

# Fluoride Removal from Double Four-Membered Ring (D4R) Units in As-Synthesized Ge-Containing Zeolites

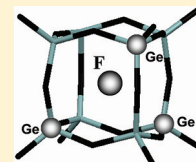
Xiaolong Liu,<sup>†</sup> Ugo Ravon,<sup>‡</sup> and Alain Tuel<sup>\*,†</sup>

<sup>†</sup>IRCELYON -Institut de recherches sur la Catalyse et l'Environnement de Lyon, UMR 5256 CNRS-Université de Lyon, 2 avenue Albert Einstein, 69626 Villeurbanne, Cedex, France

<sup>‡</sup>KAUST Catalysis Center (KCC), 4700 King Abdullah University of Science and Technology, Thuwal 23955–6900, Kingdom of Saudi Arabia

**ABSTRACT:** Fluoride anions can be removed from the framework of as-prepared Ge-containing zeolites ITQ-13 and ITQ-17 without modification of the crystallinity and crystal habit. By contrast to all-silica ITQ-13 for which fluoride could not get out from D4R units, F is completely removed from Ge rich zeolites, even from D4R cages. This has been explained by the relaxing effect of germanium, making F less necessary for the stabilization of the small D4R units. Si/Ge ratios are similar in as-prepared and treated zeolites, indicating that the framework composition is not affected by the removal of anions. The fluoride-free zeolites possess XRD patterns similar to those of the as-made solids but their <sup>29</sup>Si NMR spectra are significantly different, revealing the sensitivity of the method to the environment of silicon atoms in the framework. The extent of fluoride that can be removed from D4R units depends not only on the framework Ge content but also on the zeolite topology: for similar contents, F is much more easily eliminated from ITQ-17 than from ITQ-13.

**KEYWORDS:** fluoride, germanium, D4R units, zeolites, ITQ-13, ITQ-17



## INTRODUCTION

Silica-based zeolites are generally synthesized under hydro- or solvothermal conditions following two different routes. In the “basic route”, the hydroxide anion OH<sup>-</sup> is used as mineralizing agent and zeolites crystallize at high pH values, typically higher than 11.5.<sup>1</sup> The second route, known as the “fluoride route” is performed at near neutral or slightly basic pH values in the presence of F<sup>-</sup> anions, which improve the solubility of silica species and catalyze the formation of Si–O–Si bonds.<sup>2,3</sup> For zeolites that can be prepared following the two routes, the choice of the mineralizing agent is of prime importance as it greatly affects the properties of the final solid. In particular, high silica zeolites prepared under alkaline pH conditions possess a relatively high concentration of framework connectivity defects, essential to balance the positive charge of organic templates.<sup>4</sup> In fluoride media, charges are balanced by F<sup>-</sup> anions and the corresponding zeolite frameworks are almost defect-free.<sup>5–7</sup> Moreover, a remarkable and general trend of the fluoride route is that large crystals can be grown, because of a smaller nucleation rate at moderate pH values.<sup>8</sup> The fluoride route has been extensively developed during the last two decades and has led to a variety of new materials, essentially high-silica or even all-silica zeolites.<sup>9–17</sup> In addition to their charge-compensating role, fluoride anions play a structure directing effect in the synthesis of all-silica zeolites. Indeed, many of the newly discovered zeolites contain specific subunits like double four-membered rings (D4R) units that cannot be obtained in the pure silica form in the absence of fluoride.<sup>16–19</sup>

We have recently reported that fluoride anions could be easily exchanged by SiO<sup>-</sup> defects in the framework of as-made all silica zeolites, except when they are located inside D4R units.<sup>20</sup> When fluoride resides in [4<sup>1</sup>5<sup>2</sup>6<sup>2</sup>] cages, as it is the case

for silicalite-1 (MFI framework type), the exchange is complete and totally reversible.<sup>20,21</sup> It occurs without dissolution of the zeolite and preserves the original crystal morphology. In the case of ITQ-13, in which F<sup>-</sup> anions reside in two different cages of the framework,<sup>17,22</sup> the exchange was very selective and concerned only [4<sup>1</sup>5<sup>2</sup>6<sup>2</sup>] cages. Two main reasons had been put forward to explain the absence of exchange in the small D4R units. First, the impossibility to obtain all-silica D4R from basic synthesis gels suggests that F<sup>-</sup> ions are essential to the stability of all-silica D4R, at least in as-made zeolites. Under such conditions, the replacement of F<sup>-</sup> by OH<sup>-</sup> or a framework defect is inconceivable. Second, 4 membered-rings windows are too small to allow F<sup>-</sup> to diffuse out of D4R cages and exchange is only possible in cages containing 5- or 6-membered rings.

