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Hollow polycrystalline Y zeolite shells obtained from selective desilication of Beta-Y core-shell composites

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Abstract

Hollow polycrystalline Y zeolite spheres have been obtained by combining zeolite crystallization and selective dissolution steps. Beta-Y core shell composites were first obtained by hydrothermal recrystallization of a synthesis mixture containing as-made Beta crystals in the presence of Y zeolite seeds. Under such conditions, Beta zeolite crystals served not only as cores but they also progressively dissolved and provided the necessary Si species for the formation of the shell. The proportion of Beta zeolite remaining in the composite strongly depended on the composition of the solution, in particular the amount of Al and the alkalinity. It could not be decreased below 45-50 wt. % without formation of contaminating phases, mainly zeolites with GME, GIS and LTA topologies. Successive additions of Al could significantly reduce the amount of Beta zeolite in the composite but to the detriment of faujasite crystal size. Hollow shells with less than 10 wt. % Beta have been obtained by selective removal of Beta zeolite from a composite containing 20 wt. % Beta and obtained after two successive recrystallizations in the presence of aluminum. These shells are built up from faujasite nanocrystals with a high silicon content, making them potentially interesting in diffusion-limited catalytic reactions.

Key words: Hollow zeolite; Faujasite; Crystallization; Dissolution; Capsules

1. Introduction

In many applications, the properties of zeolites depend not only on their intrinsic physical characteristics such as the dimensionality and size of the pore system but also on macroscopic parameters, in particular the average crystal dimension. Crystal length can indeed be a major obstacle to catalysis when reactions are subject to diffusion limitations, i.e. when the size of reactant and/or product molecules is similar to the pore dimensions[1–3]. In the last decades, many strategies have been developed to minimize the effect of internal diffusion on reaction rates and the subject is still of great interest for both academic and industrial researches. Among those strategies, demetalation techniques consist in generating an additional array of macro/mesopores in individual crystals by selectively dissolving some parts of the framework under alkaline (desilication), acidic (dealumination) or hydrothermal conditions [4–11]. Desilication can also be combined with recrystallization of the zeolite framework to generate hollow single crystals, as recently reported for silicalite-1 and ZSM-5 [12–15]. Since diffusion in mesopores is generally several orders of magnitude faster than in micropores, those microporous-mesoporous hierarchical zeolites showed improved catalytic properties for many established reactions of the petrochemical industry as well as in the valorization of large molecules contained in biomass [16–19]. Alternatively, transport can be significantly improved using nanosized zeolites, typically with individual crystals smaller than a few hundreds of nanometers. Nanosized crystals are generally obtained by modifying standard hydrothermal crystallization conditions for example by shortening the crystallization period, increasing supersaturation or by adding growth inhibitors to the synthesis gel [20–22]. One of the most famous example of growth inhibition concerns the preparation of zeolite nanosheets with specific structure directing agents containing a di-

quaternary ammonium head group and a long hydrophobic surfactant chain [23,24]. These molecules force the zeolite framework to grow perpendicularly to the alkyl chains, leading to a multi-lamellar stacking of sheets with a thickness corresponding to a few unit cells. However, the synthesis of zeolite crystals with a size below 500 nm is not generally obvious and decreasing the size may result in changes in the zeolite properties and composition. For example, in the case of zeolite Y with the FAU topology, a decrease in crystal size is usually associated with an increase in framework aluminum content and most of nanometric Y zeolites are characterized by Si/Al ratios below 2 [25–27]. Moreover, nanometric crystals are difficult to manipulate in the form of powders at large scale and further processing is usually required to design agglomerates with size and shape adapted to practical applications.

Polycrystalline hollow zeolite spheres – also named capsules - constitute a very interesting approach to agglomerate zeolite nanocrystals within a very thin shell while keeping macroscopic objects that can be easily handled and sieved [28–31,14]. In addition, zeolite hollow spheres may find applications in encapsulation, drug delivery, membrane science, catalysis, ... [14]. They are generally prepared using controlled deposition of nanocrystals on various templates such as carbon beads, silica or polystyrene spheres, potentially followed by hydrothermal crystallization in a precursor gel solution. If most of literature data concern zeolites with MFI and *BEA framework types, examples of Al-rich zeolite capsules of FAU and LTA structures have also been reported [29]. In the case of silica, spheres not only serve as support for zeolite seeds deposition but they are also gradually dissolved during the hydrothermal process and provide silica species for shell growth. As a silica-zeolite core-shell structure is first formed, the quality of the final zeolite shell depends on the balance between amorphous silica dissolution and

