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Hollow structures by controlled desilication of Beta zeolite nanocrystals

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Abstract

The present work examines the different parameters that affect desilication of nanometric Beta zeolite crystals in alkaline solutions. The influences of different synthesis parameters such as the nature of the zeolite (size of the crystals, composition), the alkalinity, the temperature and the amount of added Al species on the morphology and properties of hollow structures are discussed. Addition of sodium aluminate to the alkaline solution protects the surface from desilication and favors dissolution at the center of the crystals, leading to the formation of hollow structures. The size, morphology and crystallinity of those structures depend mainly on zeolite composition, treatment temperature and alkalinity of the solution. If hollow structures are totally amorphous when desilication is carried out under stirring, their crystallinity and thermal stability are significantly improved in the presence of tetraethylammonium (TEA⁺) cations.

Key words: Beta zeolite, desilication, hollow crystals, recrystallization, aluminum zoning

1. Introduction

Inorganic hollow nano structures have received great attention over the last decade due to their potential and promising applications in catalysis, separation, optical and electrochemical devices, drug delivery and controlled release of therapeutic molecules [1-9]. Whereas drug delivery requires a slow dissolution of inorganic amorphous capsules in the organism, materials devoted to catalytic applications need to be robust, with a porosity permitting molecular transport through the shell [10-13]. Among them, hollow zeolite single crystals are particularly interesting because they possess a defect-free purely microporous shell whose thickness can be controlled down to a few nanometers [14-24]. Compared to amorphous oxide capsules, crystalline zeolite walls are generally much more stable, which is a great advantage for applications that necessitate harsh conditions of pH or temperature. Moreover, the well-defined microporosity of the zeolite framework acts as a membrane that selects molecules in accordance with their size and shape and isolates the internal cavity from bulky undesirable molecules. This feature was recently highlighted in the catalytic hydrogenation of substituted aromatics over Pt and Ni nanoparticles encapsulated in hollow silicalite-1 crystals [25,26].

Hollow single crystals are usually prepared by controlled desilication/recrystallization of Al-zoned crystals with an Al-rich surface and a Si-rich core [17-19,27,28]. In the particular case of the zeolite Socony Mobil-5 (ZSM-5) with **MFI** framework type, the gradient of composition can be directly formed during synthesis when tetrapropylammonium (TPA⁺) cations are used as structure-directing agents [29,30]. Hollow crystals have also been obtained from silicalite-1, the Al-free analog of ZSM-5,

taking advantage of the difference in dissolution rates between highly defective cores and well-crystallized rims [31]. For other types of zeolites, crystals are rather homogeneous in composition and, therefore, desilication or dealumination techniques are not selective and lead to porous crystals with randomly distributed mesopores [32-35]. We have recently reported the preparation of hollow Y zeolite from crystals with an artificial Al-zoning obtained by post-synthesis modification of a standard NaY zeolite (**FAU** framework type) [36]. In short, the zeolite was first dealuminated with silicon tetrachloride and crystals were desilicated in the presence of protective Al species that prevented surface dissolution. However, the shell of hollow Y zeolites remains relatively thick and synthesis conditions make that crystals cannot be obtained within a broad range of composition, in particular with low Si/Al ratios. Similar restrictions were observed during the preparation of hollow Beta crystals by seed-assisted dissolution/recrystallization of CIT-6, a zincosilicate zeolite with the same ***BEA** topology as Beta. In the absence of organic molecules, hollow Beta crystals can only be obtained with low Si/Al ratios, typically $\text{Si/Al} < 10$ and a wall thickness comprised between 100 and 150 nm [37,38].

Interesting materials have been obtained by crystallization of Beta zeolite over various templates but the relatively thin shells were composed of roughly packed nanocrystals [39,40]. Recently, researchers have proposed a method to obtain hollow Beta by selective desilication of nanocrystals with sodium hydroxide in the presence of various Al sources [41]. TEM pictures of the treated zeolite showed hollow spherical particles between 300 and 500 nm in diameter with a cavity of ca. 200-300 nm. The corresponding XRD pattern was characteristic of the ***BEA** framework type, suggesting that the crystallinity of the zeolite had been at least partially preserved. However the

stability of the materials upon calcination was not mentioned and calcined solids were not characterized in terms of crystallinity, composition and porosity. Therefore, the preparation of hollow Beta single crystals with a size smaller than 1 μm is still a matter of great interest.

The present work examines the different parameters that affect desilication of nanometric Beta zeolite crystals in alkaline solutions including the possibility to protect the outer surface of the crystals by in-situ formation of an Al-rich rim. The influences of different synthesis parameters such as the nature of the zeolite (size of the crystals, composition), the alkalinity, the temperature and the amount of added Al species on the morphology and properties of hollow structures are discussed. While the formation of hollow crystals generally results in a drastic collapse of the structure, we show that the presence of TEA^+ cations in the desilicating solution prevents complete amorphization of the zeolite and enables to improve the crystallinity of hollow particles, likely by recrystallization of dissolved species.