In the present work the concept of anion exchange has been extended to Ge-containing zeolites. It is well-known that Ge directs the synthesis of zeolites toward structures containing D4R units.<sup>23,24</sup> By increasing the average T–O distance and decreasing the T–O–T bond angle, incorporation of Ge relaxes the zeolite structure and diminishes geometric constraints in small D4R cages.<sup>25,26</sup> Ge-rich D4R units are so stable that some zeolites like ITQ-13 have even been obtained in the absence of HF.<sup>27</sup> Such zeolites represent a real opportunity to better understand the diffusion of fluoride through the framework, in particular through 4MR windows. Two series of zeolites, namely (Si,Ge)ITQ-13 and (Si,Ge)ITQ-17 (ITH and BEC framework types, respectively) have been prepared with various germanium contents in the presence of

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hexamethonium cations ( $\text{HM}^{2+}$ ) as structure directing agent. Typically, ITQ-13 can be obtained within a broad range of compositions, from the pure-silica polymorph to zeolites with Si/Ge ratios close to 3.<sup>17,22,27</sup> As already reported  $\text{F}^-$  can be easily removed from  $[\text{4}^1\text{S}^2\text{6}^2]$  cages of all-silica ITQ-13 but not from D4R cages.<sup>20</sup> ITQ-17 can also be prepared with different Si/Ge molar ratios but the pure-silica form cannot be obtained in the presence of  $\text{HM}^{2+}$  cations.<sup>16,28–30</sup> Moreover, all fluoride anions in ITQ-17 reside in D4R units. For these two series, as-synthesized zeolites were systematically treated in basic media and products were analyzed, to quantify the extent of defluorination, and characterized.

## EXPERIMENTAL SECTION

**Materials.** All zeolites were synthesized from gels containing tetraethyl orthosilicate (TEOS, 98%, Aldrich), germanium oxide ( $\text{GeO}_2$ , 99.99%, Aldrich) and homemade hexamethonium hydroxide solutions (Table 1). Hexamethonium bromide ( $\text{HMBR}_2$ ), prepared by

**Table 1. Chemical Analysis of the Different Samples**

sample name	Si/Ge ratio		$\text{HM}^{2+}/$ u.c.
	Gel	ratio	
$[\text{SiO}_2]$ ITQ-13			2.01 <sup>c</sup>
ITQ-13-1	20	20.8	
ITQ-13-2	10	9	
ITQ-13-3	5	4.5	1.97 <sup>c</sup>
ITQ-13-3 <sup>a</sup>	5	4.8	1.85
ITQ-13-4	3	3.2	1.88 <sup>c</sup>
ITQ-13-4 <sup>b</sup>	3	3.5	1.92
ITQ-17-1	15	12.2	
ITQ-17-2	10	8	
ITQ-17-3	5	6.1	
ITQ-17-4	3	4.7	1.08 <sup>c</sup>
ITQ-17-4 <sup>a</sup>	3	4.7	1.05

<sup>a</sup>After fluoride removal. <sup>b</sup>After a treatment period of 48 h to completely remove fluoride species (see text). <sup>c</sup>In as-made zeolites, the weight loss was corrected to take into account the presence of 4F/u.c. and 2F/u.c. for ITQ-13 and ITQ-17, respectively.

reaction of dibromohexane with trimethylamine in ethanol, was converted into the hydroxide form by reaction with  $\text{Ag}_2\text{O}$ . For ITQ-13, the preparation followed the recipe reported by Corma et al.<sup>17</sup> Gels with the composition  $\text{SiO}_2-x\text{GeO}_2-0.25\text{SHM}^{2+}-0.5\text{HF}-5\text{H}_2\text{O}$  ( $0 < x < 0.333$ ) were placed in stainless-steel Teflon-lined autoclaves and heated at 175 °C for 2 weeks under slow stirring (60 rpm). ITQ-17 was prepared following the same procedure except that the gel was dehydrated at room temperature for 48 h before crystallization. During the dehydration period, the  $\text{H}_2\text{O}/\text{SiO}_2$  ratio decreased to ca. 2. After crystallization, solids were recovered by filtration, washed with distilled water, and dried overnight at 110 °C.

**Exchange Procedure.** Typically, one gram of as-made zeolite was dispersed in 25 mL of  $\text{NH}_4\text{OH}$  (1 wt % aqueous solution) and heated statically at 175 °C for 24 h in closed Teflon-lined autoclaves. After that period, solids were recovered by filtration, washed and dried at 110 °C overnight.