zeolite crystallization rates. Micrometric Beta zeolite crystals have also been used in the non-calcined form as sacrificial templates for the formation of BEA-FAU composite spheres [32,33]. Capsules were composed of an external layer of Y zeolite nanocrystals covering debris of beta crystals, with an internal void resulting from the partial dissolution of the core. Nonetheless, the zeolite core was not completely dissolved and the fraction of Beta zeolite remaining in the shell was far from negligible, as evidenced by XRD. Moreover, the coexistence of zeolites with FAU and BEA structures made the characterization of the shell difficult, in particular the determination of the Al content and the individual size of Y zeolite crystals.

The aim of the present work was to develop and optimize the synthesis of FAU-type hollow capsules. It was achieved by the detailed investigation of the influence of synthesis parameters on the nature and characteristics of FAU-type capsules obtained by controlled dissolution of Beta-Y zeolites core-shell structures. Experiments were directed towards the optimization of Beta zeolite core dissolution in order to obtain shells with a minimum of impurities while keeping Y nanocrystals as small as possible. The main discovery of the present study was the effect of step-wise addition of Al source in the synthesis gel which led to a decrease of the amount of Beta zeolite in the composite below 5 wt. %, while being accompanied with a significant growth of Y zeolite crystals and the ultimate formation of other contaminating phases, essentially A and P zeolites.

2. Experimental section

2.1. Synthesis

2.1.1. Synthesis of micrometric Beta zeolite crystals

Beta zeolite with micrometric crystals were prepared following a literature procedure [34]. Typically, 0.0792 g of sodium hydroxide (NaOH, Carlo Erba), 2.137 g of tetraethylammonium bromide (TEABr, Aldrich) and 0.2081 g of sodium aluminate (Riedel de Haën, 50-56% Al_2O_3 , 40-45% Na_2O) were dissolved in 4.38 mL of water under stirring. 0.67 mL of ammonium hydroxide (NH_4OH , Fluka) were then added and the mixture was stirred until it becomes clear. Then, 4.33 g of Ludox® HS-30 (Aldrich) were added dropwise and the final mixture was stirred for 2 hours at room temperature. The synthesis gel was finally placed in a 23 mL Teflon® lined stainless steel autoclave and heated at 140°C for 10 days under static conditions. After crystallization, the mixture was cooled down to room temperature and used as is for secondary crystallization of Y zeolite in the presence of seeds. When necessary, the crystalline powder (approx. 1.7 g) was separated from the liquid phase (7.4 mL) by centrifugation, washed and dried at 80°C. Chemical analysis of the obtained zeolite by ICP-OES gave $\text{Si}/\text{Al} = 9.6$.

2.1.2. Synthesis of nanometric Beta zeolite crystals

10.21 g of tetraethylammonium bromide (TEABr, Aldrich) were dissolved in 20 mL water. Then 10.61 g of an aqueous solution of tetraethylammonium hydroxide (TEAOH 35 wt. %, Aldrich) and 29.7 mL of ammonium hydroxide (NH_4OH , Fluka) were added and the mixture was stirred for about 10 minutes. A second solution was prepared by dissolving 0.46 g of sodium hydroxide (NaOH, Carlo Erba) and 2.48 g of sodium aluminate (Riedel de Haën, 50-56% Al_2O_3 , 40-45% Na_2O) in 28.6 mL of water.

The second solution was slowly added to the first one, followed by dropwise addition of 51.73 g of Ludox® HS-30 (Aldrich) under vigorous agitation. The gel mixture was stirred for 1 hour, placed in 100 mL Teflon®-lined autoclaves and heated at 140°C for 9 days.

After crystallization, the zeolite was recovered by filtration, washed with distilled water and dried overnight at 80°C. Chemical analysis of the obtained zeolite by ICP-OES gave Si/Al = 8.6.

2.1.3 Synthesis of Y zeolite seeds

Faujasite crystals were obtained using a synthesis recipe of the literature [35]. To a solution containing 9.6 g of sodium hydroxide and 6.92 g of sodium aluminate (Riedel de Haën, 50-56% Al₂O₃, 40-45% Na₂O) in 93 mL of water, 60 g of Ludox® HS-40 (Aldrich) were added dropwise and the mixture was vigorously stirred for 10 minutes. After aging at room temperature for 24 hours under static conditions, the gel was placed in 100 mL Teflon®-lined autoclaves and heated at 100°C for 24 hours. At the end of the crystallization period, autoclaves were cooled down at room temperature and the solid phase was recovered by centrifugation, washed and dried overnight at 80°C. The Si/Al atomic ratio of 2.4 was obtained from chemical analysis and solid-state NMR of the dried zeolite.