2. Experimental

2.1. Zeolite Beta synthesis

Beta zeolites as starting materials were synthesized following the procedure reported by Cambor et al. [42,43]. In a typical preparation, 68.27 g of TEAOH (Aldrich, 35 wt. % aqueous solution), 0.353 g of NaCl (Carlo Erba), 0.96 g of KCl (Carlo Erba) and 31 g of H_2O were mixed together. Then, 19.69 g of SiO_2 (A200 from Evonik) were slowly added and the obtained gel was vigorously stirred until complete homogenization. Finally, a solution containing 0.22 g of NaOH (Carlo Erba) and 1.193 g of NaAlO_2 (Riedel de Haën) in 13.3 g of H_2O was added into the above mentioned gel and stirred for 15

minutes. The thick gel, with the following composition: 1.97 Na₂O: 1.00 K₂O: 12.5 (TEA)₂O: 1.00 Al₂O₃: 50 SiO₂: 750 H₂O: 2.9 HCl was then transferred into 100 mL autoclaves and heated under dynamic conditions (60 rpm) at 135 °C for 24 hours. After crystallization, the autoclaves were quenched in cold water; the solid was recovered by centrifugation, washed abundantly with deionized water and dried at 110 °C overnight. The zeolite was then calcined in air at 580 °C for 12 hours.

Beta zeolites with different framework Al contents (SiO₂/Al₂O₃ = 100/1, 50/1 and 40/1) were synthesized by modifying the gel composition as reported in the literature (Table 1) [42,43]. The K/(K+Na) ratio was also varied from 0 (pure Na synthesis) to 0.6 in order to change the mean crystal size of the final zeolite. All samples were crystallized at 135 °C under the same conditions as previously described and calcined in air at 580 °C prior to modification.

2.2. Post-synthesis treatments

In a standard treatment (Table 2, entry 1), 0.55 g of NaOH and 0.175 g of NaAlO₂ were dissolved in 25 mL of deionized H₂O. Then, 0.5 g of calcined Beta zeolite were added and the suspension was stirred at room temperature for 30 minutes. It was then transferred into a 46 mL Teflon-lined, stainless-steel autoclave and heated at 90 °C for 5 hours under static or dynamic (60 rpm) conditions. After treatment, the zeolite was recovered by centrifugation, washed abundantly with deionized water and dried at 110 °C overnight. Additionally, the zeolite can be calcined in air at 580 °C for 12 hours.

Different treatments were also performed by changing the temperature (from 90 to 140 °C), the heating period (from 4 to 8 hours), the amounts of NaOH and NaAlO₂, and by replacing partially or totally NaOH by TEAOH/TEABr mixtures. Table 2 summarizes

the amounts of chemicals and the experimental conditions used in the different treatments.

High-silica beta zeolites were obtained by dealumination of a solid prepared with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$ in the precursor gel. The as-made zeolite (1 g) was dispersed in 100 mL of a 10 M HNO_3 solution and the mixture was heated at 80 °C for 4 hours under stirring. The solid was then filtered, washed abundantly with deionized water, dried at 110 °C and finally calcined in air at 580 °C for 12 hours. Part of the calcined zeolite was dealuminated once again using the above procedure.

2.3. Characterization techniques

X-ray powder diffraction (XRD) patterns were recorded on a D8 advance A25 diffractometer ($\text{CuK}\alpha$ radiation) from 4 to 80° with 0.02° steps and 0.5 s per step.

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.

N_2 adsorption/desorption isotherms were measured at 77 K 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.

^{29}Si and ^{27}Al MAS NMR spectra were obtained on a Bruker Avance III 500WB 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 μs ($\pi/3$) and 100 s for ^{29}Si , 1 μs ($\pi/12$) and 1 s for ^{27}Al , respectively. ^1H - ^{29}Si CP/MAS NMR spectra were obtained using a standard cross-polarization sequence with

5 ms contact time and a recycle delay of 10 s. Chemical shifts were referenced to tetramethylsilane (TMS) and $\text{Al}(\text{H}_2\text{O})_6^{3+}$ for Si and Al, respectively.

3. Results

3.1. Standard treatment

3.1.1. Static conditions

The starting zeolite Beta-1, which was prepared with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$ in the precursor gel appears in the form of particles with diameters in the 200-400 nm range and ill-defined morphologies, built up from the aggregation of regularly oriented small crystallites (Fig. 1-a). The framework composition obtained by chemical analysis of the calcined solid gives $\text{SiO}_2/\text{Al}_2\text{O}_3 = 26$, similar to the value reported in the literature for similar materials (Table 1) [42]. The zeolite is highly crystalline and pure as evidenced by powder XRD (Fig. 2-a). In contrast to ZSM-5, treating the Beta nanocrystals in sodium hydroxide solutions does not lead to hollow structures but to the formation of shapeless zeolite debris, with a significant loss of crystallinity (Fig. 1-b). Dissolution is homogeneous, which is likely a consequence of the aggregated nature of the particles and of the absence of a marked Al-zoning like the one often observed in ZSM-5 crystals [27-30]. Nonetheless, in the case of NaY crystals, we have shown that internal dissolution could be controlled if aluminum species were added to the desilicating alkaline medium [36]. Aluminum is supposed to react with siloxy groups at the external surface of zeolite crystals and to form an Al-rich layer less prone to desilication. Following this hypothesis, zeolite Beta-1 was treated in the presence of NaAlO_2 as

