Zeolites

DOI: 10.1002/ange.201306744

Quasi All-Silica Zeolite Obtained by Isomorphous Degermanation of an As-Made Germanium-Containing Precursor

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Abstract: *Ge-containing ITQ-22 zeolites have been almost completely degermanated under strong acidic conditions without modifications of the framework topology. Simultaneous to Ge extraction, the framework was partially dissolved; mesopores were formed but the structure was maintained through the re-incorporation of some of silicon species at vacant sites. The presence of many defects in the degermanated framework enabled the incorporation of tetrahedral aluminum, opening the way to the preparation of new and stable acid catalysts with original topologies.*

Owing to the presence of pores and cavities of molecular dimensions in their structures, zeolites are inorganic crystalline materials that are widely used in catalysis, adsorption and separation. The necessity for molecules to diffuse through the zeolites channels means that large-pore zeolites (in which channels are delimited by more than 12-membered rings) with three-dimensional pore structures are generally preferred. However, medium- or even small-pore zeolites are also potentially interesting in catalysis because they can change the nature of the products in a reaction, following the so-called "shape selectivity" concept. For this reason, the presence of interconnected pores with different sizes in the same zeolite structure would be particularly interesting for reactions necessitating both fast diffusion of the reagents and shape selectivity. Such zeolites have been recently reported, the most significant examples being ITQ-47, the synthetic counterpart of the natural boggsite and ITQ-22.[1,2] ITQ-22 was the first zeolite with a fully interconnected system of small (8MR), medium (10MR), and large (12MR) pores. This zeolite is obtained in the presence of germanium, using hexamethonium (HM) or 1,5-bis(methylpyrrolidinium)pentane (MPP) cations as organic structure directing agents (OSDAs).[3] Since ITQ-22 is synthesized in the absence of fluoride anions, high framework Ge contents are generally observed in the final zeolites, particularly in the small D4R units of the structure, making the preparation of the zeolite quite expensive. Moreover, high Ge contents decrease the hydrothermal stability of the zeolite by facilitating the hydrolysis of T–O–T bonds in the framework. Stabilization of germanium-containing zeolites can be achieved either by direct synthesis of materials with higher Si/Ge ratios or by post-synthesis treatments of Ge-rich solids.[4] Theoretical methods to find structure-directing molecules that better stabilize the structures, along with an optimization of the synthesis conditions can lead to materials with lower Ge contents in the framework. However, this method is limited to a small number of zeolite structures and data concerning the preparation of Si-rich ITQ-22 have not yet been reported. Concerning post-synthesis treatments, it was reported that ITQ-17 could be stabilized by simultaneous Ge extraction and Al incorporation in the framework under mild acidic conditions.[5,6] However, Ge extraction was limited (the Si/Ge ratio in the treated zeolite never exceeded 10) and the impact of the treatment on the crystallinity was not clearly illustrated.

ITQ-22 samples with various Ge contents were prepared following literature procedures using MPP cations as OSDA (Table 1).[2]

Table 1: Chemical composition and structural properties of as-made and treated ITQ-22 zeolites.

Sample[a]	Ge [wt.%] As-made	Treated[b]	S_{BET} [m^{2}g^{-1}][c]	V_P [cm^{3}g^{-1}] V_{micro}	V_{meso}
ITQ-22(10)	8	0.71	492	0.185	0.112
ITQ-22(5)	16.5	0.66	483	0.18	0.135
ITQ-22(3)	22	0.83	477	0.17	0.148

[a] The value between parentheses is the Si/Ge ratio in the gel. [b] Treated 2 times with HCl 37 wt.%. [c] Measured on treated samples evacuated at 250°C under vacuum.