2.1.4 Synthesis of Beta-Y core-shell structures

The standard protocol for the preparation of Beta-Y core shell structures was adapted from the work of Zheng et al. [32]. Typically, 0.1436 g of sodium hydroxide (NaOH, Carlo Erba), 0.298 g of sodium aluminate (Riedel de Haën, 50-56% Al₂O₃, 40-45% Na₂O) and 0.3107 g of Y zeolite seeds were dispersed in the reaction mixture containing as-made micrometric Beta zeolite crystals. The mixture was vigorously stirred for 2 hours and heated at 90°C for 22 hours. After this period, the autoclave was cooled down and the solid phase recovered by filtration, washed and dried overnight at 80°C.

In the case of core-shell structures with nanometric beta crystals, the direct crystallization of Y zeolite was not possible because of the high alkalinity of the reaction medium. Therefore, an artificial reaction mixture was made by dispersing 1.7 g of dried Beta nanocrystals in 7.4 mL of the liquid phase corresponding to the synthesis of micron-sized Beta crystals. Core-shell structures were then obtained following the standard protocol described above for micrometric crystals.

2.1.5. Selective desilication in sodium carbonate solutions

Desilication experiments were performed by treating 1 g of calcined zeolite in 30 mL of a 1 M solution of sodium carbonate (Aldrich) at 80°C for 2 hours under gentle stirring. In the case of successive treatments (max. 3), the solid was recovered by centrifugation and used without drying in the next experiment. The solid was finally recovered, washed and dried overnight at 80°C.

2.2 Characterization

X-ray powder patterns were recorded from 4 to 80° 2-theta on a Bruker (Siemens) D5005 diffractometer using CuK α 1 radiation at $\lambda = 1.5406 \text{ \AA}$, with steps of 0.02° and 1 s per step. X-ray powder patterns were recorded on a D8 advance A25 diffractometer using CuK α 1 radiation at $\lambda = 1.5406 \text{ \AA}$ equipped with a Ni filter and 1-D fast multistrip detector (LynxEye, 192 channels on 2.95°). Measurements were performed at room temperature under air, from 4 to 80° with 0.02047° step and 0.5 s per step.

Scanning Electron Microscope (SEM) images were collected on a FEI ESEM-XL30 microscope under high vacuum (FEG source). A dispersion of the sample crushed in ethanol was deposited on standard holey carbon-covered copper TEM grids. A high

voltage of 20 kV was used in order to enhance the contrast between regions of the crystals with different densities, which revealed the existence of hollow structures.

Chemical analysis of the different zeolites was performed by ICP-OES after solubilization of the solids in HF-HCl solutions.

TEM images were obtained on a JEOL 2010 LaB6 microscope operating at 200kV. Samples were crushed in ethanol and deposited on the same grids as those used for SEM analysis.

N₂ adsorption / desorption isotherms were measured at 77K on a Belsorp-mini (BEL-Japan) sorption apparatus. Circa 80 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. ²⁹Si spectra were recorded using a one-pulse sequence with a pulse length of 4 μs (π/3) and a recycle delay of 100 s to ensure complete relaxation of the magnetization between consecutive scans. For ²⁷Al experiments; the pulse length was 1 μs (π/12) and the recycle delay was 1 s. Chemical shifts were referenced to tetramethylsilane (TMS) and Al(H₂O)₆³⁺ for Si and Al, respectively.

Quantitative determinations of Y and Beta zeolite proportions in composites were obtained using a calibration curve comparing experimental XRD and NMR spectra with those of mechanical mixtures (Fig. 1). More specifically, 6 solids containing 0, 20, 40, 60, 80 and 100 wt. % Y were prepared by physically mixing Y and Beta zeolites. XRD patterns and NMR spectra were recorded using the same amount of powder and similar acquisition parameters. Under such conditions, the absolute intensity of XRD lines at 6.2 and 7.5° (2-theta) corresponding to zeolites Y and Beta, respectively, varied linearly with the

composition. For NMR spectra, the contribution of Beta zeolite was systematically subtracted and the remaining part of the signal was deconvoluted to estimate the Si/Al ratio of the newly formed Y zeolite. The precision of the results was strongly affected by the presence of impurities in the batch, whose NMR spectrum generally overlapped with that of faujasite.