described in example #1 of a very recent patent [41], corresponding to the “standard conditions” here in the experimental section (Table 2, entry 1). After a standard treatment, the morphology of the zeolite is drastically modified and most of the crystals appear hollow in TEM pictures (Fig. 1-c). In contrast to experiments carried out in the absence of additional Al species, the presence of aluminum effectively prevents complete dissolution of the crystals. The overall size of the crystals does not markedly change suggesting that hollow structures do not result from the secondary crystallization of species in solution but actually from selective desilication of original crystal cores under alkaline conditions. The shells possess a uniform thickness of ca. 20-30 nm with relatively smooth surfaces, in contrast with the jagged surface of non-treated Beta crystals and points towards a probable amorphization of the zeolite framework. Partial amorphization of the zeolite is confirmed by the decrease of reflections in the powder XRD pattern and the presence of an intense and broad signal between 15 and 35° (2 θ), characteristic of amorphous matter (Fig. 2-b,c). Nonetheless, the persistence of Beta reflections suggests that amorphization is not complete and that the crystalline framework is not totally destroyed by the alkaline treatment at 90 °C. Information about the formation of the internal cavity has been obtained by looking at crystals recovered after a short treatment period, typically 1 hour (Fig. 1-d). While the outer surface of the crystals still shows well-defined crystallites, a large cavity is already present with a smooth and regular wall, suggesting internal amorphization of the zeolite framework. As for Y zeolites, the presence of additional Al species in solution retards surface desilication with respect to the bulk and the cavity, which initially forms at the center of the crystals, grows by a progressive core-to-surface dissolution. The ²⁹Si NMR spectrum of hollow Beta zeolite crystals is complex and shows many peaks between -70 and -120

ppm (Fig. 3-b). Peaks between -90 and -120 ppm correspond to Si atoms in crystalline Beta zeolite while the broad and intense signal around -90 ppm can be unambiguously attributed to the amorphous non-framework material detected by XRD [Fig.2-b,c]. The ^{27}Al MAS NMR spectrum is composed of a unique signal at 54 ppm attributed to Al tetrahedra with 4 Si atoms in the coordination sphere $[\text{Al}(\text{OSi})_4]^-$ [44]. It contrasts with the spectrum of the original bulk Beta zeolite by the absence of signal at 0 ppm, assigned to extraframework octahedrally coordinated Al oxide species generated upon calcination of the zeolite in air. The chemical shift is very similar to that observed for Al species in zeolite frameworks but the signal is broader and likely results from the superposition of contributions from the crystalline zeolite and amorphous phase. It has already been reported that desilication of zeolite frameworks with NaAlO_2 solutions could form amorphous $\text{Na}_x\text{Al}_x\text{Si}_{1-x}\text{O}_2$ phases with ^{27}Al NMR chemical shifts around 55 ppm and ^{29}Si NMR chemical shifts between -85 and -110 ppm, depending on the composition [45,46]. These species, which are difficult to distinguish from framework Al and Si atoms on the basis of NMR alone, can lead to an incorrect interpretation of NMR spectra, in particular an underestimation of the dealumination level.

3.1.2. Dynamic conditions

Despite a high proportion of hollow crystals in TEM pictures of the treated zeolite, the batch is found not to be homogeneous. Some crystals are more or less transformed and a few of them even appear intact with the morphology they had before desilication (arrow in Fig. 1-c). These heterogeneities can result either from structural differences between individual crystals in the zeolite batch or from ill-adapted experimental conditions during the treatment. In the particular case of ZSM-5 nanocrystals with a homogeneous morphology and size, it was reported that most of the crystals treated

with NaOH were hollow but some of them remained plain, pointing out differences in structure or composition [18]. Generally, treatments are more homogeneous when they are performed under dynamic conditions, which favors a better contact between the crystals and the solution. For zeolite Beta, stirring the solid during desilication had a strong effect on the morphology and crystallinity of the final zeolite. The powder XRD pattern of the treated zeolite is consistent with a totally amorphous material and zeolite peaks that were still observed after a static treatment have totally disappeared (Fig. 2-d). It seems that stirring accelerates the dissolution of the zeolite and facilitates the formation of amorphous phases from Si and Al species in the solution. The solid appears in the form of hollow spheres with a smooth surface and approx. 40 nm thick walls (Fig. 1-e, f). High resolution images do not show any crystalline region, thus supporting the amorphous nature of the spheres and the complete destruction of the zeolite framework. The absence of crystalline zeolite in the solid was further confirmed by ^{29}Si MAS NMR. The spectrum consists of a unique and broad signal at -90 ppm and peaks characteristic of Beta zeolite that were still visible on the solid treated under static conditions are no longer present (Fig. 3-c). According to the literature, the observed ^{29}Si chemical shift corresponds to an aluminosilicate with $1 < \text{SiO}_2/\text{Al}_2\text{O}_3 < 6$, which was confirmed by chemical analysis ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 4.5$; Table 3) [46].

The broad ^{29}Si NMR line corresponding to a completely amorphous phase has been subtracted from the spectrum of hollow crystals obtained under static conditions. By comparing intensities of NMR signals before and after subtraction, the fraction of amorphous matter in the solid can be estimated to $\approx 75\%$. The resulting signal, which represents the crystalline part of hollow structures, is composed of four lines at ca. -98, -104, -109 and -114 ppm (Fig. 3-d). It differs from the spectrum of the original calcined

zeolite by the presence of intense signals at -98 and -104 ppm that were almost absent before treatment. The ^{29}Si NMR spectrum of the untreated zeolite is composed of 3 main peaks at -114.5, -110 and -104.3 ppm along with a weak signal at -98.5 ppm (Fig. 3-a). Signals at -114.5 and -110 ppm are assigned to $\text{Si}(4\text{Si})$ framework atoms while the peaks at -104.3 and -98.5 correspond to $\text{Si}(3\text{Si}, 1\text{Al})$ and $\text{Si}(2\text{Si}, 2\text{Al})$, respectively. Based on the decomposition of the spectrum, the calculated $\text{SiO}_2/\text{Al}_2\text{O}_3$ framework ratio is 21.8, a value slightly lower than that obtained by chemical analysis. The difference likely results from an overestimation of the $\text{Si}(3\text{Si}, 1\text{Al})$ signal at -104.3 ppm, which generally overlaps with the signal of silanol groups $\text{Si}(3\text{Si}, 1\text{OH})$ in zeolite frameworks [44]. For the treated solid, a similar decomposition of the spectrum of the zeolitic fraction gives $\text{SiO}_2/\text{Al}_2\text{O}_3 = 10.2$, supporting a severe desilication of the framework under alkaline conditions.

