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High-silica hollow Y zeolite by selective desilication of dealuminated NaY crystals in the presence of protective Al species

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†Electronic Supplementary Information (ESI) available: NMR spectra of parent and hollow zeolite Y, SEM pictures of NaY dealuminated with SiCl₄ and NaY treated in the absence of acid leaching, XRD patterns of zeolites treated with NaOH and without acid leaching and IR spectra of the zeolites at each step of the process.

Abstract

Highly crystalline hollow Y zeolite has been obtained by post-synthesis modification of conventional NaY crystals. The top-down transformation involves substantial dealumination of the zeolite framework by silicon tetrachloride followed by acid leaching and finally selective dissolution of the crystal core in the presence of protective aluminium species. The formation of internal cavities depends on the extent of dealumination of the zeolite as well as on the efficiency to remove extraframework Al species prior to realumination. Hollow Y zeolite crystals possess more or less regular internal cavities of ca. 0.8 μm diameter with external size and shape similar to those of the original NaY crystals. They differ from those recently reported in the literature by much higher Si/Al ratios, higher crystallinities and pure microporous shells of ca. 0.12 μm thickness. As a result of these differences, the family of hollow faujasites is significantly enlarged towards more siliceous and less defective materials. Their formation is most likely based on the presence of an Al-rich surface generated by NaAlO₂ species during the last stage of the process, which protects the outer parts of the crystals from desilication.

1. Introduction

Mainly motivated by catalytic, adsorption and separation applications, the design of zeolites with diverse crystal sizes and well controlled morphologies remains a topic of intense research and development.¹⁻⁷ Over the last decades, the influence of crystal size on the catalytic properties of zeolites has been widely studied and it is generally accepted that a decrease of the characteristic diffusion length improves the catalytic efficiency and can have a major influence on selectivities.^{8,9} By contrast, studies on the effects of the morphology remain scarce. One of the reasons is that modification of the crystal habit is almost systematically associated with a change in dimension, at least along one of the axes of the crystal, which generally hides the real impact of the morphology. Unusual morphologies such as needles, plates or sheets do not only improve mass transport throughout the crystals, they also enable the exposure of preferential crystal faces, which may be particularly interesting for facilitating the diffusion when frameworks contain pore systems of different sizes.¹⁰⁻¹⁴ Specific morphologies may also be used to create unique materials associating the intimate properties of zeolite frameworks with those of original architectures. Famous examples include polycrystalline zeolite spheres and hollow zeolite single crystals in which a large internal cavity is completely isolated and communicates with the outside only by sub-nanometric micropores.¹⁵⁻²¹ Hollow single crystals have recently received considerable interest because of their ability to encapsulate noble metal and transition metal oxide nanoparticles with controlled size and composition.²²⁻²⁵ These yolk-shell systems have been used as nanoreactors in various catalytic reactions with remarkable shape selectivity in the hydrogenation of substituted aromatics and poison resistance in the CO oxidation in the presence of propylene.^{26,27} These characteristics have been attributed to the presence of the microporous zeolite shell around the nanoparticle, which acts as a barrier for large molecules. Nonetheless, these systems are to date limited to ZSM-5 and silicalite-1 zeolites, both with the **MFI** framework type. Indeed, the formation of hollow structures by selective desilication requires a heterogeneous composition of the crystals due to either an aluminium zoning with Al-rich surfaces for ZSM-5 or a higher density of structural defects in the inner parts of the crystals for silicalite-1. For most other types of zeolites with homogeneous crystal compositions, the desilication is not selective and leads to the formation of mesopores randomly distributed throughout the crystals. Desilication of Y zeolite crystals in alkaline solutions has been widely studied and the corresponding hierarchical structures, which combine micro- and mesopores, have shown improved transport properties, catalyst lifetime and selectivities, particularly for reactions involving large molecules.²⁸⁻³⁰ The mesopore size distribution is generally fairly broad but it can be significantly reduced when desilication is performed in the presence of surfactant molecules such as CTAB.^{31,32} However, mesopores obtained in the presence of CTAB possess a relatively small opening of ca. 3 nm and their connection with the crystal surface means that they cannot be used for the encapsulation of nanoparticles, particularly when these nanoparticles have a diameter higher than 4-5 nm. Recently, Yuan et al. have shown that mesostructured hollow faujasites can be obtained by desilication of crystals which have previously been partially dealuminated by silicon tetrachloride.³³ For the authors, the design of crystals with a Si-rich surface and an Al-rich core introduced by SiCl₄ treatment was a critical factor for the formation of the internal cavity. However, the low extent of dealumination implied that the crystallinity of the zeolite was significantly affected by the alkaline treatment