Attempts to decrease the framework Ge content using slightly acidic solutions (HCl, 10^{-2} M) as for ITQ-17 were not successful.[5,6] The composition of the zeolites remained unchanged, even after stirring for 24 h at 150°C (Table S1, Supporting Information). One of the zeolites (sample ITQ-22(5) in Table 1) was then selected and subjected to treatments with more concentrated solutions (from 10^{-2} M to 12 M), the highest concentration corresponding to a 37 wt.% commercial solution). After each treatment, the zeolite was immediately characterized by X-ray diffraction (XRD) to evaluate the effect of the acidity on the framework. As shown in Figure 1, the crystallinity of the zeolite was retained, even after a treatment in concentrated HCl solutions.

No addition phases were formed, in particular lamellar phases, as was observed in the case of UTL zeolite.[8,9] However, although the diffraction peaks remained intense and well resolved, their relative intensities gradually changed

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201306744.

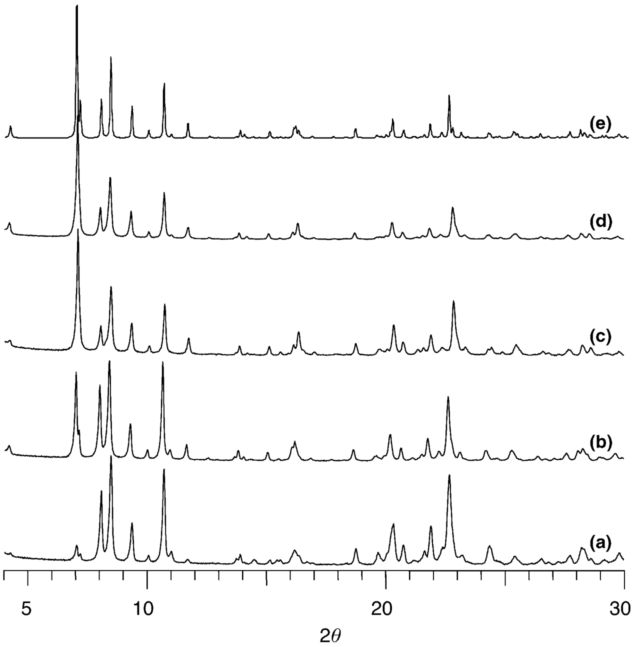

Figure 1. XRD patterns of ITQ-22(5): As-made (a), calcined (b), treated 2 times with 37 wt.% HCl (c), and calcined after HCl treatment (d). Pattern (e) was simulated assuming a pure silica framework.[7]

with the acid concentration, particularly in the region below 10° (2θ; Figure S1, Supporting Information). More specifically, the intensity of the (001) diffraction peak at $2\theta \approx 7°$ increased with the acid concentration and it became the most intense peak after treatments in concentrated solutions. Such an increase can be explained either by a partial removal of organic molecules from the pores or by a modification of the framework composition of the zeolite. Indeed, at low angle values, peak intensities are very sensitive to the nature of the molecules adsorbed inside the pores and/or to the presence of framework heteroatoms, particularly heavy atoms, such as Ge.[10] A thermo-gravimetric analysis confirmed that the zeolite treated in 12 M HCl solution contained less than 10% of the organic molecules initially present in the pores and that 90% of MPP cations had been removed (Figure S2, Supporting Information). However, XRD intensities of the treated solid did not match at all with those observed on the pattern of the calcined initial zeolite, which suggested that the treatment not only removed OSDA molecules from the channels but also probably modified the framework composition (Figure 1b). By contrast, the pattern fitted almost perfectly that calculated for a hypothetical all-silica framework, thus indicating that the zeolite was most likely enriched in silicon after acid treatment (Figure 1e).

Chemical analysis of the sample confirmed a high degree of degermanation of the zeolite after a treatment in concentrated HCl (Table 1). Indeed, the Ge content decreased from 16.5 wt.% in the initial zeolite (Si/Ge = 5.6; 17 Ge atoms/unit cell (u.c.)) to 1.2 wt.% after a treatment (Si/Ge = 100; 1.12 Ge/u.c.). A second treatment was then applied to the zeolite to evaluate the possibility to extract more Ge atoms from the framework. Though the Ge content decreased to 0.66 Ge/u.c. (Si/Ge = 185), no changes could be observed in the XRD pattern, indicating that the structure of ITQ-22 is stable in a quasi-all-silica form.