Solids obtained under static or dynamic standard conditions (Table 2, entry 1) retain their hollow structure after calcination at 580 °C in air without significant changes in size and shape. However, in the case of static syntheses for which zeolite peaks were still present after desilication, the intensity of the XRD pattern decreases upon calcination, suggesting an additional loss of crystallinity at high temperature (Fig. 2-c). The pattern of the calcined solid is almost flat and similar to that obtained when syntheses were performed under stirring. This may be attributed to the high Al content of the zeolitic fraction of hollow spheres as well as a high density of defects resulting from framework desilication. Calcined hollow spheres obtained under static or dynamic conditions are almost totally closed and non-porous with BET surface areas typically below 35 m²/g (Table 3). The slightly higher surface area observed on the solid treated under static conditions likely originates from the heterogeneity of the batch, in particular the presence

of non-affected crystals, as those shown in Fig. 1-c. The corresponding adsorption/desorption isotherms are characteristic of non-microporous solids (type III) with low surface area, with a hysteresis loop at $p/p_0 > 0.85$ resulting from inter-particle voids (Fig. 4).

3.2. Influence of NaOH concentration

Despite a better homogeneity of the batch, stirring does not really improve the synthesis of hollow zeolite structures since solids are totally amorphous and non-porous, which means that they cannot be used as porous hosts for the encapsulation of catalysts. Experiments carried out under static and dynamic conditions tend to show that the loss of crystallinity of hollow structures can be directly related to the extent of desilication of the zeolite. The desilication level depends on many factors such as the composition of the zeolite framework, the temperature and duration of the treatment and the OH^- concentration. Both the NaOH and NaAlO_2 concentrations influence the alkalinity of the desilicating solution. Under static conditions, decreasing the NaOH concentration by a factor of two effectively improves the crystallinity of the zeolite after treatment (Table 2, entry 2). Compared to a standard procedure, zeolite reflections in the XRD pattern are much more intense and they do not totally disappear upon calcination (Fig. S1 in ESI). However, many crystals look intact or barely transformed, evidencing a poor desilication of the zeolite (Fig. S2 in ESI). A systematic study of the influence of the pH value showed that crystals were not modified at $\text{pH} < 13.5$ under static conditions, which means that the NaOH concentration cannot be used as a relevant parameter to optimize the formation of hollow structures. On the other hand, higher NaOH concentrations (Table 2, entry 3) increase the desilication rate of the

zeolite and treated solids are always contaminated with large NaP crystals that recrystallize from species in solution. The same observation can be made upon increasing the desilicating temperature: as it will be discussed later, the fraction of zeolite NaP in the batch increases with temperature and reaches 100% after a treatment of 5 hours at 135 °C.

3.3. Influence of NaAlO₂ content

Changing the amount of NaAlO₂ has only a minor influence on the pH value but a strong impact on the morphology of the corresponding hollow structures (Fig. 5). We have already mentioned that the crystals were severely damaged in the absence of NaAlO₂. Besides a very little modification of the pH value, the absence of sodium aluminate mostly prevents the protective effect of Al species against desilication of the surface. Nonetheless, decreasing the amount of NaAlO₂ by 50% in the desilication solution (Table 2, entry 4) still leads to well-defined hollow structures under static conditions (Fig. 5-b). The size, wall thickness and crystallinity of hollow crystals are similar to those obtained with the full amount of sodium aluminate. At 25% NaAlO₂ (Table 2, entry 5) the corresponding hollow crystals are less well-defined with many fragments and a large proportion of broken shells (Fig. 5-c). The effect of decreasing the amount of NaAlO₂ is even much more pronounced when treatments are performed under stirring conditions. Already at 50% of the initial amount of NaAlO₂, crystals are almost totally destroyed and the percentage of undamaged shells is negligible (Fig. 5-d).

3.4. Effect of the zeolite composition

As mentioned above, the desilication rate of a zeolite also depends on the framework composition. In the particular case of NaY, it shows an optimum for $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios between 40 and 100, significantly higher than the Si/Al ratio of the previous Beta zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 26$) [47]. Zeolites with different compositions have thus been synthesized and treated following the standard procedure both under static and dynamic conditions. The first zeolite was prepared with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 35$ in the gel and characterized by a framework $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 20.1 (Beta-4 in Table 1). Increasing the amount of Al in the framework did not change the K and Na contents in the zeolite and the particle size remained approx. the same (Table 1). After a standard treatment under static conditions (Table 2, entry 1), the corresponding XRD pattern shows relatively intense reflections attributed to the crystalline zeolite framework and the amorphous contribution is significantly reduced as compared to a zeolite with less aluminum (Fig. S3 in ESI). Clearly, more aluminum in the framework improves the stability of the framework under alkaline conditions, in particular compared to zeolite Beta-1 with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 26$. TEM images show that the treated zeolite is very heterogeneous, with hollow structures coexisting with some intact crystals (Fig. S4 in ESI). Those intact crystals, which were not observed in the batch of the zeolite containing less aluminum, most likely contribute to the higher intensity of XRD reflections after desilication. The quality of the sample could be significantly improved by treating the zeolite for 5 hours at 110 °C (Table 2, entry 6). Most of the intact crystals observed after desilication at 90 °C disappeared at higher temperature without co-crystallization of contaminating phases such as NaP. The batch is homogeneous, hollow structures being similar in size and shape to those obtained at 90 °C from a zeolite with a lower framework Al content (Fig. 6-a). The ^{29}Si NMR signal obtained after subtraction of the amorphous phase from the spectrum of

