Fluorine-Containing Organic Molecules: A New Class of Structure-Directing Agents for the Synthesis of Molecular Sieves

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The addition of specific organic molecules to otherwise purely inorganic synthesis gels is generally required to direct the hydrothermal crystallization of a large variety of zeolites and zeolite-like materials from these gels. Since the pioneering work of the late Professor Barrer,[1] the use of water-soluble organic molecules, preferentially amines and quaternary ammonium cations, as structure-directing agents (SDAs), has allowed the invention of a large variety of different zeolite topologies.[2−5] An ever-increasing complexity of the chemical structure of SDAs has resulted in a parallel expansion of zeolite structure types.[6,7]

It has been long recognized that the so-called template organic molecules are in most cases filling the zeolite cavities in a very efficient manner. The pore-filling ability of SDAs and their matching to the zeolite cavities have as a consequence that the chemical interaction between the zeolite inorganic framework and the occluded SDAs takes place basically through the hydrogen atoms belonging to the organic molecule. Although some alcohols and primary and secondary amines have been used as SDAs, most if not all the hydrogen atoms of these molecules are nevertheless attached to carbon atoms. Therefore, the apparently wide diversity of SDA molecules that has been used for zeolite synthesis overshadows the fact that the chemical character of these molecules has remained basically unchanged.

It is well-known that organic molecules where hydrogen atoms are partially or totally replaced by fluorine atoms exhibit a remarkable change in surface properties.[8] These fluorine-containing molecules are in general more hydrophobic than their all-hydrogen counterparts.[9] Based upon these grounds, it would be possible to think of the use of fluorine-containing molecules as templates for zeolite synthesis. Indeed, very recently mesoporous materials have been obtained using fluorinated surfactants.[10] In this context, it is important to remark that C−F bonds are stable under the conditions required for the hydrothermal crystallization of most zeolitic materials, provided that temperature and pH are not too high.

We report in this work a new concept in zeolite synthesis. We propose that the replacement of hydrogen atoms by fluorine atoms in SDAs can have a profound influence on the crystallization process of the synthesis gel, leading in some cases to the formation of crystal phases different from those obtained from all-hydrogen molecules.

The fluorine-containing molecules used in this work have been prepared by reacting commercial *o*-, *m*-, or *p*-fluorobenzyl chloride with pyrrolidine, dimethylamine, or benzyldimethylamine. In this way, 1-(fluorobenzyl)-pyrrolidines (F-BP) and difluorinated dibenzyldimethylammonium cations (DBDM) were obtained and used as SDAs for the synthesis of AlPO and SAPO materials. The chemical compositions of the gels was (mole bases) 1:1:1:x:40 R:Al_2O_3:P_2O_5:SiO_2:H_2O (where R stands for the organic molecule and x was 0 for AlPO and 0.5 for SAPO gels), and the gels were heated statically at 150 °C for 72 h. The quaternary monofluorinated DBDM cations were also obtained and used together with their all-H counterpart for the preparation of silica gels in a fluoride medium. The molar composition of these gels was 0.54:0.54:1:7.93 R:HF:SiO_2:H_2O. The gels were heated at 135 °C for 46 d.

AlPO-5 crystals (framework type code AFI), an aluminophosphate with 12MR one-dimensional channels, were obtained using benzylpyrrolidine (BP). However, the nature and crystallinity of the phase obtained by using their monofluorinated derivatives depended strongly on the position of the fluorine atom in the aromatic ring, which evidences a marked regioselectivity of the template in the course of the crystallization process. The fluorine atom in the meta position increases the crystallinity of the AlPO-5 (100%) as compared with that of the all-H counterpart (62%). The organic content of these samples was 1.2 and 1.0 molecules per unit cell for mF-BP and BP, respectively, as determined by elemental analysis. The lowest crystallinity corresponds to the template molecule containing F in the para position (just traces of AlPO-5). Interestingly, the effect is much more pronounced if silica is present in the synthesis gel. In this case, poorly crystalline SAPO-5 (AFI, ∼33% crystallinity) is obtained using the F-free amine, whereas a noticeable increase in crystallinity (61%) is obtained by using mF-BP (Figure 1). The latter sample contains 1.2 template molecules per unit cell according to chemical analysis data. In contrast, AlPO-C (framework type code APC) crystals with only traces of SAPO-5 are obtained from pF-BP and oF-BP. AlPO-C is a dense aluminophosphate containing 8-MR channels that cannot accommodate the BP molecules. Therefore, the preferential crystallization of the APC phase evidences a low interaction energy between the AFI framework and these fluorine-substi-