3. Results and discussion

A first set of experiments was carried out using a micrometric Beta zeolite prepared according to the procedure of the literature used for Beta-Y core-shell structures. After complete crystallization of Beta zeolite, the corresponding liquid phase contains 2.05 g/L Si with only traces of Al (< 0.1 mg/L) supporting the complete incorporation of Al in the solid phase. In order to get appropriate conditions to crystallize Y zeolite, Al was added in solution in the form of NaAlO_2 , which increased the Al concentration to 10.64 g/L. After mixing for 2 hours at room temperature in the presence of Y zeolite seeds, both concentrations dropped at 5.8 and 0.045 g/L for Al and Si, respectively. During this pre-crystallization period, temperature was too low for zeolite crystallization and the absence of significant changes in XRD pattern intensities suggest that seeds did not dissolve and that Si and part of Al species that were initially present in solution precipitated in the form of an Al-rich amorphous phase with $\text{Al/Si} > 1$. When the gel was heated at 90°C ($t = 0$), the excess of Al in the solid phase as well as in solution prevented the rapid crystallization of Y zeolite. Crystallization started after ca. 18 hours when the synthesis medium had been enriched with silicon species, resulting from the solubilization of the Si-rich Beta crystals (Fig. 2). Indeed, between $t = 0$, which corresponds to the beginning of the second crystallization step at 90°C and $t = 18$ h, the amount of Beta zeolite decreased by ca. 30

% whilst that of zeolite Y remained unchanged. After 18 h, zeolite Y crystallized whilst Beta continued to dissolve regularly to reach approx. 50% of the initial amount at 38h. During the whole crystallization period, samples were taken at regular intervals and the corresponding solid phases were analyzed by XRD (Fig. 3). Whereas Beta and Y were the only two zeolites detected at short synthesis time, new diffraction lines attributed to A and P zeolites appear after 24 hours. After 38 h, XRD intensities no longer changed suggesting that the reaction medium had reached an equilibrium. The Al concentration in the liquid phase has dropped below 10 mg/L and crystallization of Y zeolite stopped likely because available Al species have been almost totally consumed. The corresponding XRD pattern showed that the solid still contained a significant proportion of Beta zeolite that has not been dissolved with traces of A and P zeolites.

SEM pictures of a non-contaminated solid obtained after 23 h of crystallization revealed that large octahedral crystals characteristic of Y zeolite seeds have been totally dissolved during the recrystallization period (Fig. 4). Chemical analysis of the powder gave an overall value of the Si/Al ratio of 3.7. Assuming that the composition of the remaining Beta crystals and that the newly formed Y zeolite are similar to those of the original zeolites (Si/Al = 9.6 and 2.4 for Beta and Y, respectively), this corresponds to a mixture with 42 wt. % Y and 58 wt. % Beta. These proportions were confirmed by the relative intensities of reflections corresponding to Y and Beta zeolites in the XRD pattern of the solid (Fig. 3). They slightly differ from those of the literature (approx. 50 wt. % Beta in the composite estimated from XRD patterns) but the nature of seeds as well as the silicon source differed from a recipe to another. The ^{29}Si solid-state NMR spectrum of the Beta-Y composite showed many signals between -80 and -120 ppm. It could be decomposed into high-field signals corresponding to zeolite Beta and low-field peaks assigned to Y zeolite (see