hollow structures shows well-defined lines between -90 and -115 ppm, characteristic of an aluminum-rich compound, resulting from the desilication of the zeolite framework. Deconvolution of the signal gives a $\text{SiO}_2/\text{Al}_2\text{O}_3$ value of 9.4, similar to that previously obtained on Beta-1 zeolite containing less aluminum.

A second solid Beta-5 prepared with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$ in the gel was characterized by a higher framework $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 35.8 (Table 1). As for the previous zeolites, changing the amount of Al in the framework did not change the particle size but the zeolite mainly differs from the others by a lower $\text{K}/(\text{K}+\text{Na})$ ratio (Table 1). The structure of the zeolite completely collapses when the zeolite is treated under standard static conditions, as evidenced by the absence of characteristic reflections in the XRD pattern (Fig. S5 in ESI). As a consequence, less aluminum in the zeolite induces a loss of stability of the framework under alkaline conditions since a crystalline phase was still present after treating a zeolite with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 26$. The amorphous nature of the solid is supported by bubble shaped particles with smooth regular shells, very similar to those obtained for solids treated under dynamic conditions (Fig. 6-b).

Because of the difficulty to obtain Beta zeolites with much higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios following the same synthesis route, as-made Beta-5 crystals were dealuminated in concentrated HNO_3 (10 M solution). Chemical analysis of the calcined zeolite gave $\text{SiO}_2/\text{Al}_2\text{O}_3 = 56.2$, showing that the zeolite has been severely dealuminated by the acid treatment. Moreover, ^{27}Al NMR confirms that all aluminum atoms are at framework positions and that the acid treatment did not produce a detectable amount of extra-framework oxide species. XRD confirms that the structure of the zeolite totally collapses under standard desilication conditions, as already observed for a solid with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 35.8$ (Fig. S6 in ESI). However, whereas very regular hollow structures were formed for

$\text{SiO}_2/\text{Al}_2\text{O}_3 = 35.8$, the solid is less well-defined for $\text{SiO}_2/\text{Al}_2\text{O}_3 = 56.2$ with the coexistence of irregular hollow particles and unshaped zeolite debris as it can be seen in the TEM images (Fig. 6-c). Increasing again the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the Beta zeolite to 109.3 confirms that the Al content of the zeolite is a key parameter for the formation of hollow structures, even under static conditions. Indeed, TEM images of the high-silica zeolite treated under static standard conditions no longer feature hollow-structured particles and most of the solid is in the form of shapeless fragments (Fig. 6-d).

Experiments carried out on zeolites with various Al contents clearly demonstrate that the structuration of amorphous alumina-silica mixed oxides into hollow spheres drastically depends on the composition of the original zeolite. The formation of hollow spheres requires a high Al concentration in the alkaline medium, provided not only by addition of NaAlO_2 but also by the dissolution of the zeolite framework. When high-silica zeolites are used, they dissolve faster than Al-rich analogs but the amount of Al released in solution is not sufficient to form stable alumina-silica mixed oxides.

3.5. Effect of the zeolite crystal size

The equilibrium between zeolite dissolution and amorphous shell formation can also be controlled by changing the zeolite crystal size while keeping unchanged the framework composition. It was previously reported that the crystals size could be easily modified by changing the $\text{K}/(\text{K}+\text{Na})$ ratio in the synthesis gel [42]. In addition to the standard zeolite obtained with $\text{K}/(\text{K}+\text{Na}) = 0.33$ in the synthesis gel, two other samples were synthesized with $\text{K}/(\text{K}+\text{Na}) = 0$ (Beta-2) and $\text{K}/(\text{K}+\text{Na}) = 0.6$ (Beta-3), which is the maximum that can be achieved when NaAlO_2 is used as aluminum source (Table 1). TEM images of the resultant samples effectively show that the crystal size increases

with the K/(K+Na) ratio, from 0.06 μm at K/(K+Na) = 0 to 0.8 μm at K/(K+Na) = 0.6 (Fig. 7-a,c). On the other hand, the Al content in the zeolite does not significantly change since chemical analyses reveal $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of 27.6 and 26.6 for K/(K+Na) = 0 and 0.6, respectively (the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio was 26 for a standard synthesis) (Table 1). Both zeolites have been subjected to a standard treatment (Table 2, entry 1) under static conditions and the resulting solids analyzed by XRD and TEM. After the treatment, the zeolite with smaller crystals exhibits a totally amorphous XRD pattern while the zeolite with larger crystals still shows intense reflections corresponding to the crystalline zeolite framework (Fig. S7 in ESI). Amorphization of the small crystals is supported by the morphology of the solid, which differs from the morphology of the original zeolite and consists of shapeless clusters of particles of 30 to 50 nm in size. In contrast, large crystals show very regular hollow structures with 50 nm thick shells in which Beta nanocrystals can be easily distinguished (Fig. 7-c,d). Despite similar $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, the two zeolites differ not only by their size but also by their potassium content. After exchange with Na^+ cations to decrease the K content from 0.4 to 0.08 wt. %, large crystals treated under standard conditions show the same hollow structures, suggesting that the nature of occluded cations only has a minor influence on the desilication process and that the final morphology mainly depends on the original crystal size.

