Zeolites

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Evidence for F$^-$/SiO$^-$ Anion Exchange in the Framework of As-Synthesized All-Silica Zeolites**

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Zeolites are crystalline microporous aluminosilicates with unique properties in adsorption, separation, and catalysis. For several decades, zeolites were prepared under alkaline conditions (OH$^-$ route) by hydrothermal crystallization of gels containing organic cations (structure-directing agents or SDAs) and inorganic species.[1–3] At the end of the 1970s, a breakthrough emerged with the introduction of F$^-$ ions as mineralizing agents in the synthesis of silicalite-1, the all-silica zeolite with the MFI framework type.[4] Since then, the F$^-$ route led to the discovery of a number of new materials, particularly silica-rich zeolites with low-density frameworks.[5–13] Many of these new frameworks contain specific subunits such as double four-membered ring units (D4R) with an F$^-$ ion located in the center.[12–15] In addition to the discovery of novel structures, the F$^-$ route leads to large well-defined zeolite crystals with a low density of lattice defects.[16–19] For zeolites that can be obtained by following both the F$^-$ and OH$^-$ routes, the question remains as to whether or not the two routes have some connection. In particular, although F$^-$ ions are located in the framework of zeolites prepared in fluoride media, this is not the case for SiO$^-$ defects when the same zeolites are prepared under alkaline conditions.[20–25] From experimental observations and geometry optimization, Koller et al. have suggested that defect sites were preferentially located in six-ring units of silica frameworks.[26] These rings are actually the best candidates to accommodate the Q^3 sites that result from the cleavage of two Si–O–Si bridges without creating too much strain in the structure. However, techniques such as NMR and IR spectroscopy were not sufficiently structure-sensitive to precisely define which six-rings of the framework SiO$^-$ defects were preferentially located.

Herein, we show for the first time that F$^-$ and SiO$^-$ defect sites can be reversibly exchanged in the framework of as-synthesized all-silica zeolites, except when F$^-$ ions are located at the center of D4R units. Preliminary experiments were performed on all-silica zeolites with MFI and MRE framework types, for which both synthesis routes have been widely documented.

Silicalite-1, which was prepared in the presence of HF and denoted [F]-MFI, is pure, and SEM images show that it forms large and regular twinned crystals (Figure 1 a). The unique signal at approximately −60 ppm in the ^{19}F NMR spectrum characterizes F$^-$ ions in a [$4^1 5^2 6^2$] cage of the structure.[20,24] This signal completely disappears upon treatment of the zeolite for 24 h under highly alkaline conditions (Figure 2). This treatment does not affect the crystallinity, as evidenced by X-ray diffraction and SEM, but results in significantly modified ^{29}Si and ^{1}H NMR spectra. The loss in ^{29}Si NMR resolution observed upon treating [F]-MFI suggests the creation of framework defect sites (Figure 2).[17] This was further confirmed by ^{1}H NMR spectroscopy: the appearance of a resonance at $\delta = 10.2$ ppm on the spectrum of the treated zeolite is clear evidence that structures such as SiO$^-\cdots$HOSi hydrogen bonds have been created (see the Supporting Information).[26] All characteristics of the treated zeolite appear to be similar to those of defective zeolites prepared under alkaline conditions, except for the crystal size. Indeed, all chemical modifications could be performed without any change in crystal size, thus suggesting the absence of dissolution and recrystallization from ammonium hydroxide solutions at pH 13.5 (Figure 1 b). Similar experiments have been performed starting from [OH]-MFI, an as-synthesized all-silica MFI zeolite obtained following the OH$^-$ route. The

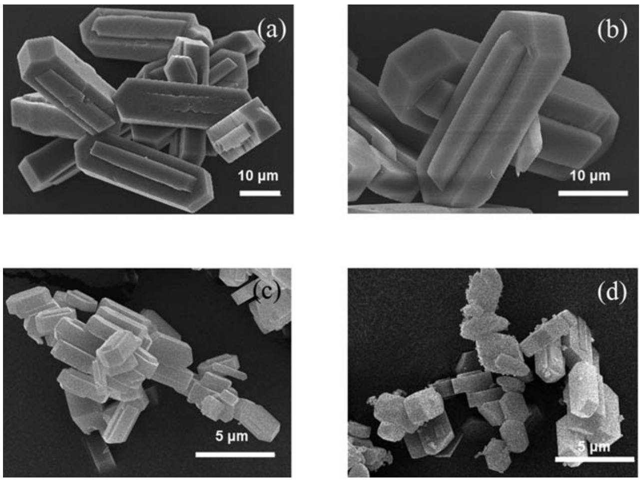

Figure 1. SEM pictures of a) [F]-MFI, b) [F]-MFI treated under alkaline conditions (pH 13.5), c) [OH]-MFI, and d) [OH]-MFI treated with ammonium fluoride solution (pH 6; for further details, see the experimental section).