**Physicochemical Techniques.** The crystallinity of the zeolites was determined by X-ray diffraction on a Bruker (Siemens) D5000 diffractometer using  $\text{CuK}\alpha$  radiation. Diffractograms were collected between 3 and 70° ( $2\theta$ ) with steps of 0.02° and 1 s per step.

Solid state NMR spectra were recorded on a Bruker DSX 400 spectrometer equipped with a 2.5 mm, probe head.  $^1\text{H}$ - $^{29}\text{Si}$  CP/MAS experiments were carried out at 10 kHz using a standard Cross-Polarization sequence with 5 ms contact time and 10s delay.  $^{19}\text{F}$  NMR spectra were obtained at 376.3 MHz using a one-pulse sequence with 3

$\mu\text{s}$  ( $\pi/4$ ) pulses and 5 s between pulses.  $^1\text{H}$  NMR spectra were recorded at 10 kHz with 3  $\mu\text{s}$  pulses and 1 s delay.  $^1\text{H}$ ,  $^{29}\text{Si}$  and  $^{19}\text{F}$  chemical shifts were referred to tetramethylsilane (TMS) and  $\text{CFCl}_3$ , respectively.

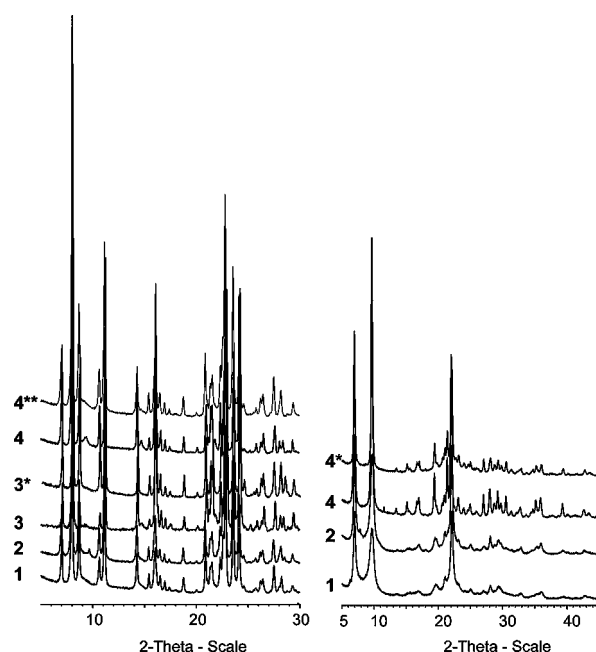
Elemental analysis data were obtained from the IRCÉLYON-CNRS Analytical core facilities; metal contents were determined by inductively coupled plasma optical emission spectroscopy (HORIBA Jobin Yvon Activa ICP-OES).

SEM pictures were obtained on a Hitachi S800 Microscope.

Thermal analysis data were obtained on a Netzsch STA 449F1 apparatus. Samples were heated in air from 25 to 1000 °C at a heating rate of 2 °C/min.

## RESULTS AND DISCUSSIONS

For Si/Ge ratios between 3 and 10, ITQ-13 and ITQ-17 can crystallize from very similar compositions, the only difference being the water content in the gel. Relatively high  $\text{H}_2\text{O}/\text{SiO}_2$  ratios ( $5 < \text{H}_2\text{O}/\text{SiO}_2 < 8$ ) favor the formation of ITQ-13 whereas ITQ-17 is preferentially obtained when Si/Ge is lower than 2. A selection of XRD patterns of ITQ-13 and ITQ-17 zeolites are shown in Figure 1. All ITQ-13 products are highly

