (Figure 10, top-left). In addition, there seems to be an intermediate phase where the low-angle diffraction slightly increases from 5.4 to 5.7 2θ ; this phase transformation is especially observed after 30 minutes of treatment. However, this meta-stable phase again transforms to the initial framework after some more time immersed in ethanol (red and green lines). A similar behavior is found for the material obtained with pFBP (Figure 10, bottom-right), where a new low-angle diffraction at higher angles (5.7 vs the initial 5.3 2θ) is observed after 30 minutes, but again this nascent structure transforms in the initial one with time, which further decreases its XRD intensity after 24 hours (although the XRD profile still remains). A similar phase-transformation after 30 minutes of treatment is observed for the framework obtained with mFBP, where a shift of the low-angle diffraction from 5.3 to 5.5 2θ is appreciated. However, in this case the initial framework is not recovered (at least in the times analyzed in this work), but after this initial phase-transformation the framework collapses upon increase of immersion time, in sharp contrast to the observations in water where this mFBP-framework was the most stable one. TGA results (Figure 9, green lines) show that in this case the desorption of the organic matter from the framework is notably less effective than

when treated in water since, even after 24 hours, still a large proportion of organics (which desorb between 200 and 900 °C) is appreciated.

Discussion

Our work shows that, under a high concentration of organics (2SDA:40H₂O), BP molecules and their fluorinated derivatives are able to produce different AlPO frameworks by a self-assembly process of the molecules through the establishment of π - π type interactions. Interestingly, the assembly procedure is dependent on the aggregation behavior of the organic molecules; in this way, the material obtained with oFBP, which shows the lowest trend to aggregate in water solution, is the less stable one, and is transformed into the more stable AFI phase soon after it is formed in the synthesis medium. The other three molecules, which show a stronger aggregation trend, are able to produce stable AlPO-based frameworks with very large organic contents. The high number of diffractions in the middle-angle region (from 15 to 35 2 θ) suggests a strong topological ordering of the AlPO network in AlPO-BP and AlPO-mFBP phases; in contrast, the AlPO-pFBP framework shows a very intense low-angle diffraction, suggesting a strong ordering of the space between the AlPO network, but few very and wide diffractions and with low intensity in the middle-angle region, suggesting a poorer short-range ordering of the AlPO network in this framework; attempts to solve the structure of the frameworks were unsuccessful due to the poor quality of the XRD patterns and the presence of amorphous/unreacted material (purification by sonication was not possible due to their instability in water).

The high organic contents found, close to 50 %, are rare among these AlPO frameworks; to our knowledge, there are only two examples in the literature with such high organic contents, of layered AlPO frameworks obtained with butyl-, hexyl- and

octyl-amines [38], with organic contents up to 50 %, and with an aromatic molecule, phenyl-ethyl amine [39], with an organic content of 47 %; both materials comprise bilayers of the organic molecules located between AlPO sheets. Therefore, the high organic content found in our material together with the low angle observed for the first diffraction (around $5.4\ 2\theta$, corresponding to a distance of $16.5\ \text{\AA}$) suggest the presence of bilayers of BP and related molecules within the AlPO network, similarly as occurs in the framework obtained by Dorner et al. [39]. However, such framework is clearly different from ours since it contains octahedral Al.

The high organic content points to low-dimensional AlPO frameworks. Common 3D-frameworks cannot host such large number of guest molecules; even JDF-20 [9], with very large pore-openings of 20-membered rings, contains only 22 % of organic matter. On the other hand, 1D-chain structures usually contain $\text{PO}_{2b}\text{O}_{2t}$ ($\text{P}(\text{Q}_2)$) and PO_bO_{3t} ($\text{P}(\text{Q}_3)$) [40] which are not observed in our ^{31}P NMR spectra. Therefore, it seems clear that the three frameworks obtained in this work must consist of 2D-layered AlPO structures containing only AlO_4 and PO_{3b}O_t . The most common framework compositions satisfying these conditions are $\text{Al}_3\text{P}_4\text{O}_{16}^{3-}$, of which several different sheet structures have been found [40]; such Al/P ratio of 0.75 is lower than the one we found (0.9), but this might be explained by the presence of unreacted pseudoboehmite as observed by ^{27}Al NMR. Assuming such inorganic composition, the materials would contain close to 3 molecules per $\text{Al}_3\text{P}_4\text{O}_{16}^{3-}$, suggesting that they might be protonated to achieve charge-balance and to enhance the interaction by establishment of H-bonds between the proton (attached to N) and the terminal O in PO_{3b}O_t units. We should note that most of these low-dimensional frameworks have traditionally been obtained under solvothermal conditions, but rarely crystallize in aqueous gels [39,41-44] as our materials.