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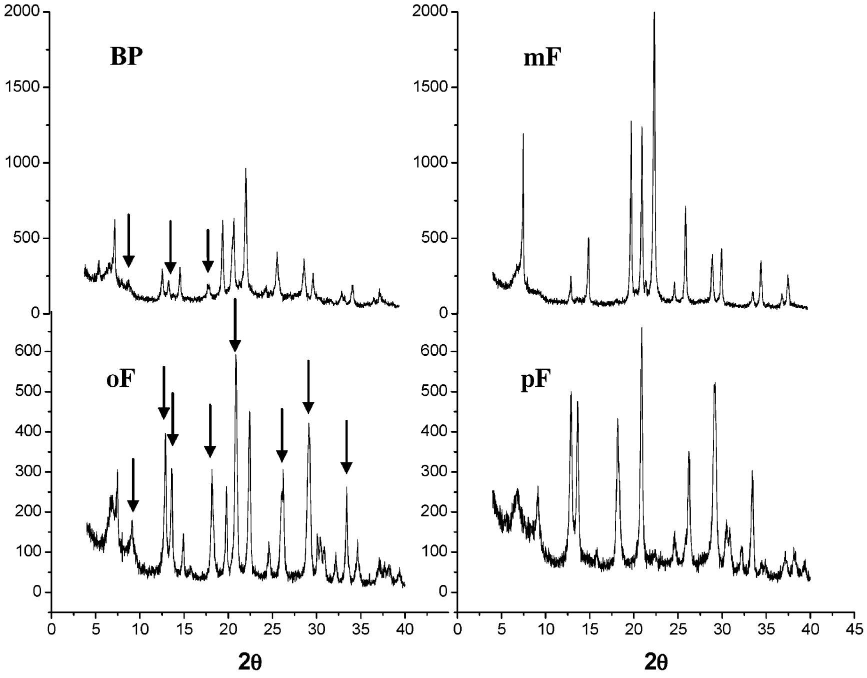

Figure 1. XRD pattern of SAPOs obtained with benzylpyrrolidine (BP, peaks of APC indicated by arrows) and its fluorinated derivatives in ortho (oF, main peaks of APC indicated by arrows), meta (mF, all peaks from AFI phase), and para (pF, mainly peaks from APC phase).

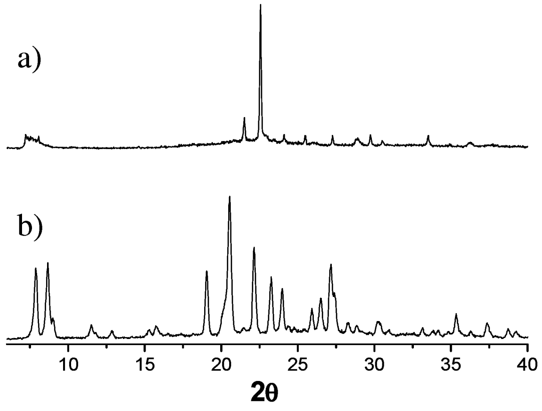

Figure 2. XRD pattern of (a) Beta sample obtained with DBDM and (b) EUO sample obtained with oF-DBDM.