The zeolite treated two times in concentrated HCl solutions was further characterized by nitrogen adsorption. The zeolite was degassed under vacuum at 250 °C, a temperature lower than that corresponding to the decomposition of OSDA molecules (ca. 350 °C). Data reported in Table 1 showed that the BET surface area and pore volume are similar to those reported for directly calcined ITQ-22 zeolites, thus supporting the complete removal of OSDA molecules from the pores upon acid treatment.[11] The isotherm was characteristic of microporous solids (type I) with a hysteresis loop closing at $p/p_0 \approx 0.45$ (Figure S3, Supporting Information). The hysteresis loop is generally observed on post-synthesis treated zeolites in which internal mesopores obtained either by dealumination under alkaline pH conditions or by desilication at low pH values, are connected to the surface by micropores.[12,13] TEM images confirmed the highly porous character of the zeolite crystals in agreement with a mesoporous volume of 0.135 $cm^3 g^{-1}$ obtained from nitrogen adsorption data.

In contrast to mesopores created by dealumination or desilication, mesopores obtained by degermanation have a regular shape and seemed to be all oriented along one of the directions of the crystals (Figure 2).[14,15] The presence of mesopores in the treated zeolite suggests that the framework is partially dissolved under the acidic conditions. However, the zeolite weight loss, which is limited to 35 wt.% and corresponds approximately to the removal of both Ge species (16.5 wt.%) and organic molecules (15 wt.%), which implies that some of the dissolved Si species are probably re-incorporated into the framework.

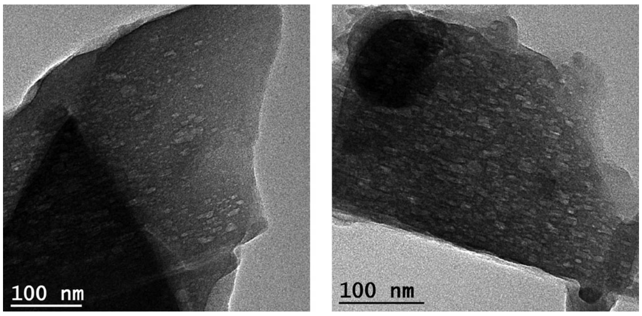

Figure 2. TEM pictures of ITQ-22(5) treated 2 times with 37 wt.% HCl solutions.

As with dealumination, degermanation most probably creates many defects in the framework that can be detected using spectroscopic techniques. The ^{29}Si MAS NMR spectrum of the original zeolite showed several signals between $\delta = -100$ and -120 ppm, characteristic of framework silicon atoms with different chemical environments (Figure 3).

Though the assignment of the different NMR signals was not reported for ITQ-22, it is generally accepted that chemical shifts between $\delta = -90$ and -100 ppm correspond to silanol groups, those between $\delta = -100$ and -110 ppm to Q^4 atoms with at least one Ge atom in the first coordination sphere and