Fluorescence results clearly evidence that the molecules are developing π - π type interactions when occluded within these frameworks; however, the aggregation extent is again different among the phases obtained with the three molecules: BP and mFBP incorporates both monomers and aggregates, some of them (for BP) with very strong π - π interactions (shown by the large shift of the emission band to 400-500 nm), while the framework obtained with pFBP incorporates exclusively aggregates. Hence, these results confirm the self-assembly process of the organic molecules to produce the crystallization of these frameworks containing a high amount of organics, possibly arranged as organic bilayers. The different shifts observed in the aggregates emission band points to different types of stacking of the aromatic molecules within the bilayer depending on the presence of fluorine.

The relatively low strength of the intermolecular forces which conform the frameworks (π - π in the organic bilayer and weak H-bonds of PO_{3b}O_t species with protons from pyrrolidine) enables an easy un-assembly process just by treatment at room temperature in water. Worth is noting that the relative stability of the different materials found in water and in ethanol is distinct: in water, the most resistant framework is the one obtained with mFBP, but this is the less resistant one in ethanol, with the material obtained with BP being now the most stable one. Treatment of the materials with ethanol enables only dissolution of the self-assembled organic molecules of the framework; hence, the lower resistance of mFBP suggests a lower stability of the organic self-assembled layer, i.e. a lower aggregation force and lower interaction with the AlPO network. In fact, this is in line with the highest aggregation trend observed in water for BP, suggesting also a stronger aggregation within the framework and hence a stronger resistance to dissolution by ethanol. However, we should note also that the solubility of mFBP in ethanol might be slightly higher than

that of BP, what could also affect the distinct resistance of the frameworks to dissolution. On the other hand, treatment with water involves both dissolution of the organic molecules (they might be protonated, increasing their solubility in water) and dissolution/hydrolysis of the AlPO layers. The fact that, in this case, the most resistant material is the one obtained with mFBP might be due to a higher framework stability and consequently stronger resistance to hydrolysis of the AlPO network. However, we should also keep in mind when comparing with the BP-framework that the solubility of mFBP in water is slightly lower than that of BP, what could also enhance its stability against hydrolysis. The ability of these frameworks to un-assemble in water might be surprising if one considers that indeed these frameworks crystallize (and are stable with time) from aqueous gels. However, we note that the concentration of the organic molecules in the aqueous phase of the synthesis gel during crystallization is rather high since these molecules are quite in excess over Al and P species, what could explain the stability of the frameworks in the synthesis gels (with high concentration of dissolved organics) compared to that in organic-free water (during un-assembly process).

Figure 11 shows a scheme of the concepts proposed here. The organic molecules that self-assemble (through π - π type interactions) into large supramolecular bilayer aggregates (BP, mFBP and pFBP) organize the inorganic units around forming an inorganic network, giving place to the crystallization of layered frameworks as long as the crystallization temperature is relatively low. SDAs that do not self-assemble (oFBP) tend to direct the crystallization of AFI. The layered frameworks are held together by weak intermolecular forces between the molecules in the organic bilayer (hydrophobic π - π) and between terminal network O atoms and protons from pyrrolidine rings (hydrophilic $\text{PO}_4 \cdots \text{NHR}_3$, through a single H-bond possibly sterically

hindered). The weak forces sustaining the layered framework allow the organic bilayer to be easily removed by immersing the solid in water, producing an X-Ray amorphous solid. It is plausible that such solid could keep some structural feature of the AlPO-layered precursor, although this is just a mere hypothesis and no direct proof is provided in this report; work is currently under way in order to provide evidence for this. This strategy of un-assemblable frameworks could be applied for the delamination of nanoporous catalysts in order to maximize their activity, as was proposed for MCM-22 by swelling the material with surfactants [33].