3.6. Attempts to recrystallize dissolved species

Desilication primarily produces silica species that react with Al initially introduced in the form of NaAlO_2 to give amorphous aluminosilicates in close contact with the zeolite crystals. Under certain conditions, desilication is accelerated and the whole crystal can even be totally transformed into an amorphous hollow sphere with a compact, non-

porous shell. Changing experimental parameters influences the desilication rate of the zeolite but hollow structures are never totally crystalline and they always contain some amorphous matter. In the case of silicalite-1 and ZSM-5, two zeolites with the **MFI** framework type, we have previously reported that dissolved species may recrystallize on the surface of the crystals, provided that desilication is performed under specific conditions [14,15]. Recrystallization not only requires appropriate temperature and gel composition, it also necessitates the presence of organic molecules that serve as template for zeolite recrystallization. For ZSM-5, experiments are generally performed at 170 °C in TPAOH solutions, which provide both alkalinity for framework desilication and TPA^+ cations for zeolite growth.

Beta zeolites usually crystallize at temperatures between 135 and 150 °C in the presence of tetraethylammonium (TEA^+) cations [42,43]. Moreover, in most synthesis procedures, the $\text{H}_2\text{O}/\text{SiO}_2$ ratio in the gel is generally lower than 25, which is 6 times less than in the present standard desilication procedure. The influence of temperature was first evaluated by treating zeolite Beta-1 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 26$) at 135 °C for 5 hours in a standard solution using NaOH and NaAlO_2 (Table 2, entry 7). Increasing temperature not only accelerates the dissolution of the zeolite, it also dramatically impacts the nature of the final solid. The powder XRD pattern shows intense narrow peaks different from those of the original Beta zeolite, indicating that a new crystalline phase was formed at high temperature (Fig. S8 in ESI). This phase was identified as being zeolite NaP, a small pore zeolite with low framework $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, typically < 6 [48]. An experiment performed with decreasing the amount of NaAlO_2 by 75% (Table 2, entry 8) gave similar results, revealing that the Al concentration has little influence on the formation of NaP, in contrast with temperature which appears to be a key parameter. Apart from decreasing

temperature, the formation of NaP can be impeded by limiting Beta dissolution, which provides the necessary Si species for zeolite crystallization. Recrystallization can also be directed towards a desired zeolite structure by addition of organic molecules to the desilicating solution, for example TEA⁺ cations for the **BEA** structure.

Further treatments were thus performed in the presence of TEA⁺ cations using zeolites with high Al contents to limit dissolution at 135 °C. NaOH was first replaced by TEAOH to maintain a constant OH⁻/SiO₂ ratio in the desilication medium (Table 2, entry 9). For zeolite Beta-4 with SiO₂/Al₂O₃ = 20.1, changing Na⁺ for TEA⁺ has a strong influence on the nature and crystallinity of the treated solid. In particular, extra phases such as NaP that were formed at 135 °C with NaOH are not detected in the XRD pattern (Fig. S9 in ESI). Despite the presence of a moderate amount of amorphous phase, reflections of Beta zeolite are still intense, suggesting a protective role of TEA⁺ cations against framework amorphization and structure collapse. Desilication of the zeolite is nonetheless supported by the presence of hollow crystals with a regular shell in TEM pictures, quite similar to those obtained with NaOH from a zeolite with lower Al content (Beta-1; SiO₂/Al₂O₃ = 26) (Fig. 8-a). However, a significant proportion of the starting crystals look unmodified, probably because of the high Al content of the original zeolite (those crystals are identified by arrows in the picture). The ²⁹Si NMR spectrum of the treated zeolite (Fig. S10 in ESI) shows peaks corresponding to the zeolite framework along with a broad signal due to amorphous aluminosilicates. The signal corresponding to the crystalline zeolite is different from that obtained with NaOH at 90 °C, but the presence of intact crystals in the batch made difficult a reliable estimation of the SiO₂/Al₂O₃ ratio in hollow crystals.

More homogeneous batches have been obtained by decreasing the Al content in the zeolite. Since lower Al content increases the solubility of the framework and leads to the formation of NaP at 135 °C even in the presence of TEA⁺ cations, desilication parameters were modified. Compared to the standard procedure, the amount of NaOH was decreased by 50% and TEA⁺ cations were introduced in the form of TEABr, with TEA/SiO₂ = 0.45 (Table 2, entry 10). For zeolite Beta-1 with SiO₂/Al₂O₃ = 26, most of the treated crystals show a hollow morphology with a quite uniform shell (Fig. 8-b). Some intact crystals are still observed but their proportion is so small that they do not markedly affect NMR intensities and chemical composition. The zeolite remains highly crystalline after treatment despite the presence of a weak background signal characteristic of amorphous matter in the XRD pattern (Fig. 2-e). Intensities slightly decrease upon calcination in air at 580 °C but the structure does not completely collapse, as it was the case when the zeolite was treated in the absence of TEA⁺ at 90 °C. Chemical analysis of the zeolite gives SiO₂/Al₂O₃ = 11.2, a value significantly higher than those obtained in the absence of TEA⁺ (Table 3). Amorphous matter in hollow crystals is also evidenced by the presence of a broad signal at -90 ppm in the NMR spectra of as-made and calcined zeolites (Fig. 9-a,b). After subtraction of the amorphous phase from the ²⁹Si NMR spectrum of calcined hollow crystals, the corresponding signal, which characterizes the zeolite framework, can be deconvoluted into four main lines between -95 and -115 ppm (Fig. 9-c). Intensities differ from those obtained after a standard treatment at 90 °C (compare with the spectrum in Fig. 3-d), giving SiO₂/Al₂O₃ = 23, a value not very different from that of the parent zeolite (SiO₂/Al₂O₃ = 26).