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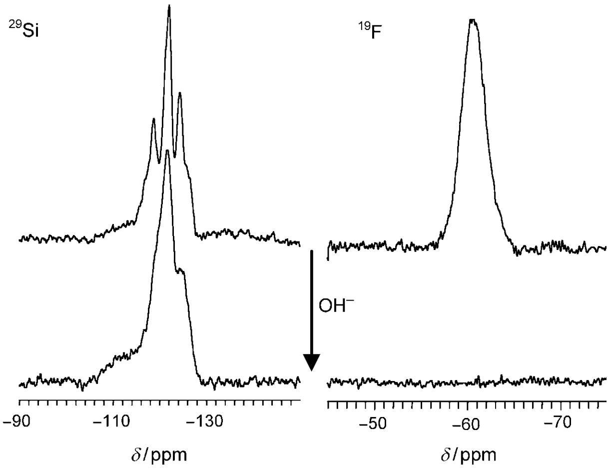

Figure 2. ^{29}Si and ^{19}F NMR spectra of silicalite-1 prepared in a fluoride medium before (top) and after (bottom) treatment with NH_4OH.

zeolite was treated with an ammonium fluoride solution at around neutral pH value (pH 6) for 1 day. Once more, modifications of the chemical composition were immediately confirmed by ^{19}F NMR spectroscopy. An intense signal at approximately $\delta = -60$ ppm, which is not present in the spectrum of the pristine zeolite, strongly suggests that F^{-} ions were incorporated into the framework. It is interesting to note that both the chemical shift and line width of the signal are strictly the same as those observed on [F]-MFI. Concurrent with the incorporation of F^{-} ions, the density of lattice defect sites decreases, as evidenced by the higher resolution of the ^{29}Si NMR spectrum and the complete disappearance of the proton signal at $\delta = 10.2$ ppm (see the Supporting Information). X-ray diffraction and electron microscopy confirmed that the transformation occurs without loss of crystallinity and keeping the size and habit of the crystals unchanged (Figure 1c,d).

Although crystals of [F]-MFI are relatively large, the [F]→[OH] transformation is complete and not limited to the surface, as evidenced by the complete disappearance of the ^{19}F NMR signal (Figure 2). The [OH]→[F] modification is more difficult to quantify, but the disappearance of the signal at $\delta = 10.2$ ppm in the ^{1}H NMR spectrum and the fluoride content in the treated zeolite (3.6 F^{-} ions per unit cell) indicate that most of SiO^{-} defect sites are concerned.

Additional experiments were performed on all-silica ZSM-48 (MRE framework type) to examine the role of the zeolite structure on the exchange process. ZSM-48 is a disordered zeolite with a framework containing one-dimensional 10-MR channels.[27] Aggregates of very thin needles were formed under alkaline conditions, whereas crystals obtained using the fluoride route are rather large, well-shaped, and characteristic of the fluoride route (see the Supporting Information). As for silicalite-1, F^{-} ions can be completely removed from the framework without changes in the crystal morphology. The creation of lattice defects is clearly evidenced by the increase of the signal at $\delta = -100$ ppm in the ^{29}Si NMR spectrum and the appearance of a signal at $\delta = 10.2$ ppm in the ^{1}H NMR spectrum. Conversely, the introduction of F^{-} ions in the framework of a zeolite prepared under alkaline conditions is accompanied by the appearance of a strong signal at $\delta = -67$ ppm in the ^{19}F NMR spectrum and a decrease of the number of defects (^{1}H NMR signal at $\delta = 10.2$ ppm in Figure 3). As a result, the hydrophobic character of the zeolite is increased and the signal at $\delta = 5.8$ ppm, which is characteristic of water molecules, also disappears. In the absence of large crystals, which are characteristic of zeolites obtained at near neutral pH values, it is likely that the process occurs without dissolution of the initial zeolite. Data obtained on ZSM-48 tend to show that this type of modification is not restricted to silicalite-1 but more work is necessary before generalizing the process to all-silica zeolites. The reversibility of the exchange process was demonstrated on [F]-MFI: F^{-} ions could be removed and further reinserted in the framework without changes in the crystallinity (see the Supporting Information).