Conclusions

In this work we propose a new strategy for the synthesis of un-assemblable metastable AlPO-based layered materials that can be easily decomposed by deaggregation of the organic molecules composing the frameworks. By using the aggregation trend of benzylpyrrolidine and its fluorinated derivatives, we have produced three new AlPO layered frameworks with extremely large organic contents. We have observed that the crystallization of these frameworks is strongly dependent on the aggregation ability of the molecule in water; in this way, the ortho-fluorinated derivative, which shows the lowest trend to aggregate in water, is not able to produce a stable self-assembled framework. In contrast, benzylpyrrolidine and the meta- and para-fluorinated derivatives do, and indeed they form aggregates within the space between the inorganic entities in the frameworks.

Such aggregation of the organic molecules within the frameworks driven by weak hydrophobic interactions enables a simple un-assembly of these structures by immersion of the samples in water.

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Tables

Sample	C	H	N	C/N	% organic (C)	Al/P
BP-125-192h	36.04	5.13	3.70	11.4 (11)	43.96	0.91
mFBP-125-192h	33.46	4.78	3.47	11.2 (11)	45.37	0.89
pFBP-125-192h	34.57	4.59	3.59	11.2 (11)	46.88	0.92

Table 1. CHN analyses of AlPO frameworks. The organic percentage was determined from the C content.

Figure Captions

Figure 1. Height-normalized fluorescence emission spectra of BP-H⁺ chloride (top-left), oFBP-H⁺ chloride (top-right), mFBP-H⁺ chloride (bottom-left) and pFBP-H⁺ chloride (bottom-right) aqueous solutions at different concentrations. The excitation wavelength was 260 nm.

Figure 2. XRD patterns of the AlPO frameworks obtained at 125 °C with BP (192h, top-left), oFBP (3h, top-right), mFBP (192h, bottom-left) and pFBP (192h, bottom-right).

Figure 3. TGA (solid line) and DTA (dashed line) of the AlPO materials obtained after 8 days (with BP, black, mFBP, blue, and pFBP, green) or 3 hours (with oFBP, red) of crystallization.

Figure 4. ¹³C CP MAS NMR of AlPO frameworks (and corresponding assignment); inset: detail of the C-F ¹³C resonance region.

Figure 5. ²⁷Al MAS NMR of AlPO frameworks; inset: detail of the tetrahedral ²⁷Al resonance region.

Figure 6. ³¹P MAS NMR of AlPO frameworks; inset: detail of the range between -16 and -24 ppm ³¹P resonance region.

Figure 7. Height-normalized fluorescence emission spectra of the different frameworks. The excitation wavelength was 260 nm.

Figure 8. XRD patterns of AlPO frameworks after treatment with water at room temperature for different times.

Figure 9. TGA (solid lines) and DTA (dotted lines) of the original AlPO frameworks (blue lines) and after treatment with water (red lines) or EtOH (Green lines) at room temperature for 24 hours.

Figure 10. XRD patterns of AlPO frameworks after treatment with EtOH at room temperature for different times.

Figure 11. Schematic picture showing the concepts proposed in this work.

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Un-Assemblable Layered Aluminophosphates from Self-Assembling Structure- Directing Agents: Effect of Fluorine

Luis Gómez-Hortigüela, Ana Sanz, Teresa Álvaro-Muñoz, Fernando López-Arbeloa
and Joaquín Pérez-Pariente*

Supporting Information.

Figure 1-SI. Comparison of XRD patterns of the different AlPO phases.

Figure 2-SI. XRD patterns of AlPO-BP phase. Evolution of crystallinity with time: the structure is stable with time.

Figure 3-SI. XRD patterns of AlPO-mFBP phase. Evolution of crystallinity with time:
the structure is stable with time.

Figure 4-SI. XRD patterns of AlPO-pFBP phase. Evolution of crystallinity with time:
crystallinity notably increases with time.

Figure 5-SI. XRD patterns of AlPO-oFBP phase. Evolution of crystallinity with time:
the structure is rapidly transformed into AlPO-5, suggesting a lower stability.

Figure 6-SI. SEM pictures of the AlPO phases obtained after 192 hours (with BP, top-left, mFBP, bottom-left, and pFBP, bottom-right) or after 3 hours (with oFBP, top-right) of crystallisation.

Figure 7-SI. SEM pictures (two magnifications) of the AlPO phase obtained after 192 hours with pFBP after treatment of 24 hours in water.