Very similar results were obtained on a zeolite with less aluminum (Beta-5; SiO₂/Al₂O₃ = 35.8) (Fig. 8 c, d). The amount of amorphous phase, estimated from ²⁹Si NMR

spectra, decreases from ca. 65 to 20% with addition of TEA⁺ cations. Moreover, the composition of the zeolitic fraction of hollow structures changes, the framework being more silicic in the presence of TEABr. As observed with the previous zeolite Beta-1 with SiO₂/Al₂O₃ = 26, the ²⁹Si NMR signal obtained after subtraction of the amorphous phase is very similar to that of the untreated zeolite (Fig. S11 in ESI).

The same desilication treatment was less effective with more silicic zeolites (SiO₂/Al₂O₃ = 56.2 and 109.3), as already observed at 90 °C. The presence of TEA⁺ cations did not substantially improve the stability of the zeolite framework and the crystallinity was severely damaged under alkaline conditions, particularly for the less aluminic compound.

Assuming that some of the dissolved species recrystallize, the presence of amorphous matter in treated zeolites suggests that recrystallization is never complete, even in the presence of TEA⁺ cations. Thermogravimetric analysis (TGA) of hollow structures obtained from zeolite Beta-5 with SiO₂/Al₂O₃ = 35.8 shows a weight loss between 250 and 700 °C that can be attributed to the combustion of TEA⁺ cations in air (Fig. S12 in ESI). The weight loss, which represents approx. 6.3 wt. % of the total mass of solid, has to be compared with 11.3 wt. % in the original bulk crystals. Moreover, the ¹H-¹³C CP/MAS NMR spectrum of the treated solid is strictly similar to that of the original as-made zeolite, with two peaks at 4 and 51 ppm, characteristic of TEA⁺ cations in the porosity (Fig. S13 in ESI). The presence of organic molecules in hollow structures supports the assumption of a partial recrystallization of aluminosilicate species present in the solution. If recrystallization actually occurs under desilication conditions, it does not concern the totality of the dissolved species. Indeed, taking into account that ≈ 50 wt. % of the solid phase is lost upon desilication and that hollow structures contain ≈ 15-20

wt. % of amorphous matter, the weight loss observed in TGA indicates that only 25 % of Si(Al) species originally present in the zeolite have recrystallized in the form of Beta zeolite. TGA data can also be explained by a simple occlusion of organic molecules in hollow structures during desilication, without involving a hypothetical recrystallization. Under such conditions, the TEA⁺ cation does not act as a structure directing agent but as a protecting molecule that interacts with the negatively charged surface of the crystals and limits desilication.

Solids prepared in the absence of TEA⁺ contain exclusively Na⁺ as charge-compensating cations. The absence of protons makes that NMR signals obtained under ¹H-²⁹Si CP/MAS conditions are extremely weak, even after long accumulation periods. When TEA⁺ cations are present in the solid, hydrogen atoms of ethyl chains can be used as a proton reservoir for CP/MAS NMR experiments. Since polarization transfer decreases very rapidly with the distance and is generally limited to the nearest neighbors, NMR spectra identify Si atoms in close proximity with ethyl chains of the organic cation. The ¹H-²⁹Si CP/MAS NMR spectrum of zeolite Beta-1 (SiO₂/Al₂O₃ = 26) treated at 135 °C in the presence of TEABr differs from that recorded using a standard “one-pulse” sequence (Fig. 10). In particular, the broad signal around -90 ppm, which characterizes amorphous matter almost completely disappears under polarization transfer. The spectrum essentially contains signals corresponding to the “zeolitic part” of hollow structures with intensities similar to those of the original as-made Beta zeolite (Fig. 10-c). Those results strongly suggest that TEA⁺ cations are in close contact with Si atoms of the zeolite framework and they support partial recrystallization of the zeolite framework from species in solution.

The benefit of the presence TEA^+ cations during the hollowing process is clearly evidenced by the modification of the N_2 adsorption/desorption isotherm. For zeolite Beta-1, a type-IV isotherm is obtained in the presence of TEA^+ with a hysteresis loop closing at $p/p_0 = 0.45$, characteristic of meso or macropores with entrances smaller than 4 nm [49]. By comparison with isotherms obtained on other hollow zeolites such as silicalite-1 or ZSM-5, it is reasonable to assume that the hysteresis is a consequence of the partial accessibility of the large internal cavity to nitrogen molecules [14,15]. However, the amount of nitrogen that can be adsorbed in a calcined hollow structure is quite low, with BET surface areas and micropore volumes generally below $150 \text{ m}^2/\text{g}$ and $0.06 \text{ cm}^3/\text{g}$, respectively (Table 3). These values represent approx. 25% of the surface and volume accessible in the original zeolite (Table 1). Amorphous matter, which is observed in NMR spectra and XRD patterns, probably blocks the access to some of the zeolite micropores and limits the adsorption. Oxygen diffusion seems to be also affected since calcined compounds are always greyish, even when they have been heated in air at 580°C for long periods.