experimental section and Fig. 1). The proportion of Beta zeolite in the mixture obtained from the decomposition of the spectrum was 57 %, in excellent agreement with the value deduced from the overall Si/Al ratio. Moreover, the deconvolution of the signal of the newly formed Y zeolite into 5 different environments $\text{Si}(\text{OSi})_n(\text{OAl})_{4-n}$ ($0 \leq n \leq 4$) gave Si/Al = 2.35, close to the value of the original seeds. The batch contained mainly oval-shaped crystals with a size similar to that of the original Beta zeolite (Fig. 4). Broken crystals confirmed the presence of hollow structures in the batch with a shell of ca. 100-200 nm thick. Moreover, SEM pictures of some of the intact crystals presented a contrast of intensity between a dark center and a brighter periphery, suggesting that they could also possess an internal cavity. The existence of a density gradient in some of the crystals was clearly evidenced by SEM-EDX mapping which showed a more intense color at the external surface for all elements constituting the zeolite framework (Fig. 4-d and 4-e). The contrast was particularly pronounced for silicon and oxygen atoms which are the most abundant constituents of the zeolite shell. More details on the intimate morphology and structure of zeolite shells were obtained by TEM. Shells are polycrystalline and built up from the stacking of nanocrystals with a size comprised between 30 and 50 nm (Fig. 5-a). The low cohesion between individual nanocrystals makes that they are defective and fragile, as evidenced by the high proportion of broken objects in TEM pictures. As the solid phase contains a huge amount of unreacted Beta zeolite, the composition and the nature of nanocrystals forming the shell were not easy to estimate. Nonetheless, a synthesis performed under similar conditions but in the deficiency of Y seeds (5 wt. % instead of 24 wt. %) led to a significant amorphization of the zeolite and to crystals with a totally different morphology. Indeed, as discussed further, hollow structures were observed as a result of partial dissolution of the crystals but their surface was smooth. Since temperature is too

low for Beta zeolite to crystallize within 22 hours under experimental conditions, it is reasonable to assume that crystals observed in the zeolite shell are FAU-type crystals, formed when enough seeds are added to the synthesis gel.

3.1. Amount of seeds

As already mentioned above, addition of seeds is essential for the recrystallization of Y zeolite and the formation of hollow structures. In addition to directing the crystallization towards FAU-type structures, the dissolution of seeds generates Si and Al species that significantly modify the composition of the synthesis gel. This is particularly the case of the present synthesis in which the amount of seeds represents 24 wt. % of the total amount of silica (solid + liquid) of the Beta zeolite reaction mixture. With 5 wt. % seeds, approx. 45 % of the Beta zeolite has been dissolved but the amount of recrystallized Y zeolite was very low, typically 10 wt. % of the solid phase as evidenced by XRD. Most of the compound was in the form of hollow capsules with smooth surfaces, supporting the internal dissolution of Beta crystals without recrystallization on the outer surface (Fig. 5-b). In the absence of recrystallization, the batch was contaminated with an amorphous phase, clearly evidenced on TEM pictures as well as by a broad background between 15 and 40° in the XRD pattern. When the amount of seeds was increased to 10 wt. %, the XRD pattern of the corresponding solid was quite similar to that obtained in a standard experiment with 24 wt. % seeds. The high intensity of reflections attributed to Y zeolites and the quasi absence of amorphous phase confirmed that recrystallization took place and that faujasite was the major zeolite formed along with traces of A and P. Hollow crystalline structures were observed with size and shape similar to those obtained in a standard experiment but TEM pictures also revealed the presence of many bulk crystals

and smooth capsules previously observed at 5 wt. % seeds. In contrast, an excess of seeds (34 wt. %) did not noticeably improve faujasite recrystallization as the relative intensities of XRD lines at 6.2 and 7.5° did not significantly change as compared to a standard procedure. Moreover, TEM pictures showed that the solid contained a huge proportion of large octahedrons, most probably seeds crystals that did not dissolve in the reaction medium.

3.2. Nature of the seeds

Experiments have been performed using zeolite seeds of FAU-type structure but with different framework compositions. The absence of large octahedra characteristic of seed crystals in the batch after a standard experiment suggest that seeds are partially dissolved during the process and contribute to modify the chemical composition of the gel. Four commercial faujasites with various Al contents and different cations have been used, namely CBV-100, 300, 500 and 720 from Zeolyst. CBV-100, a NaY zeolite with Si/Al = 2.55 is chemically similar to Y seeds prepared in this study. CBV-300 (Si/Al = 2.55; 2.8 wt. % Na₂O) and 500 (Si/Al = 2.6; 0.2 wt. % Na₂O) are obtained from CBV-100 by partial or complete exchange of Na⁺ with NH₄⁺. Finally, CBV-720 is a protonic dealuminated Y zeolite with Si/Al = 15. Whatever the nature of the cation, all Al-rich seeds led to a significant level of recrystallization with a weight proportion of Y zeolite in the final solid comprised between 45 and 70 %, as estimated from XRD patterns. The best results were obtained with CBV-300 suggesting that the Al content in the zeolite is not the only factor that can affect the recrystallization of Y zeolite capsules. Compared to CBV-100, the amount of Y zeolite in the batch has almost doubled in the presence of ammonium cations. However, SEM pictures clearly showed the presence of large octahedral faujasite crystals

with size and shape different from those of CBV-100 and resulting from the recrystallization of dissolved species. Such large crystals were also observed with NaY seeds but only after several additions of sodium aluminate in the gel (see section 3.4).