and that many mesopores were formed in the shell. These mesopores were beneficial to the activity of the zeolite in the conversion of 1,3,5-triisopropyl benzene, but they might nonetheless be detrimental to other reactions for which the zeolite shell must act as a size-selective membrane. The synthesis of hollow Y zeolite crystals with high crystallinity, high Si/Al ratios and purely microporous shells is highly motivated and remains a challenge. Hollow Y crystals would significantly enlarge the possibilities offered by hollow MFI-type zeolites in size-selective catalysis, in particular because of their difference in pore size. Moreover, the presence of an internal cavity with relatively thin walls would also allow deeper understanding of the effects of crystal size and external surface on transport and catalytic properties of dealuminated faujasites.

In the present work, we report a top-down method for the synthesis of highly crystalline high-silica hollow Y zeolite capsules, starting from conventional NaY crystals. Our materials have been obtained following a multi-step process combining dealumination, acid leaching, and selective desilication in the presence of aluminium species. Compared to previous work, these materials possess higher framework Si/Al ratios, excellent crystallinities and purely microporous shells.³³

2. Experimental section

Hollow Y zeolite crystals have been obtained from a parent NaY following is a 3-step synthesis process involving dealumination, acid leaching and alkaline treatment. At each step, the solid was characterized in order to follow chemical and structural modifications of the zeolite framework and identify possible mechanisms for the selective desilication.

2.1. Synthesis of parent Y zeolite

A gel of NaY zeolite was first prepared with standard reactants to obtain a molar composition of $4 \text{ Na}_2\text{O} - 1 \text{ Al}_2\text{O}_3 - 10 \text{ SiO}_2 - 180 \text{ H}_2\text{O}$.³⁴ It was aged for 24h at room temperature and then heated at 100°C for another 24h to promote the crystallization. The obtained zeolite was filtered, washed with distilled water and dried at 90°C. The as-synthesized dry zeolite crystals were then subjected to the following three-step procedure.

2.2.1. Step 1: dealumination procedure

According to the method of Beyer et al., 2 g of the original Y zeolite were placed in the powder form in a tubular quartz reactor.³⁵ The reactor temperature was then increased under nitrogen flow to 350°C at a rate of 10°C.min⁻¹ and kept at this value for 2 hours to achieve a complete dehydration of the zeolite. After cooling down to 250°C, the nitrogen flow passing through the zeolite bed was saturated at room temperature with silicon tetrachloride. Temperature was then increased to 560°C with a rate of 10°C.min⁻¹ and the zeolite was treated at this temperature for 1 hour. Then the reactor was purged for 1 hour with pure nitrogen. After cooling to room temperature the sample was washed with deionized water and dried overnight at 90°C.

2.1.2. Step 2: acid leaching

The dealuminated zeolite was then treated with a 0.1 M hydrochloric acid solution. 1 g of sample was dispersed in 20 mL of HCl solution and stirred in a round-bottomed flask for 4 hours at a temperature of 80°C. The solid was recovered by filtration, washed with deionized water and dried overnight at 90°C.

2.1.3. Step 3: Alkaline desilication with Al-containing reactant

The dried, dealuminated and acid-leached sample was dispersed into an aqueous solution of sodium aluminate (Riedel de Haën, 0.01 M) with a solid-to-liquid ratio of 1:60. After a short time of homogenization, the solution was put in an oil bath, progressively heated at 60°C and kept for 4 hours under vigorous stirring. Subsequently, the suspension was filtered, washed with deionized water and dried overnight at 90°C.

2.2. Characterization techniques

X-ray powder diffraction (XRD) patterns were recorded on a D8 advance A25 diffractometer (CuK α 1 radiation at $\lambda = 1.5406 \text{ \AA}$) equipped with a Ni filter and 1-D fast multi-strip detector (LynxEye, 192 channels on 2.95°). Measurements were performed at room temperature under air, from 4 to 80° with 0.02047° steps and 0.5 s per step.