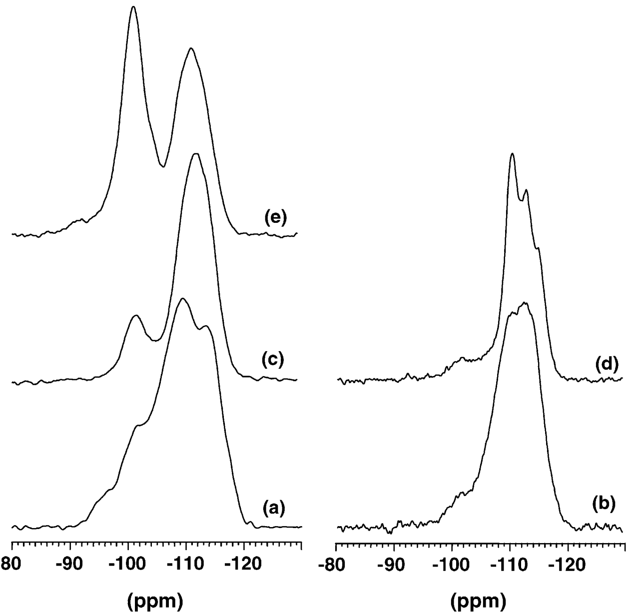

Figure 3. ^{29}Si MAS NMR spectra of ITQ-22(5): As-made (a), calcined (b), treated (c), treated and calcined (d) and ^{1}H-^{29}Si CP/MAS NMR spectrum of the treated zeolite (e).

those between $\delta = -110$ and -120 ppm to Q^4 silicon atoms surrounded by 4 Si atoms.[10,16] The spectrum of the zeolite treated two times with concentrated HCl was drastically different and composed of two main signals at approximately $\delta = -100$ and -115 ppm. Most of the contribution between $\delta = -100$ and -110 ppm had disappeared, thus supporting the removal of Ge atoms from the zeolite framework. The NMR signal at $\delta = -115$ ppm corresponds to $Si(OSi)_4$ silicon atoms in the framework whilst the smaller signal at $\delta = -100$ ppm results from the presence of silanol groups. Indeed, the intensity of this line considerably increased when proton polarization was transferred to silicon atoms using a ^{1}H-^{29}Si CP/MAS sequence (Figure 1 e).[17]

The stability of the treated zeolite was confirmed by heating the solid in air at 550 °C. The structure was preserved, as evidenced by X-ray diffraction, with a powder pattern similar to that of the non-calcined material (Figure 1 d). Calcination considerably reduced the population of silanol groups, the ^{29}Si MAS NMR spectrum being composed of a main signal at $\delta = -115$ ppm along with a shoulder at $\delta = -100$ ppm (Figure 3 d).

The possibility to incorporate Al in a highly mesoporous and thermally stable [Si]-ITQ-22 would be very interesting for specific catalytic reactions, particularly those involving bulky molecules. Al can be incorporated in ITQ-22 along with germanium directly during synthesis, leading to materials with unique shape selectivity effects owing to the particular pore topology.[2,11] However, low pH values systematically remove Al from zeolite frameworks and it was not possible to obtain aluminosilicate materials by degermanation of [Al]-ITQ-22. In the case of ITQ-17, it was reported that aluminum could be incorporated simultaneously to Ge removal under weakly acidic conditions.[6] For ITQ-22 this was not feasible because degermanation was only effective under very concentrated solutions. Nevertheless, Al incorporation could be achieved by taking advantage of the high density of hydroxy nests in the framework of degermanated [Si]-ITQ-22. The treated zeolite was dispersed in an acidic solution (HCl, pH 2) of aluminum sulfate and the mixture was stirred at 90 °C overnight. X-ray diffraction confirmed that the crystallinity of the zeolite was not altered and incorporation of aluminum was evidenced by chemical analysis (the solid contained 0.75 wt. % Al, corresponding to a molar ratio Si/Al $\approx$ 60) and ^{27}Al MAS NMR (Figure S4, Supporting Information). The spectrum was composed of one signal at approximately $\delta = 52$ ppm, characteristic of four-coordinate species in silica frameworks.[18] In addition, Al species were stable in the framework and they retained their tetrahedral coordination upon calcination in air at 550 °C.

The same treatments (two consecutive treatments with 12 M HCl solutions) were also applied to ITQ-22 zeolites with different Ge contents (Table 1). In all cases, the results were similar, suggesting that the degermanation process does not depend on the amount of Ge originally present in the framework.