On the other hand, the use of the dealuminated CBV-720 as seeds did not lead to the formation of FAU-type zeolite capsules. The XRD pattern of the solid showed mainly peaks of Beta zeolite with only a weak line at 6.2° corresponding to faujasite. The intensity of the peak clearly indicates that Y seeds have been almost totally dissolved in the reaction mixture and that recrystallization did not occur. The absence of capsules could be attributed on one hand to a deficit of Al species in the crystallization gel and, on the other hand, to the inappropriate composition of the dealuminated zeolite to serve as seeds for the growth of Y crystals.

3.3. Alkalinity

Beta zeolite dissolution can be improved by increasing the alkalinity of the synthesis medium. A standard experiment was modified by increasing the OH^- concentration in the synthesis mixture from 1.21 to 1.55 mol/L. Since Na concentration in the gel also affects the crystallization of the zeolite, the alkalinity was increased by addition of TEOH, keeping the $[\text{Na}^+]$ concentration unchanged. The XRD pattern of the solid recovered after 23h of crystallization confirmed that the extent of Beta zeolite dissolution has increased from ca. 50 to 85 % as compared to a standard synthesis. Y was the major zeolite formed along with traces of P, which amount did not exceed that obtained in a less alkaline medium. A semi-quantitative estimation of the solid composition from XRD intensities gave 20 wt. % Beta and 80 wt. % Y, which was supported by ^{29}Si MAS NMR. If all species resulting from the dissolution of Beta cores had recrystallized into Y zeolite, the relative

proportions in the solid phase would have been 13 and 87 wt. % for Beta and Y, respectively. The discrepancy with solid-state NMR analysis confirms that some of the dissolved species remained in solution and contributed to enrich the liquid phase in Si at the end of the crystallization process. The deconvolution of the signal corresponding to the recrystallized Y zeolite in the ^{29}Si MAS NMR spectrum gave a framework Si/Al ratio close to 2, which is significantly lower than ratios obtained from standard synthesis. This supports data from the literature suggesting that higher alkalinities favor framework Al incorporation during synthesis of faujasites [36,37]. Increasing the alkalinity not only affects the composition but also the morphology of the zeolite aggregates. In particular, individual crystals constituting oval-shaped aggregates were smaller and most of aggregates were dense and did not present a clear hollow structure (Fig. 5-c).

3.4. Amount of Al

Important information on the mechanism of transformation of one zeolite to another can be obtained by looking at the evolution of the composition of the liquid phase during crystallization. In the particular case of the transformation of FAU-type zeolites in highly alkaline solutions, the dissolution of FAU crystals releases Si and Al species but whilst Si concentration rapidly increases to reach a plateau, Al is quickly reincorporated into the framework of a new zeolite [38]. As a consequence, the transformation generally stops because of an Al deficiency in the reaction medium. During the transformation of Beta into Y zeolite, we have observed that crystallization of Y zeolite stopped after 38 hours when the Al concentration in the liquid phase dropped below 10 mg/L. More aluminum in solution could therefore increase the recrystallization yield of Y zeolite as well as the extent of dissolution of zeolite Beta. An experiment performed using an excess of Al (1.33 times

the amount used in a standard experiment) effectively increased Beta conversion as evidenced by a less intense XRD signal at ca. 7.5° but the sample was contaminated with significant amounts of zeolites with LTA, GIS and GME topologies. In order to avoid the presence of co-zeolites in the batch, crystallization was performed in several steps with a limited Al concentration at each step. For example, instead of one step with 135 % Al – 100 % corresponding to standard conditions – zeolite Y was first crystallized with 75 % Al followed by a second recrystallization after 22 hours with 60 % Al. Under such conditions zeolite Y could be obtained with more than 100 % Al but the initial Al concentration never exceeded that of a standard experiment. Moreover, recrystallization steps could be repeated as long as Beta dissolution was observed. A first synthesis was performed with 75 % Al at the first step followed by 40 % Al at the second, i.e. with a total amount of Al corresponding to 115 % of a standard experiment. The amount of Beta zeolite in the solid phase effectively decreased as compared to a standard experiment and Y zeolite was the only zeolite formed, impurities with GIS, LTA and GME topologies being observed only at trace levels. Quantitatively, the Beta zeolite conversion was estimated by the decrease of the intensities of the corresponding XRD signals. Compared to a unique Al addition for which approx. 50 % of Beta zeolite had been dissolved, this two-step method led to 70 % dissolution. An EDX analysis by SEM of the shell gave a Si/Al ratio close to 4.5, approximately half the value obtained in a standard synthesis ($\text{Si/Al} = 8.5\text{-}10$), thus supporting a lower amount of the Si-rich Beta zeolite in the solid phase. Solid-state NMR also confirmed that the proportion of Beta zeolite decreased from ca. 55 % in a standard synthesis to 35 % when Al was added in two steps. When the second Al addition was increased to 60 %, which corresponds to a total Al addition of 135 %, the extent of dissolution reached 80 % but the amount of contaminating phases increased.