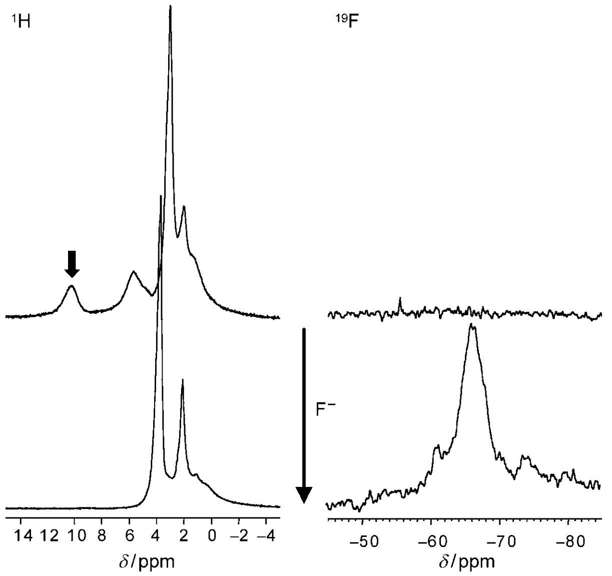

Figure 3. ^{1}H and ^{19}F NMR spectra of all-silica ZSM-48 prepared under alkaline conditions before (top) and after (bottom) treatment with NH_4F.

The procedure was further tested on ITQ-13 (ITH framework type), a zeolite with three sets of interconnected medium pore channels.[13,28,29] In contrast with zeolites with MFI and MRE framework types, all-silica ITQ-13 cannot be obtained under alkaline conditions.

Fluoride ions are located at two different crystallographic positions in the framework. In the all-silica polymorph, half of the F^{-} ions are located in the center of the D4R units whereas the remainder are close to the four-membered ring shared by two fused [$4^15^26^2$] cages. The two types of F^{-} ions are easily distinguished by NMR spectroscopy: the ^{19}F NMR spectrum of all-silica ITQ-13 consists of signals at $\delta = -38$ and -66 ppm, which are assigned to F^{-} ions in D4R and [$4^15^26^2$] cages, respectively (Figure 4).[28]

Upon treatment at a high pH value for 24 h, the ^{19}F NMR signal at $\delta = -66$ ppm disappears while that at $\delta = -38$ ppm remains unchanged. Fluoride ions can be completely removed

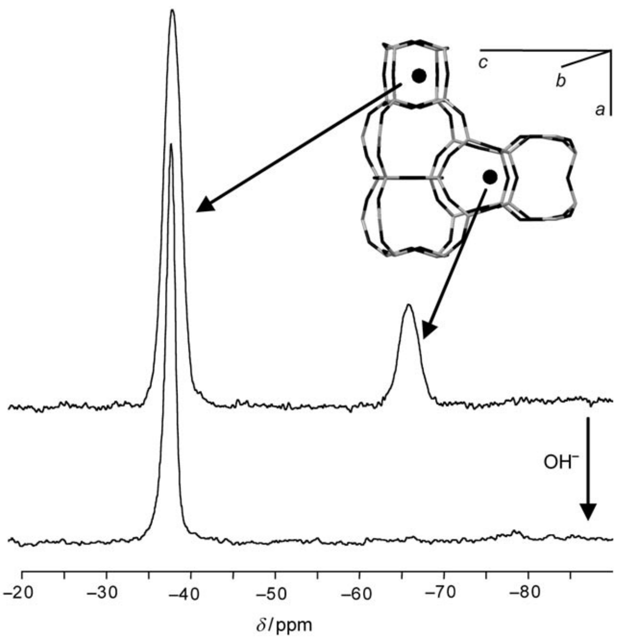

Figure 4. ^{19}F NMR spectra of all-silica ITQ-13 before (top) and after (bottom) treatment with NH_4OH and approximate position of the corresponding fluoride ions in the framework cages.

from [$4^15^26^2$] cages as was previously shown for zeolites with MFI and MRE framework types. In contrast, the F^- ions in D4R units cannot be exchanged, which is probably the reason why all-silica ITQ-13 does not crystallize in the absence of fluoride ions in the synthesis gel. Fluoride ions are essential for the stabilization of all silica D4R units and, therefore, for the crystallization of the zeolite framework. A possible dissolution and subsequent recrystallization of the zeolite during the treatment was refuted by the impossibility to directly synthesize an all-silica ITQ-13 with F^- ions located exclusively in the D4R cages.