Scanning Electron Microscope (SEM) images were collected on a FEI ESEM-XL30 microscope under high vacuum (FEG source). Surface analysis by SEM is usually performed using low voltages (< 5kV) on gold-coated solids. In the present case, bulk analysis was performed on uncoated crystals using a high voltage of 20 kV. Under such conditions, electrons penetrate deeply in the solid and give direct information about the presence of hollow structures by enhancing the contrast between regions of the crystal with different densities. A dispersion of the sample crushed in ethanol was deposited on standard holey carbon-covered copper TEM grids. Transmission electron microscopy (TEM) images were obtained on a JEOL 2010 LaB6 microscope operating at 200 kV. A dispersion of the sample crushed in ethanol was deposited on standard holey carbon-covered copper TEM grids.

N₂ adsorption / desorption isotherms were measured at 77K on a Belsorp-mini (BEL-Japan) sorption apparatus. Circa 50 mg of sample was outgassed under vacuum in a cell at 300°C overnight prior to adsorption.

²⁹Si and ²⁷Al MAS NMR spectra were obtained on a Bruker DSX 400 spectrometer equipped with a double-bearing probe-head. Samples were spun at 10 kHz in 4 mm zirconia rotors. Spectra were recorded with pulse lengths and recycle delays of 4 μ s ($\pi/4$) and 100 s for ²⁹Si, 1 μ s ($\pi/6$) and 1 s for ²⁷Al, respectively. Chemical shifts were referenced to tetramethylsilane (TMS) and Al(H₂O)₆³⁺ for Si and Al, respectively. Semi-quantitative NMR intensities were obtained using determined amounts of zeolite and by collecting spectra with the same number of scans.

DRIFTS experiments were performed at ambient pressure with a modified high temperature DRIFT cell (from Spectra-Tech) fitted with KBr windows. The reaction cell was modified to eliminate bed by-pass by inserting some PTFE tape between the ceramic crucible and the metallic base plate. The cell was placed in a collector assembly and fitted in a Tensor 27 FT-IR spectrometer (Bruker) equipped with a mercury cadmium telluride (MCT) detector cooled with liquid nitrogen.

Approximately 2-3 mg of catalyst powder was deposited onto a silicon carbide (SiC) bed inside the crucible. The infrared spectra were recorded with a resolution of 4 cm^{-1} and monitored using the OPUS software. Samples were first degassed *in situ* at $250\text{ }^{\circ}\text{C}$ for 1 h in a 20 mL min^{-1} flow rate of He. Spectra were subsequently recorded at $200\text{ }^{\circ}\text{C}$ by accumulating 64 scans and then were normalized using the area of the silica overtone band at 1875 cm^{-1} . The DRIFTS spectra are reported as $\log(1/R)$, where R is the sample reflectance. This pseudo-absorbance gives a better linear representation of the band intensity against surface coverage than that given by the Kubelka–Munk function for strongly absorbing media such as those based on oxides.

X-ray Photoemission Spectroscopy (XPS) measurements were performed on an ESCA KRATOS Axis Supra spectrometer using Al $K\alpha$ radiation ($h\nu = 1486.6\text{ eV}$). Surface Si/Al atomic ratios were calculated using integrated areas of Si_{2s} and Al_{2p} peaks.

3. Results

Conventional NaY crystals with a homogeneous composition were first dealuminated (step 1), then leached with hydrochloric acid (step 2) and finally desilicated using an Al-containing alkaline solution (step 3) (see Scheme 1). Desilication was accompanied by a partial realumination in the presence of Al species, giving Al-zoned crystals with an Al-rich surface and a Si-rich core (see discussion in section 4). As pointed out in the introduction, the overall Al content, the nature of Al species (4-coordinate framework and 5- or 6-coordinate extra-framework species) and their radial distribution in crystallites determines the success of the synthesis of Al-containing hollow zeolites. Elemental analyses, X-Ray Diffraction data, XPS, EDAX SEM & TEM, Si and Al solid state NMR analyses of solids recovered after each of the three main steps of the process are presented here to address this point.

The parent NaY zeolite was in the form of interpenetrating octahedrons forming round-shaped aggregates of about $1.2\text{ }\mu\text{m}$ diameter. The solid was pure and highly crystalline, as evidenced by X-ray diffraction (see Figure 1), and the silicon to aluminium ratio of the framework obtained by chemical analysis and from the deconvolution of the ^{29}Si MAS NMR spectrum was 2.45 ± 0.05 (see Table 1 and Figure S1).