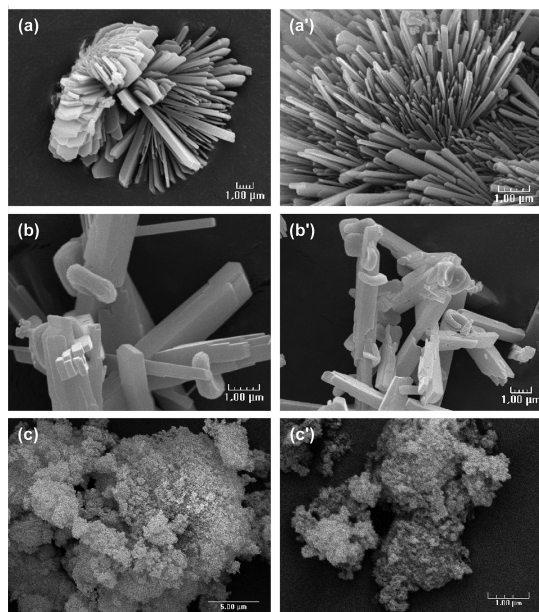


**Figure 1.** XRD patterns of ITQ-13 (left) and ITQ-17 (right) samples. Numbers refer to sample names in Table 1.

crystalline and do not contain any contaminating phase, even at low Si/Ge ratios. Moreover, the intensity and resolution of the patterns do not significantly change with the Ge content, suggesting that the incorporation of germanium has a minor influence on the crystallinity. For ITQ-17, diffractograms are all pure but reflections tend to broaden at low Ge content ( $\text{Si}/\text{Ge} > 10$ , sample ITQ-17-1), suggesting a slightly lower crystallinity. Actually, the synthesis of highly crystalline ITQ-17 zeolites is limited to a quite narrow range of composition in the presence of  $\text{HM}^{2+}$  cations and silica-rich materials are difficult to obtain in the absence of seeds. However, no other phases such as ITQ-13 were detected by XRD.

The chemical analysis of the different samples shows that the Ge content in the various samples increases with the amount of germanium introduced in the gel (Table 1). The maximum of germanium incorporation, determined in calcined dehydrated

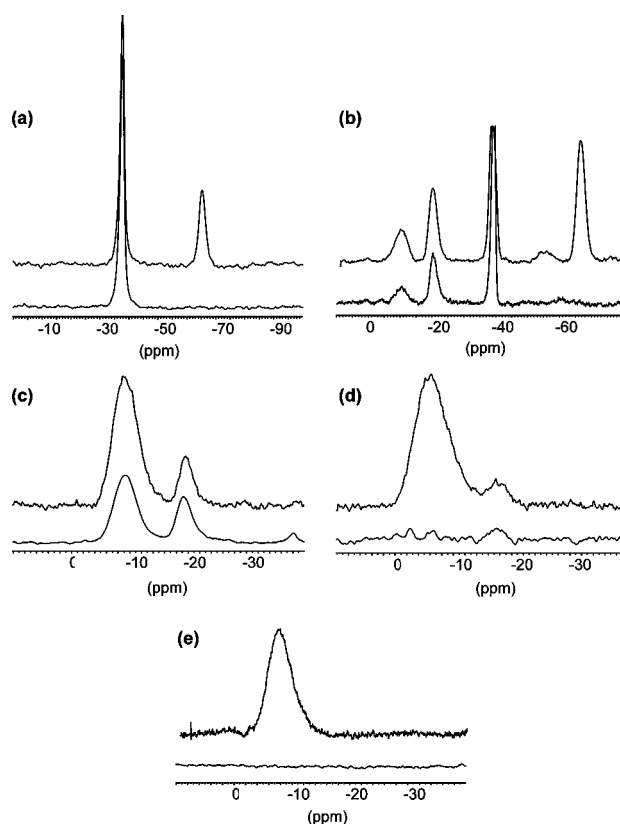
zeolites, was ca. 23 wt % in both ITQ-13 and ITQ-17, corresponding to a Si/Ge atomic ratio of 4.5. SEM pictures show that ITQ-13 zeolites are pure and highly crystalline materials, thus supporting XRD data (Figure 2). Crystals



**Figure 2.** SEM pictures of various zeolites before (left) and after (right) fluoride removal: (a, a') all-silica ITQ-13, (b, b') ITQ-13-3, and (c, c') ITQ-17-4.

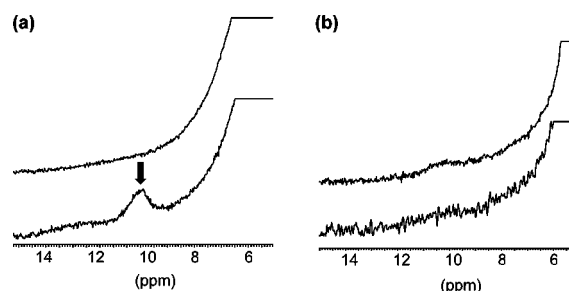
appear as aggregated elongated plates, which size increases with the germanium content. Crystals of the all-silica material, which are approximately 5  $\mu\text{m}$  long, are aggregated to form round-shaped particles of ca. 20 nm diameter. At high Ge content, crystals are less packed and their size is two or three times that obtained in the absence of germanium.