Table 4 summarizes the main characteristics (morphology, crystallinity) of the solids obtained after treating the different Beta zeolites under various conditions. It appears that the optimal conditions for the preparation of hollow Beta crystals involve treatments in the presence of TEA^+ cations using zeolites with relatively high Al contents (entries highlighted in grey). The corresponding hollow structures possess a morphology quite different from amorphous solids obtained in the absence of TEA^+ cations with thin walls made of aggregated nanocrystals (Figs 8 b-d).

4. Conclusion

Despite the absence of a marked Al-zoning in nanometric Beta zeolite crystals, hollow structures have been obtained by selective desilication of the crystal cores in alkaline conditions at moderate temperatures. The morphology, composition and crystallinity of these structures depend not only on the desilication conditions but also on the size and composition of the original zeolite particles. Among all parameters that influence the crystallinity of the obtained structures, stirring appears to be one of the most critical since hollow spheres obtained under dynamic conditions are generally totally amorphous, particularly for Beta zeolites with high Al contents.

Dissolved framework species could partially recrystallize into Beta zeolites in the presence of TEA⁺ cations but hollow structures are never totally crystalline and always contaminated with some amorphous aluminosilicates, which drastically limits their adsorption capacity after calcination. Under optimized conditions, more than 50% of the original crystallinity could be preserved in hollow structures, particularly for zeolites with relatively high Al contents ($\text{SiO}_2/\text{Al}_2\text{O}_3 < 40$). Even though experimental procedures still need to be improved to remove totally amorphous material from the hollow structures, the present study nonetheless contributes to a better understanding of the desilication process and paves the way to synthesis methods to prepare highly crystalline hollow zeolite particles with controlled composition and morphology.

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Figure captions

Figure 1 TEM pictures of the original Beta-1 zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 26$) before (a) and after a standard treatment (Table 2, entry 1) under static conditions in the absence (b) and in the presence (c) of NaAlO_2 . Image (d) represents zeolite crystals recovered after 1 h in the presence of NaAlO_2 . Images (e) and (f) correspond to the same zeolite after a treatment of 5 h with NaAlO_2 under stirring (60 rpm).

Figure 2 XRD patterns of Beta-1 zeolite: (a) original; (b) after a standard treatment (Table 2, entry 1) under static conditions; (c) after a standard treatment under static conditions and calcination; (d) after a standard treatment under stirring conditions and (e) after a treatment at 135 °C in the presence of TEABr.

Figure 3 ^{29}Si (left) and ^{27}Al (right) NMR spectra of: (a) calcined Beta-1 zeolite; (b) after a standard treatment (Table 2, entry 1) under static conditions; (c) after a standard treatment (Table 2, entry 1) under stirring (60 rpm); (d) spectrum (b) after subtraction of the amorphous phase.

Figure 4 Nitrogen adsorption/desorption isotherms for zeolite Beta-1 before (a) and after various desilicating treatments: standard under static conditions (Table 2, entry 1) (b), standard under stirring (Table 2, entry 1) (c, dashed line) and in the presence of TEA^+ cations (Table 2, entry 10) (d).

Figure 5 TEM pictures of Beta-1 zeolite treated under static conditions with different amounts of sodium aluminate: (a) standard conditions (1 NaAlO₂) (Table 2, entry 1); (b) 0.5 NaAlO₂ (Table 2, entry 4); (c) 0.25 NaAlO₂ (Table 2, entry 5) and (d) 0.5 NaAlO₂ under stirring (60 rpm) (Table 2, entry 4).

Figure 6 TEM pictures of Beta zeolites with various Al contents treated under static conditions for 5 h. (a) Beta-4 at 110 °C (Table 2, entry 6); (b) Beta-5 at 90 °C (Table 2, entry 1); (c) dealuminated Beta-5 (SiO₂/Al₂O₃ = 56.2) at 90 °C (Table 2, entry 1) and (d) dealuminated Beta-5 (SiO₂/Al₂O₃ = 109.3) at 90 °C (Table 2, entry 1).

Figure 7 TEM pictures of: Beta-2 prepared with K/(K+Na) = 0 in the gel before (a) and after (c) a standard treatment under static conditions (Table 2, entry 1); Beta-3 prepared with K/(K+Na) = 0.6 before (b) and after (d) a standard treatment under static conditions (Table 2, entry 1).

Figure 8 TEM pictures of Beta-4 (a), Beta-1 (b) and Beta-5 (c, d) zeolites after a treatment at 135 °C in the presence of TEA⁺ cations (Table 2, entry 10). Arrows in picture (a) indicate the presence of intact or slightly modified crystals.

Figure 9 ²⁹Si NMR spectra of Beta-1 zeolite: after a treatment at 135 °C in the presence of TEA⁺ cations (Table 2, entry 10) (a); after treatment and calcination (b) and deconvolution of the “zeolitic part” of spectrum (b) after subtraction of the amorphous phase (dashed line) (c).

Figure 10 ^{29}Si NMR spectra of Beta-1 zeolite treated at 135 °C in the presence of TEA+ cations (Table 2, entry 10) recorded under MAS (a) and ^1H - ^{29}Si CP/MAS (b) conditions. (c) corresponds to the spectrum of the original Beta-1 zeolite recorded under ^1H - ^{29}Si CP/MAS conditions. The dashed line in (a) corresponds to an amorphous phase obtained at 90 °C under stirring.