Upon dealumination with SiCl_4 , the crystallinity of the zeolite was maintained but XRD reflections were shifted to high-angle values, indicating a decrease of the unit cell parameter a_0 .³⁶ It has already been reported that the unit cell axes of Y zeolites vary almost linearly with the aluminium content in the framework.

In particular, Fichtner-Schmittler et al. have shown that the linearity was verified for a wide range of compositions, i.e. for zeolites containing 5 to 52 Al atoms per unit cell, which corresponds to Si/Al ratios between 2.7 and 37.³⁷ If we assume the validity of this relationship, the framework Si/Al atomic ratio of the dealuminated Y zeolite can be estimated at 29 ± 3 (see Table 1). This value significantly differed from that obtained by chemical analysis ($\text{Si/Al} = 18.4$), thus suggesting the presence of extra-framework Al species in the porosity. This was supported by ^{27}Al MAS NMR studies. Extra-framework aluminium was clearly evidenced by the presence of intense signals at ca. 30 and 0 ppm in the ^{27}Al MAS NMR spectrum, assigned to 5- and 6-coordinate Al species, respectively, and that were not present on the spectrum of the parent zeolite (see Figure 2).³⁸ Extra-framework Al species appear when aluminium trichloride (AlCl_3),

formed during dealumination of the zeolite with SiCl_4 , is hydrolysed upon washing and transformed into non-soluble aluminium hydroxide, which remains inside and partially blocks the zeolite micropores. Because some of the extracted Al atoms were expelled from the zeolite during the treatment and subsequent washing, it was not possible to estimate the degree of dealumination of the framework by measuring the relative proportion of 4-coordinate Al species in the NMR spectrum. More information was obtained when analysing the relative intensities of ^{29}Si MAS NMR signals. The ^{29}Si MAS NMR spectra of the dealuminated zeolite was mainly composed of a single peak at -108 ppm assigned to Q^0 species, i.e. Si atoms in a purely siliceous environment (see Figure 2).³⁸ It strongly differed from the spectrum of the original NaY zeolite, which was composed of five peaks corresponding to the five possible environments of Si atoms in the framework $\text{Si}(\text{OSi})_{4-n}(\text{OAl})_n$ ($0 \leq n \leq 4$). A weak signal at ca. -105 ppm was also observed, attributed either to Q^1 species $\text{Si}(\text{OSi})_3(\text{OAl})$ or to silanol groups $\text{Si}(\text{OSi})_3\text{OH}$.

Based upon the relative intensities of these two signals, an approximate value of the framework Si/Al ratio of the dealuminated zeolite could be estimated between 30 and 35, in good agreement with values obtained by X-ray diffraction. The spectrum also contained a broad signal at -112 ppm whose assignment is still a matter of debate. Often associated with the presence of amorphous silica even when the latter was not detected by XRD, its significant decrease upon calcination rather suggested an unusual silanol group in the framework, in spite of the lack of any noticeable effect of cross polarization on its intensity.^{39,40}

The BET surface area and microporous volume of the zeolite decreased by more than 20 % after dealumination, possibly resulting from a partial pore blocking by extra-framework Al species (see Table 2).

The N_2 adsorption/desorption isotherm remained a Type-I isotherm with a quasi-horizontal plateau for p/p_0 values between 0.1 and 0.9, confirming that the dealumination synthesis step (step 1) did not create a noticeable population of mesopores in the crystals (see Figure S2). TEM and SEM images of the dealuminated zeolite did not either reveal any change in the overall size and surface morphology of the crystals (see Figure S3).

It was previously reported elsewhere that SiCl_4 treatment resulted in Y crystals with a Si-rich surface and an Al-rich core, and that this gradient of composition was a critical factor for the formation of hollow structures upon desilication.³³ However, several contradictory studies have shown that the difference of composition between the surface and the bulk of Y zeolite crystals dealuminated with SiCl_4 was highly dependent on the extent of dealumination as well as the leaching procedure.⁴¹ In particular, it was found that the outer surface of zeolites Y dealuminated with SiCl_4 above 360°C and washed with water is Al-enriched in contrast to the original zeolite, which has generally a silicon-rich surface. Nonetheless, most of the techniques used to estimate the gradient of concentration in zeolite crystals do not discriminate between framework and extra-framework Al species and the real framework dealumination profile is hard to estimate. SEM-EDX line analysis of one of the dealuminated crystals in two different directions showed that the Si/Al ratio of the zeolite increased from the surface to the core, thus supporting a heterogeneous composition with an Al-rich surface (see Figure 3).