$^{19}\text{F}$  NMR spectra for the series of ITQ-13 zeolites are shown in Figure 3. As previously reported,  $^{19}\text{F}$  chemical shift is not only sensitive to the geometry of the surrounding cage but also to its chemical nature. The influence of the geometry is clearly evidenced in the spectrum of the all-silica ITQ-13 sample. For this zeolite, approximately half of fluoride species reside in  $[4^15^26^2]$  cavities of the framework while the other half is occluded in the small D4R units. These two types of fluoride species can be easily distinguished by their  $^{19}\text{F}$  NMR chemical shifts at  $-66$  and  $-38$  ppm, respectively (Figure 3a). As far as Ge is introduced, new resonances appear which assignments have been largely discussed in the literature. Basically, the peak at  $-55$  ppm characterizes F in Ge-containing  $[4^15^26^2]$  cages. Its intensity does not increase linearly with the Ge content because it was reported that the amount of fluoride in  $[4^15^26^2]$  cages decreases with Ge incorporation. The two other peaks in the region between 0 and  $-20$  ppm correspond to  $\text{F}^-$  anions at the center of Ge-containing D4R. Although the interpretation of these signals has been a matter of debate, it is reasonable to assign them to  $[(8-n)\text{Si}, n\text{Ge}]$  D4R with  $n = 1$  or 2 for the NMR line at  $\delta = -20$  ppm and  $n = 3$  or 4 for the signal at  $\delta = -8$  ppm. (ref. Sastre à rajouter) For clarity, these D4R units will be further designated as  $[7/6\text{Si}, 1/2\text{Ge}]$  D4R for  $n = 1$  or 2, and  $[5/4\text{Si}, 3/4\text{Ge}]$  for  $n = 3$  or 4. As a consequence, the intensity of signals at  $-38$  and  $-66$  ppm decrease with Ge incorporation, whereas that of the signal at  $-8$  ppm increases



**Figure 3.**  $^{19}\text{F}$  MAS NMR spectra of various ITQ-13 zeolites before (top) and after (bottom) fluoride removal: (a) all-silica ITQ-13, (b) ITQ-13-1, (c) ITQ-13-2, (d) ITQ-13-3, and (e) ITQ-13-4.

due to preferential location of Ge atoms in D4R units. For ITQ-13-4 sample with the highest Ge content, the unique signal at  $-8$  ppm in the  $^{19}\text{F}$  NMR spectrum indicates that all D4R units contain three or four Ge atoms. All  $^{19}\text{F}$  NMR spectra have been compared with those of zeolites treated in  $\text{NH}_4\text{OH}$  solutions for 24 h. For the all-silica ITQ-13, we have previously reported that the treatment removes selectively fluoride from  $[4^15^26^2]$  cages. Indeed, the intensity of the signal at  $-38$  ppm remains unchanged while the peak at  $-66$  ppm totally disappears. Simultaneously, a signal at 10.2 ppm characteristic of  $\text{SiO}^- \cdots \text{HOSi}$  hydrogen bonds appears in the  $^1\text{H}$  NMR spectrum (Figure 4). As previously reported for all-silica

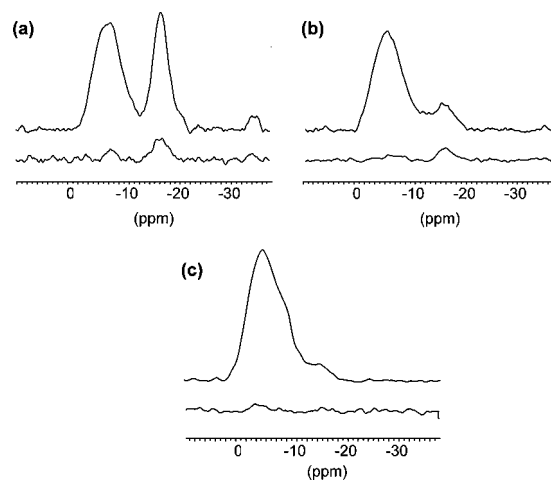


**Figure 4.**  $^1\text{H}$  MAS NMR spectra of two ITQ-13 zeolites before (top) and after (bottom) fluoride removal: (a) all-silica ITQ-13 and (b) ITQ-13-4.