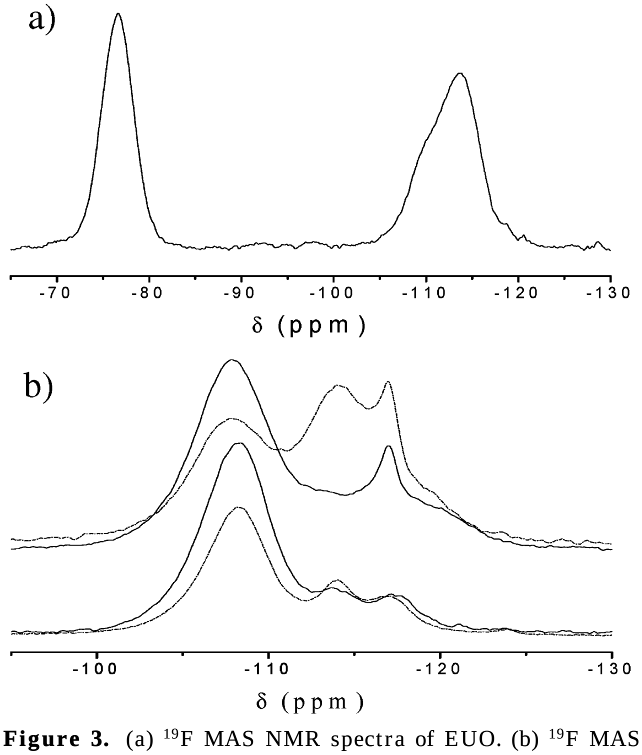

Figure 3. (a) ^{19}F MAS NMR spectra of EUO. (b) ^{19}F MAS NMR spectra of AlPO (solid line) and SAPO (dashed line) obtained with mF-BP (bottom) and mFmF-DBDM (top).

tuted derivatives. These results suggest that the stabilization of the AFI structure by the different template molecules follows the order: mF-BP > BP > oF-BP ≫ pF-BP. The nature of the interaction between the amine molecules and the AFI framework is currently under study by means of molecular mechanics methods.[11] Our results suggest that the templating of the AFI phase is hindered for the ortho- and para-fluoro amines because of a less efficient packing between the molecules; Oppositely, the meta-fluoro derivative is the best template due to electrostatic interactions developed between the fluorine atom and the framework.

Similar results have been obtained by using dibenzyldimethylammonium: the presence of fluorine atoms in the meta position of both aromatic rings increases the crystallinity of the AFI phase in the product.

Pure zeolite Beta (framework type code *BEA), a zeolite with 12MR three-dimensional channels, is obtained from silica gels in a fluoride medium by using DBDM (4 template molecules/u.c.). However, if only one H atom in the ortho position is replaced by F in one of the aromatic rings, zeolite EU-1 (framework type code EUO), composed of 10MR one-dimensional channels and large side pockets, is obtained (3 molecules/u.c.), Figure 2. The position of the F atom in the ring controls the resulting product, as only amorphous materials are obtained in the same synthesis conditions from m- and pF substituted compounds. ^{13}C MAS NMR data show

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that the template molecules are intact inside the cavities of both zeolites (DBDM) and AFI (BP) materials. The NMR spectra show signals in the region between 20 and 80 ppm corresponding to sp^3 carbon atoms belonging to the pyrrolidine, methylene, and methyl groups, and signals in the region between 120 and 140 ppm typical of aromatic carbon atoms; two additional signals at around 115 and 160 ppm appear for the fluorinated templates because of the presence of aromatic fluorine (see Supporting Information). The presence of fluorine atoms belonging to the organic compounds occluded inside the microporous crystals has been assessed by ^{19}F MAS NMR, Figure 3. Signals in the region between −105 and −120 ppm are assigned to F atoms attached to the aromatic rings.[12−14] Interestingly, three different signals appear in AFI materials, whose relative intensities, but not their position, are strongly modified by the incorporation of silicon into the framework. This complex fluorine NMR signal could eventually be due to different packing orientations of the mF-BP inside the AFI channels. An additional signal at −76.6 ppm for EU-1 corresponds to fluoride anions that compensate the charge of the DBDM cations. This signal has been detected in nonasil, where the F^- occupies the $[4^15^46^2]$ cavities that are also present in the EUO structure.[15]

The observed influence of the F atoms present in the SDA molecules is more remarkable, taking into account the small ratio of F to H atoms, which varies between 1/9 and 1/17. It is reasonable to expect that an increase of the fluorine content of the molecules would result in a stronger influence on the overall crystallization process.

To conclude, the fluorine-containing molecules can be seen as a new family of structure-directing agents for the synthesis of zeolitic materials. Several differences have already been observed between the use of these fluorinated agents and their all-hydrogen counterparts, due not only to the presence of the fluorine atom but also to its relative position in the molecule.

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Supporting Information Available: Additional figure (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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