The excess of surface aluminium as compared to the bulk was also evidenced by XPS spectroscopy, which is known to analyse solids within 5 to 10 nm under the surface (see Table 1). The value of the Si/Al

atomic ratio was approx. 20 % lower than the overall value obtained by chemical analysis. However, in a separate experiment, we showed that direct desilication of this solid with NaOH solution did not lead to the formation of hollow structures, as previously reported in the literature for Al-zoned ZSM-5 crystals.¹⁹ This behaviour supports the fact that the apparent Al-enrichment measured by SEM-EDX likely resulted from the presence of extra-framework Al deposits on the outer parts of the faujasite crystals. Moreover, the intensity of the XRD pattern significantly decreased after desilication as compared to the parent NaY, which is currently observed in the literature during desilication of faujasites (see Figure S4).

The presence of extra-framework Al species preferentially located near the surface of dealuminated faujasite crystals may have negative effects on the realumination step (step 3). The dealuminated zeolite (step1) was treated with a 0.1 M hydrochloric acid solution in order to remove as much as possible non-framework aluminium species from the pores (step 2). The Si/Al ratio obtained by chemical analysis increased to 37.7, indicating that half of Al species had been extracted (see Table 1). As expected, the acid treatment preferentially extracted Al species from the surface of the crystals. By contrast to the dealuminated zeolite, the Si/Al ratio obtained by XPS was higher than the value obtained by chemical analysis of the entire crystals (see Table 1). The treatment did not modify the crystallinity of the zeolite, as evidenced by XRD, and the absence of significant peak shift in the pattern ruled out any additional severe framework dealumination. More information about the nature of extracted species was obtained by ²⁷Al MAS NMR. Compared to the spectrum of the dealuminated zeolite, intensities of 5- and 6-coordinate extra-framework species drastically decreased after acid washing while that of framework 4- coordinate species remained almost unchanged (see Figure 2). NMR clearly demonstrated that the acid selectively removed non-framework species without changing the composition of the framework. By measuring the relative intensity of the peak at 55 ppm in the NMR spectrum, it was possible to estimate the real framework Si/Al ratio at ca. 50, slightly higher than the value estimated by XRD (Si/Al = 33). However, the low precision on the measurement of the unit cell axis a_0 for high-silica zeolites associated with the difficulty to get a quantitative deconvolution of the ²⁷Al MAS NMR spectrum means that the observed difference is not significant. As it will be discussed later, the extent of dealumination is of prime importance for the design of the final zeolite, in particular the presence of an internal cavity.

With such a composition, the faujasite framework was particularly sensitive to desilication in the presence of alkaline solutions. When the acid-treated zeolite was desilicated with NaOH solutions at moderate temperature, the structure partially collapsed and no hollow structures could be observed. SEM images revealed the presence of large mesopores throughout the crystals, suggesting that the desilication process was quite similar to that reported for less dealuminated crystals (not shown). In contrast, when desilication was carried out with sodium aluminate solutions, the structure was fully preserved and a large internal cavity was formed inside the crystals (see Figure 4-a). Transmission electron microscopy (TEM) of a 70 nm thick cross-section of resin-embedded hollow crystals clearly revealed the large internal cavity of about $0.8 \pm 0.1 \mu\text{m}$ in diameter. A porous corona that separates the purely microporous Y zeolite shell from the large central cavity could also be observed, resulting from a partial dissolution of the zeolite framework. The thickness of the microporous shell was about $0.12 \pm 0.05 \mu\text{m}$, which is significantly smaller than the average size of the $1.2 \mu\text{m}$ parent bulk crystals. The crystallinity of the microporous outer zeolite

shell was clearly evidenced by well-defined lattice fringes with the expected spacing for FAU-type zeolites (1.2 nm), as shown in Figure 4-b.⁴² Moreover, it is important to point out that neither the size nor the external morphology of the crystals was modified along the process, as it can be observed in Figure 5. Because standard measurement conditions in SEM only reveal details of the surface of the crystals, an original method was used to “see” through the crystals in scanning mode which allowed confirming the hollow nature of the crystals (Figure 5).