zeolites with MFI and MRE framework types, the removal of fluoride anions generates connectivity defects necessary to balance the charge of the templating cations.<sup>4</sup> At low Ge contents (ITQ-13-1 and ITQ-13-2; Si/Ge  $\geq 10$ ) fluoride

removal is still selective and the alkaline treatment concerns essentially species in  $[4^15^26^2]$  cages.  $^{19}\text{F}$  NMR peaks at  $-66$  and  $-55$  ppm disappear and spectra of treated materials show exclusively fluoride in D4R units. Comparing spectra of zeolites before and after treatment shows that the intensity of the line at  $-38$  ppm does not change, supporting data obtained on all-silica ITQ-13. Similarly, the signal at  $-20$  ppm is not affected, which indicates that fluoride cannot be easily removed from D4R containing 1 or 2 Ge atoms, at least under the present experimental conditions. By contrast, the slight decrease of the intensity of the signal at  $-8$  ppm suggests that fluoride can be partially removed from  $[5/4\text{Si}, 3/4\text{Ge}]$  D4R units. As an example, the intensity decreased by ca. 20% for the sample prepared with  $\text{Si}/\text{Ge} = 10$  (ITQ-13-2) and treated for 24 h. In order to see whether defluorination is limited or not by the diffusion of fluoride species through the small 4MR windows of D4R cages, longer treatments were performed, typically for 2 and 3 days at  $175^\circ\text{C}$ . Defluorination of the solid was slightly improved by increasing the treatment period but 65% of the NMR intensity at  $-8$  ppm was still present after two days and did not change after three days. The extent of defluorination drastically increases with Ge incorporation. In the particular case of ITQ-13-4 prepared with  $\text{Si}/\text{Ge} = 3$ , the unique peak at  $-8$  ppm in the  $^{19}\text{F}$  NMR spectrum almost totally disappears upon treatment and only 5% of the initial  $^{19}\text{F}$  NMR signal remained after 24 h. The modification occurred without loss of crystallinity both the XRD pattern and SEM pictures being similar on as-synthesized and treated zeolites (Figures 1 and 2). By contrast to the previous sample, a complete removal could be obtained upon increasing the treatment period from 24 to 48 h. This two days treatment did not alter the crystallinity of the zeolite, as evidenced by the high quality pattern of the modified zeolite (Figure 1). As shown in Table 1, fluoride removal does not modify the chemical composition of the framework and Ge contents are similar before and after defluorination. Moreover, no Ge was detected in the alkaline  $\text{NH}_4\text{OH}$  solutions, supporting the absence of partial dissolution of the framework during the treatment. Thermal analysis data of nontreated and treated solids confirmed that all templating molecules were still present in the channels of the framework after removal of fluoride species (Table 1). The above results are of particular importance because they show that the removal of fluoride from the framework of ITQ-13 is not limited by diffusion through 4MR windows and they strongly support the role of Ge in the stabilization of D4R units. Actually, data are consistent with the fact that silica-rich ITQ-13 cannot be synthesized in the absence of fluoride. At low Ge concentrations, fluoride, which is essential to the crystallization of ITQ-13 and to the stabilization of D4R cages, cannot be completely removed from the framework. This is particularly true for  $[8\text{Si}]$  and  $[7/6\text{Si}, 1/2\text{Ge}]$  D4R units, the  $^{19}\text{F}$  signal assigned to these units being practically unaffected by the treatment. By modifying the mean T–O bond lengths and T–O–T bond angles in the framework, incorporation of Ge relaxes the structure and, thus, minimizes the stabilizing effect of fluoride anions in D4R units. As a consequence, the presence of Ge facilitates the removal of fluoride, particularly in Ge-rich zeolites. It has been reported previously that Ge-rich ITQ-13 could be obtained directly under alkaline pH conditions in the absence of HF.<sup>27</sup> This clearly shows that  $\text{F}^-$  anions are not necessary to stabilize D4R units and may explain why a complete removal of fluoride species is possible in these zeolites.

The possibility to remove totally fluoride from the framework of Ge-rich zeolites containing D4R units has been confirmed on a series of ITQ-17 zeolites. ITQ-17 (BEC framework type) has a three-dimensional pore system with three 12-membered rings channels. The structure is built up from D4R secondary building units that delimit two types of cavities, namely  $[5^4]$  and  $[4^6]$  (or D4R) cavities.<sup>28</sup> By contrast to ITQ-13, fluoride is exclusively located in the small D4R cages, which is confirmed by  $^{19}\text{F}$  NMR. Spectra consist of two major signals at  $-8$  and  $-20$  ppm, along with a weak resonance at  $-38$  ppm (Figure 5). The peak at  $-20$  ppm assigned to



