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 AlPO 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.

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1. Introduction

Nanoporous crystalline aluminophosphates (AlPO), 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. [1], and these new materials have yielded a diversity of structural types comparable to that of the previously known aluminosilicate-based zeolites [2]. Usual AlPO 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 AlPO 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 AlPO-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, and AlO_6) and P tetrahedra $P(O_b)_n(O_t)_{4-n}$ (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 $AlPO_4$ $(OH)^-$, $AlP_4O_{16}^{9-}$, $AlP_2O_8^{3-}$, $Al_2P_3O_{12}^{3-}$, $Al_3P_4O_{16}^{3-}$, $Al_3P_5O_{20}^{6-}$, $Al_4P_5O_{20}^{3-}$, $Al_5P_6O_{24}^{3-}$, $Al_{11}P_{12}O_{48}^{3-}$, $Al_{12}P_{13}O_{52}^{3-}$, $Al_{13}P_{18}O_{72}^{15-}$ [7] or more recently $Al_6P_7O_{27}OH^{2-}$ [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

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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.

2. 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, Cu Kα 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 20 kV 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. ^{1}H to ^{13}C cross polarization (CP) spectra were recorded using $\pi/2$ rad pulses of 3 μs for ^{1}H, 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 fluorescecence spectra of the solid aluminophosphate samples were recorded by means of thin films supported on glass slides ellaborated 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 1 g of solid per 100 ml of liquid) at room temperature under continuos magnetic agitation for selected periods of times (0.5, 3, and 24 h). The resulting materials were studied by XRD, TGA, and SEM.

3. Results

3.1. 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 (Fig. 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