An overview of the final zeolite in Figure 5 shows a homogeneous batch in which hollow crystals have retained a multi-octahedral shape and an overall size of approximately 1.2 μm . Despite the large internal cavity and thin walls, the hollow Y capsules remained mechanically robust as they could withstand severe compression and grinding. As shown in Figure S5, the N_2 adsorption-desorption isotherm of hollow crystals did not change after applying a pressure of 1 ton per square inch on the powder. Considering hollow crystals as spheres of 1.2 μm diameter with an average shell thickness of 0.12 μm , the mass of hollow crystals should represent 56 % of that of the purely microporous parent crystals, which is consistent with the experimental mass balance of the complete process, which reached 58 ± 4 % (measured from five different starting batches of about 0.4 g parent NaY each).

Electron microscopy observations were entirely supported by N_2 adsorption measurements at 77 K (see Figure 6 and Table 2). By contrast to the acid treatment which had no significant effect on the isotherm of the dealuminated zeolite (see Figure S2), the adsorption branch for hollow Y zeolite continuously increased with pressure, thus supporting the existence of the internal porous corona with a quite broad mesopore size distribution. Moreover, the presence of a H2 hysteresis loop with a closure point at $p/p_0 = 0.47$ on the desorption branch showed that these internal mesopores are accessible only via entrances smaller than 4 nm, pointing towards an external defect-free purely microporous zeolite shell.^{43,44} Whereas the total BET surface area and microporous volume did not change upon alkaline treatment, the mesoporous surface area increased by over 100 m^2/g (see Table 2). Compared to parent NaY crystals, 80 % of the microporous volume was preserved in hollow crystals, the loss being essentially associated with the dealumination step (step 1) with silicon tetrachloride.

4. Formation mechanism and influence of synthesis parameters

The formation of internal cavities by selective dissolution of faujasite crystal cores follows a complex mechanism in which all steps are of prime importance and inter-related. The initial dealumination phase (step 1) regulating the silicon coordination environment is a key parameter for obtaining well-preserved hollow faujasite crystals. When the zeolite was not sufficiently dealuminated, no cavity could be created during the last step (step 3) of the process. Yuan et al. succeeded in preparing hollow Y zeolite crystals from moderately dealuminated NaY arguing that SiCl_4 treatment introduced an Al enrichment of the crystals surface, thus facilitating the preferential dissolution of the core in alkaline solutions.³³

However, in their study the desilication step was carried out with NaOH, which significantly damaged the crystallinity, as evidenced by the decrease of reflection intensities and the presence of a broad background characteristic of amorphous alumina-silica in the XRD pattern. Recently, Li et al. have shown that an acid

treatment followed by an alkaline treatment on a Y zeolite previously dealuminated by steaming led to a hierarchical material in which mesopores were randomly distributed throughout the crystals.⁴⁵ The absence of a large internal cavity could be attributed to the dealumination method, which is not reported to generate Al zoning in zeolite crystals, or to a (quite) low dealumination level. The acid leaching step (step 2) seems to be also particularly important for the formation of hollow structures. In the absence of acid treatment, the crystallinity of the final zeolite was only marginally affected but the intensity of the most intense basal reflection significantly decreased. This decrease was attributed to the presence of extra-framework species inside the porosity of the zeolite. Indeed, the intensity of X-ray peaks generally decreases with decreasing the scattering contrast between the silicate wall and the pore filling material, particularly at low angle values. Moreover, direct comparison of zeolites obtained in the presence and in the absence of acid leaching tended to show that the porosity generated by alkaline solutions was more irregular and more randomly distributed when step 2 was omitted (see Figures S6 and S7). Similar observations were recently reported by Li et al. during the hierarchisation of Y zeolite through SiCl_4 dealumination directly followed by alkaline treatment in the presence of a surfactant molecule.⁴⁶ Concerning moderately dealuminated zeolites, Yuan et al. have clearly established the importance of the acid concentration on the structural properties of the final zeolite.³³ They claimed that concentrated acid solutions (0.5 M) were necessary to further dealuminate the Al-rich core of the crystals, leading to an increasing gradient of defects from the surface to the interior. For highly dealuminated NaY crystals, we have observed that concentrated HCl solutions (0.5 M) did not enable the formation of hollow structures after alkaline treatment. As discussed later, the formation of hollow structures in highly dealuminated Y zeolites does not likely result from a gradient of defects in the crystals but rather from the presence of an Al zoning introduced during the ultimate desilication phase (step 3). Therefore, our acid washing step did not intend to further dealuminate the zeolite but only to extract part of extra-framework Al species deposited after the severe treatment with SiCl_4 . ^{27}Al MAS NMR confirmed that more diluted HCl solutions (0.1-0.2 M) exclusively removed 5- and 6-coordinate Al species from the zeolite, without changing the intensity of the signal at 55 ppm assigned to framework Al species (see Figure 2). The lack of framework dealumination at step 2 was further confirmed by the unchanged intensity of the IR band at 3735 cm^{-1} attributed to terminal silanol groups (see Figure S8).