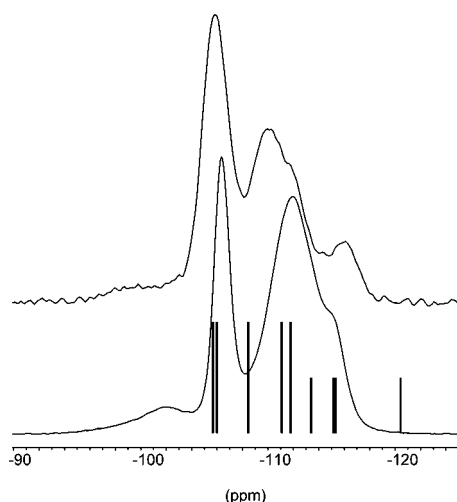
**Figure 5.**  $^{19}\text{F}$  MAS NMR spectra of various ITQ-17 zeolites before (top) and after (bottom) fluoride removal: (a) ITQ-17-1, (b) ITQ-17-3, and (c) ITQ-17-4.

$[7/6\text{Si}, 1/2\text{Ge}]$  D4R is essentially present on sample ITQ-17-1 prepared with  $\text{Si}/\text{Ge} = 15$  and its intensity completely disappears for ITQ-17-4 ( $\text{Si}/\text{Ge} = 3$ ). This sample shows a unique NMR peak at  $-8$  ppm, consistent with  $[5/4\text{Si}, 3/4\text{Ge}]$  D4R cages. Treating the samples with  $\text{NH}_4\text{OH}$  solutions almost completely removes fluoride from all ITQ-17 samples. For the lowest Ge contents ( $\text{Si}/\text{Ge} = 15$  and  $10$ ), weak NMR peaks at  $-38$  and  $-20$  ppm are still observed after treatment but their intensity represents less than 5% of the original  $^{19}\text{F}$  intensity. At higher Ge content, the totality of fluoride is removed from the framework of ITQ-17. These “fluoride-free” ITQ-17 samples remain highly crystalline, as evidenced by X-ray diffraction (Figure 1). Both the reflection intensities and the resolution of the patterns remained unchanged upon treatment. Moreover, despite  $\text{H}_2\text{O}/\text{SiO}_2$  ratios favorable to the crystallization of ITQ-13, no diffraction peaks corresponding to this zeolite were detected after treatment. By contrast to ITQ-13, ITQ-17 crystals are very small and it was not possible to get any information on the evolution of the crystal shape by SEM (Figure 2). Chemical analysis of the samples gave similar germanium contents for as-made and treated materials, suggesting that Ge was not extracted from the framework under alkaline pH conditions (Table 1).

Previous results obtained on all-silica zeolites with MFI and MRE framework types showed that the removal of fluoride anions was balanced by the creation of framework connectivity defects, which maintained the electric neutrality of the zeolite.<sup>20</sup> For the all-silica ITQ-13 solid, the formation of defects upon exchange of fluoride in  $[4^15^26^2]$  cages is evidenced by the presence of a new line at  $10.2$  ppm in the  $^1\text{H}$  NMR spectrum.

As previously reported, this line is characteristic of  $\text{SiO}^- \cdots \text{HOSi}$  hydrogen bonds in the silica framework.<sup>4</sup> Although the substitution of tetravalent Ge for Si in zeolites maintains the neutrality of the framework, the  $^1\text{H}$  NMR signal at 10.2 ppm is not observed in the spectra of treated Ge-rich zeolites. In pure silica zeolites, connectivity defects are formed by breaking Si–O–Si bridges between two neighboring atoms of the framework. At high Ge contents, the probability to form  $\text{SiO}^- \cdots \text{HOGe}$ ,  $\text{GeO}^- \cdots \text{HOSi}$  or even  $\text{GeO}^- \cdots \text{HOGe}$  connectivity defects increases. In zeolites, Ge–O bond lengths are systematically larger than Si–O bond lengths. In the particular case of ITQ-17, Ge–Si distances are ranging from 3.19 to 3.27 Å, in comparison to Si–Si distances comprised between 2.99 and 3.12 Å in the pure silica framework.<sup>31</sup> Therefore, it is reasonable to assume that the O–H $\cdots$ O hydrogen bond distance between Si and Ge atoms is increased and that the corresponding  $^1\text{H}$  NMR chemical shift is modified. Indeed, it has been reported that the proton chemical shift was very sensitive to the geometry of the hydrogen bond and that increasing the O–H $\cdots$ O distance by only 0.5 Å shifts the signal by more than 10 ppm toward high fields.<sup>32</sup> The possibility to have defects preferentially located on or immediately close to a Ge atom in Ge-rich zeolites could explain the absence of NMR line at 10.2 ppm. However, a deeper characterization of the zeolites will be necessary to identify the nature of the charge that neutralizes the template after removal of fluoride.