The presence of pores and cavities in calcined zeolites provides easy accessibility to framework sites and greatly facilitates the migration of cations during exchange processes. In the present case, modifications are performed on as-synthesized materials and F^- ions enter or exit zeolite crystals in the presence of the template. Diffusion of ions in the pores seems unlikely, particularly for one-dimensional zeolites such as ZSM-48. Indeed, pores are filled with hexamethonium cations and the tight contact between the organic molecule and silica walls does not ensure the necessary space for ionic traffic.[30,31] It is thus reasonable to assume that F^- ions could diffuse through the silica framework through small openings such as five- or six-membered ring windows. For silanolates, a true diffusion process is unlikely and exchange could occur by propagation of defect groups through the framework with breaking of Si–O–Si bonds and formation of $SiO^- \cdots HOSi$ hydrogen bonds.

Although the total negative charge of extra-framework anions is preserved, the [F]↔[OH] modification is not a simple exchange, as is the case for cations in calcined zeolites. Indeed, OH^- ions do not only substitute F^- ions in the crystal, but the framework is also locally disrupted by the formation of $SiO^- \cdots HOSi$ hydrogen bonds. Moreover, there is no experimental evidence that F^- and SiO^- defects occupy the same crystallographic sites in the structure, although ^{19}F NMR spectroscopy strongly suggests that F^- ions introduced in the framework of [OH]-zeolites possess an environment that is very similar to that observed for fluoride in the corresponding [F]-zeolites directly prepared in fluoride media.

The ability of some zeolites to exchange F^- ions for lattice defects and vice-versa opens new opportunities to better control some of their properties, such as hydrophobic character, prior to calcination. Moreover, the possibility to modify specific sites in the structure could be of practical importance in post-synthesis modifications that require the presence of silanol groups, for example the grafting of catalytic entities in zeolite pores.

Experimental Section

[OH]-MFI (silicalite-1) was prepared under alkaline pH conditions (pH 13.5) using tetraethyl orthosilicate (TEOS) and tetrapropylammonium hydroxide (TPAOH) as templating molecule, respectively. The gel with the composition $SiO_2{\cdot}0.5\,TPAOH{\cdot}30\,H_2O$ was crystallized at 175 °C for 24 days under static conditions. [OH]-MRE (all-silica ZSM-48) was prepared following the same route using a solution of hexamethonium hydroxide ($HM(OH)_2$) and a gel composition $SiO_2{\cdot}0.25\,HM(OH)_2{\cdot}30\,H_2O$.

[F]-ZSM-5 and [F]-ZSM-48 were obtained at near neutral pH (pH 7.5) by adding HF (40 wt % aqueous solution) to the above gels. The final gel compositions were $SiO_2{\cdot}0.5\,TPAOH{\cdot}0.5\,HF{\cdot}30\,H_2O$ and $SiO_2{\cdot}0.25\,HM(OH)_2{\cdot}0.5\,HF{\cdot}30\,H_2O$ for [F]-ZSM-5 and [F]-ZSM-48, respectively. These gels were heated under static conditions at 175 °C for 14 days.

All-silica ITQ-13 was synthesized following the procedure given in Ref. [28]. Zeolites were converted with NH_4F (1 $mol\,L^{-1}$, pH 6) or NH_4OH (1 wt %, pH 13.5) solutions (1 gram zeolite/25 mL solution) at 175 °C for 1 day under static conditions.

All syntheses and modifications were carried out under autogenous pressure in stainless-steel Teflon-coated autoclaves. X-ray powder diffraction patterns were recorded between 3 and 70° (2θ) on a Bruker (Siemens) D5000 diffractometer using CuKα radiation. Solid-state NMR experiments were performed on a Bruker DSX 400 spectrometer equipped with a 2.5 mm double-bearing probe head. Spectra were recorded using conventional pulse sequences for ^1H and ^{19}F nuclei and a ^1H–^{29}Si CP/MAS sequence for ^{29}Si (contact time 5 ms). Scanning electron microscopy (SEM) pictures were obtained using a Hitachi S800 microscope.

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