As mentioned above, when the third step of the treatment was carried out using sodium hydroxide instead of sodium aluminate at the same concentration, a partial amorphization of the zeolite occurred and no cavity could be created. It has already been reported in the literature that a partial realumination of the crystals could occur when a dealuminated zeolite is contacted with Al species in alkaline media.^{47,48} Depending on time and temperature of the reaction, realumination could affect selectively the surface of the crystals while keeping the inner parts intact. Therefore, we can assume that aluminium species offer protection to the silicon atoms located in the outer layers of the crystals and provide robust Si-O-Al environments which resist to desilication, thereby helping the crystal shell to maintain its integrity and generating a hollow morphology. After alkaline treatment with NaAlO_2 , the overall Si/Al ratio of the zeolite decreased from ca. 38 to 28, clearly indicating Al incorporation in the solid phase. The change in composition was even much more pronounced for species close to the surface of the crystals. Indeed, the

Si/Al ratio obtained by XPS decreased from 46.5 to 6.2, clearly supporting a surface realumination of the crystals. The local atomic environments in the final hollow crystals were further investigated by solid-state NMR. The ^{27}Al MAS NMR spectrum of final hollow crystals differed from that of the acid-treated zeolite by a decrease of the signal at 0 ppm, suggesting that alkaline solutions could partially dissolve and remove extra-framework Al species present in the pores of the structure (see Figure 2). Moreover, the signal at 55 ppm significantly increased, indicating that 4-coordinate $\text{Al}(\text{OSi})_4$ species had been created, in agreement with the decrease of the overall Si/Al ratio. The formation of such species may be an indication that some Al species have been reincorporated in the zeolite framework and support a possible realumination at high pH value. However, it was also reported that ^{27}Al NMR signals around 55 ppm could result from the formation of amorphous sodium aluminosilicate NaAlSiO_4 when silica or a Si-rich zeolite was treated with NaAlO_2 .^{33,49,50} The discrimination between Al atoms in an amorphous phase and $\text{Al}(\text{OSi})_4$ species in a zeolite framework is difficult because the corresponding ^{29}Si MAS NMR signals are also similar. The ^{29}Si MAS NMR spectrum of hollow crystals showed a very predominant peak at -108 ppm corresponding to Q^0 units, i.e. Si atoms linked to four other Si via oxygen bridges $\text{Si}(\text{OSi})_4$ (see Figure 2). The presence of an additional peak at -105 ppm, assigned to Q^3 species, did not totally exclude the presence of an amorphous phase, but the very weak intensity of the signal suggests that the proportion in the zeolite was certainly very low. Moreover, the slight gain in microporous volume of the zeolite upon alkaline treatment confirmed that micropore entrances were not blocked by amorphous matter deposited on the surface of the crystals (see Table 2). As for the signal at -101 ppm, whose intensity increased upon alkaline treatment, it was unambiguously attributed to silanol groups by DRIFTS and ^1H - ^{29}Si CP/MAS NMR studies (see Figures S8 and S9). Those silanol groups resulted from the desilication of the Si-rich crystal cores and were certainly located mainly in the internal defective corona of the zeolite shell. Finally, a peak was observed at -112 ppm whose intensity almost completely disappeared upon calcination (see Figure S8). As previously discussed, it was assigned to traces of amorphous phase along with specific hydrated sites of the zeolite framework.^{39,40}