Although powder XRD patterns of ITQ-13 and ITQ-17 zeolites are not modified after fluoride removal, significant changes are observed in  $^{29}\text{Si}$  NMR spectra. By contrast to X-ray diffraction, NMR is very sensitive to the local environment of atoms and to their interactions with molecules. Upon removing fluoride from small cavities of the framework, the environment of surrounding Si atoms is modified and  $^{29}\text{Si}$  NMR chemical shifts change. As an example,  $^{29}\text{Si}$  MAS NMR spectra of all-silica ITQ-13 before and after fluoride removal are shown in figure 6. Although the treatment removes only F species in



**Figure 6.**  $^{29}\text{Si}$  MAS NMR spectra of all-silica ITQ-13 before (top) and after (bottom) fluoride removal. Straight lines indicate the predicted chemical shifts for crystallographic sites T2, T5, T7, T6, T3, T8, (T1,T9), and T4 (from left to right) according to ref 22.

$[4^15^26^2]$  cavities, spectra are significantly different, particularly in the region between  $-108$  and  $-115$  ppm. According to Vidal-Moya et al. this region corresponds to sites T7, T6, and

T3 in the zeolite framework, which are actually the three sites forming  $[4^15^26^2]$  cages.<sup>22</sup> It is interesting to note that the line at  $-107$  ppm assigned to Si atoms in D4R remains at the same place, thus confirming that these units are not directly affected by the treatment. NMR shifts are also observed in the spectra of Ge-containing ITQ-13 and ITQ-17 zeolites but additional experiments using  $^{19}\text{F}$ – $^{29}\text{Si}$  polarization transfer will be necessary to correlate these modifications with local structural changes. Nevertheless, preliminary data obtained on Ge-rich materials ( $\text{Si}/\text{Ge} < 5$ ) seem to indicate that the environment of silicon atoms after removal of fluoride is very similar to that observed on zeolites prepared directly in the absence of fluoride.

Data obtained on samples ITQ-13–2 and ITQ-17–2 prepared with  $\text{Si}/\text{Ge} = 10$  in the gel seem to indicate that it is easier to remove fluoride from D4R cages in ITQ-17 as compared to ITQ-13. Indeed, more than 95% of fluoride is removed from ITQ-17, even from  $[7/6\text{Si}, 1/2\text{Ge}]$  D4R units. By contrast, fluoride is not removed from  $[7/6\text{Si}, 1/2\text{Ge}]$  units in ITQ-13 and only 20% of fluoride is removed from  $[5/4\text{Si}, 3/4\text{Ge}]$  D4R. Up to now, the difference between the two zeolites has not been clearly explained but structural parameters like the framework density, the topology or the accessibility to 4MR windows may have an influence on the diffusion of fluoride species through the crystal.

## CONCLUSION

ITQ-13 and ITQ-17 zeolites are generally synthesized at moderate pH values from nearly dry gels in the presence of fluoride anions. After crystallization, these anions are occluded in the framework, particularly in the center of D4R units, and serve as charge compensators for templating molecules. In the present work, we have shown that fluoride could be partially or totally removed from D4R units in both as-made zeolites. The removal is performed in the presence of templating molecules and affects neither the framework Ge content nor the crystallinity of the zeolite. The extent of defluorination depends essentially on the Ge content in the zeolite framework. For ITQ-13 zeolites with low Ge contents, fluoride is essentially removed from  $[4^15^26^2]$  cavities of the framework, in agreement with previous data obtained on pure silica zeolites, which suggested that silica-rich D4R units could not be stable in the absence of  $\text{F}^-$  anions. At higher contents, fluoride present in the center of D4R units is also removed, and a complete removal can even be achieved for  $\text{Si}/\text{Ge}$  ratios lower than 3. Experimental data show that the removal of F species from D4R cages also depends greatly on the zeolite structure, particularly for relatively high Ge contents ( $5 < \text{Si}/\text{Ge} < 10$ ).

The possibility to remove totally fluoride from Ge-rich zeolites supports the stabilizing role of germanium, which relaxes the structure, particularly when the latter contains D4R units. Indeed, fluoride-free ITQ-13 and ITQ-17 can be obtained by direct synthesis from purely hydroxide media, but only for high Ge concentrations.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: alain.tuel@ircelyon.univ-lyon1.fr.

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