Verheyen et al. have recently reported the almost complete degermanation of the calcined form of the UTL zeolite under strongly acidic conditions.[19] Degermanation of the zeolite led to the formation of a new structure by selective removal of germanium-containing 4-rings units in the framework and condensation of silanol groups. The same zeolite treated under less-severe acidic conditions (0.1 M HCl solutions) led to layered materials that could be further transformed into 3D zeolites by connecting layers together with different linkers.[8,9] As for UTL, the framework of ITQ-22 contains silica-rich layers in the *ab* plane connected to each other by Ge-containing D4R units along the *c*-direction. However, the degermanation process is most certainly different because the original structure of ITQ-22 is preserved in the absence of template, even at very low framework Ge contents. The main reasons could be that the treatment was performed on as-made material or that Ge distributions are different in both frameworks. It has been proposed that in the UTL structure, Ge atoms form 4-rings germanate units that connect D4R to the layers. In such a configuration, Ge extraction separates layers from each other with formation of $Si(OSi)_3OH$ groups, as evidenced by ^{29}Si NMR spectroscopy.[19] Although Ge has also been found to be essentially located in D4R units of the ITQ-22 structure, more stable configurations are possible in which each Ge atom is connected to four Si atoms.[20] Extraction of Ge then leads to $Si(OSi)(OH)_3$ moieties with formation of hydroxy nests capable of re-incorporating partially dissolved Si species, which maintains the integrity of the zeolite structure. Further studies are in progress to better understand why ITQ-22 and UTL, which possess similar framework compositions, behave differently under acidic conditions.

In any case, the work presented herein shows the quasi-complete degermanation of an as-made ITQ zeolite without modification of the framework topology. The process is particularly interesting because it does not necessitate the preliminary calcination of the zeolite and it allows a complete recovery of Ge in solution. There is no doubt that it will open the route to the preparation of new Si-rich large-pore zeolites that can only be prepared in the presence of germanium.[21]

Experimental Section

ITQ-22 zeolites were prepared using 1,5-bis(methylpyrrolidinium)-pentane (MPP) cations following literature procedures.[2] As-made samples were treated at 120 °C with HCl solutions (from 10^{-2} to 12 M; 30 mL solution/g of zeolite) in Teflon-lined stainless steel autoclaves under fast stirring (400 rpm) for 16 h. Treated zeolites were then washed and dried at room temperature in air.

Incorporation of aluminum was performed by stirring the dried zeolite in a solution of aluminum sulfate in HCl (pH 2) at 80 °C for 12 h (1 g zeolite/50 mL solution). The zeolite was then washed and dried at room temperature.

The germanium content in the different zeolites was obtained by ICP-OES after digestion of calcined zeolites in HF/HCl solutions.

TEM images were obtained on a Jeol 2010 LaB6 microscope operating at 200 kV.

Solid-state NMR spectra were recorded on a Bruker DSX 400 spectrometer. ^{29}Si MAS experiments were carried out at 79.4 MHz in 4 mm rotors spun at 10 kHz. Data were collected using a standard one-pulse sequence with 5 μs (π/3) pulses and 60 s delay. For ^{1}H-^{29}Si CP/MAS experiments, the contact time was fixed to 5 ms and the delay between consecutive pulses was 4 s. ^{29}Si chemical shifts were referred to tetramethylsilane (TMS).

The crystallinity of the zeolites was determined by X-ray diffraction on a Bruker (Siemens) D5000 diffractometer using $\mathrm{Cu}_{K\alpha}$ radiation. Diffractograms were collected between 4 and 80° (2θ) with steps of 0.02° and 1 s per step.

BET surface areas were measured on an ASAP 2010 (Micromeritics) apparatus by nitrogen adsorption on samples preliminary desorbed at 250 °C for 4 h.

TGA data were measured on a Mettler Toledo DGA DSC 1 STAR^{e} System apparatus. Samples (approx. 15 mg) were heated in air from 25 to 750 °C at a heating rate of $10\,^{\circ}\mathrm{C\,min^{-1}}$.

Received: August 1, 2013
Revised: October 11, 2013

Keywords: acid treatment · germanium · post-synthesis treatment · silicon · zeolites

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