5. Conclusions

We have presented a multi-step synthesis route to obtain hollow crystals from a conventional NaY zeolite. The protocol is based on a severe dealumination of the zeolite framework followed by a selective dissolution of the crystal core in the presence of protective aluminium species. Hollow Y zeolite crystals differ from those recently reported in the literature by much higher Si/Al ratios, higher crystallinities and pure microporous shells of ca. 0.12 μm thickness. With those differences, the family of hollow faujasites is significantly enlarged towards more siliceous and less defective materials. In contrast to Al-rich hollow crystals, the formation mechanism is not based on the presence of a gradient of defects generated upon acid treatment but rather on the formation of an Al-rich surface, which protects the outer parts of the crystals from desilication. We can anticipate that the present well-designed hollow Y zeolite crystals, which can be regarded as model architectures, will allow deeper understanding of the effects of diffusion and external surface on catalytic properties. Moreover, the analogy with hollow ZSM-5 crystals in terms of composition

(similar Si/Al ratios) should bring essential information on the role of the zeolite topology and pore size when crystals are used as size-selective nanoreactors with encapsulated catalysts.

Due to their high Si content, hollow crystals are particularly stable and well adapted to reactions carried out under harsh conditions. Furthermore, their overall size being similar to that of bulk NaY crystals, handling issues associated with the manipulation of large amounts of nanocrystals is totally avoided.

Transport and catalytic studies of the present hollow Y zeolite crystals are ongoing in our laboratory and will be reported elsewhere in comparison with those of classical hierarchical zeolites.

Conflicts of interest

There are no conflicts to declare.

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Scheme 1 Schematic illustration for the fabrication of hollow Y zeolite by a three-step process.

Fig. 1 XRD patterns of zeolite NaY (a) after dealumination with SiCl_4 (b) followed by acid leaching (c) and desilication in the presence of NaAlO_2 (d). Arrows point out the shift of (331) and (533) reflections of the pattern.

Table 1 Chemical analysis and unit cell value for zeolites recovered after each step of the process.

Zeolite	Si/Al				a_0 (Å) ^c
	ICP _{tot}	NMR _{fram} ^a	XRD _{fram} ^b	XPS	
NaY	2.5	2.4	2.6	2.4	24.71
Dealuminated SiCl_4	18.4	(45)	29	14.5	24.29
Washed HCl	37.7	(50)	33	46.5	24.28
Treated NaAlO_2	27.7	(37)	25	6.2	24.30

^a Values between parentheses are estimated from the relative proportion of the ^{27}Al MAS NMR signal at 55 ppm assigned to 4-coordinate framework Al species

^b Framework Si/Al ratio estimated using the Fichtner-Schmittler equation³⁷

^c Unit cell parameter of the zeolite measured on XRD patterns

Fig. 2 ^{27}Al (left) and ^{29}Si (right) MAS NMR spectra of NaY zeolite dealuminated with SiCl_4 (a) followed by acid leaching (b) and desilication in the presence of NaAlO_2 (c). Spectra were plotted in absolute intensities and collected using the same amount of zeolite and identical number of scans.

Table 2 Porous structure data obtained from analysis of N_2 adsorption–desorption isotherms at 77K on zeolites after each step of the process.

Zeolite	$S_{\text{BET}}^{\text{a}}$ (m^2/g)	$S_{\text{Meso}}^{\text{b}}$ (m^2/g)	$V_{\text{Micro}}^{\text{c}}$ (cm^3/g)	$^{\text{a}}$ BET method (constant C positive and $p/p_0 < 0.1$) $^{\text{b}}$ t-plot method (linear part between $0.34 \leq x_{\text{axis}}$ (nm) ≤ 1) $^{\text{c}}$ volume of N_2 adsorbed when the slope of adsorption branch becomes lower than $10^3 \text{ cm}^3/\text{g}$
NaY	865	6	0.31	
Dealuminated SiCl_4	669	18	0.23	
Washed HCl	687	21	0.23	
Treated NaAlO_2	709	111	0.24

Fig. 3 SEM-EDX line analysis along two directions of a faujasite crystal dealuminated with SiCl_4 . The inset shows the atomic Si/Al ratio calculated at each point

Fig. 4 TEM images of a 70 nm thick cross-section of a resin-embedded hollow crystal (a) and detail of the shell showing lattice fringes of the zeolite framework (b).

Fig. 5 SEM images at two different magnifications of parent NaY (top) and hollow crystals with a selection on a broken crystal (bottom).

Fig. 6 N₂ adsorption (open symbols)/desorption (full symbols) isotherms at 77K of parent NaY (green) and corresponding hollow crystals (black).