Nonetheless, both XRD and NMR indicated that the fraction of Beta zeolite in the solid phase decreased to ca. 20 % (Fig. 6). More than 90 % of the initial amount of zeolite Beta could even be dissolved when Al was incorporated in three successive additions of 75, 60 and 50 %, corresponding to a total Al concentration of 185 %. If Y remained the major zeolite formed, crystals were generally larger than 1 μm and they formed round-shaped aggregates of ca. 4-5 μm diameter. Internal cavities were still observed but the shell thickness had drastically increased after the third addition of aluminum. The above results suggest that the formation of pure Y zeolite capsules from the complete dissolution of Beta zeolite cores is hardly feasible, crystal growth prevailing on nucleation after the third addition of Al in the synthesis gel. However, successive additions of 75 and 60 % of aluminum seemed to be the best compromise to obtain solids with a minimum of Beta zeolite and whose shells are still made of faujasite nanocrystals (Fig. 5-d).

3.5. Morphology of the Beta zeolite core

Since faujasite recrystallization requires very specific Si, Al and Na concentrations in the gel, it strongly depends on the composition and rate of dissolution of Beta zeolite crystals originally present in solution. At constant composition, smaller Beta crystals not only dissolve faster in alkaline media but they could also offer a higher external surface for faujasite nucleation. However, the synthesis of smaller crystals with similar Al content necessitates higher pH and $[\text{NH}_4^+]$ values that are generally inappropriate to faujasite crystallization. After crystallization, small Beta crystals were then separated from their solution, washed, dried at room temperature and dispersed in the liquid phase of a standard synthesis after removal of the corresponding micrometric crystals. Except the nature of Beta zeolite crystals, all parameters were the same as those previously used, in

particular the solid-to-liquid ratio and the pH value. Two different experiments were performed with a unique (75%) and two consecutive (75% + 60%) additions of Al and the corresponding solids were compared with those obtained using larger Beta crystals (Table 1). After a unique Al addition, extents of faujasite recrystallization were similar but the size of capsules significantly differed thus reflecting the change in Beta zeolite crystal size. After the second Al addition, the influence of Beta crystals on the extent of faujasite recrystallization and the purity of the batch was much more pronounced. Although the percentage of dissolution was almost the same for both zeolites, small Beta crystals led to a lower faujasite content in the solid and to a higher amount of by-products. SEM pictures revealed the presence of quite large spherical aggregates of ca. 4-5 μm that were not present after the first addition and could be attributed to zeolite P.

3.6. Alkaline treatments with Na_2CO_3 solutions

Since successive recrystallizations in the presence of NaAlO_2 were ineffective to reduce the amount of Beta zeolite in composites below 20 wt. % while keeping nanometer-sized faujasite crystals, selective desilication methods have been experimented. A Beta-Y composite (19 wt. % Beta) obtained using two successive additions of sodium aluminate (75 and 60% Al, respectively) was treated with a 1 M Na_2CO_3 solution at 80°C for 2 hours. Comparison of XRD patterns showed that Y zeolite was still highly crystalline after alkaline treatment and that the corresponding reflection intensities did not change. By contrast, the intensity of the broad XRD line at 7.5° decreased by ca. 30%, supporting a selective elimination of Beta zeolite in the composite. This could be explained by the difference in composition between Beta and FAU zeolites, in particular the higher Si/Al ratio in Beta crystals, which makes that the latter are preferentially dissolved when capsules are

contacted with alkaline solutions at moderate temperature. A series of treatments performed at different concentrations (from 0.6 to 1 M), temperatures (80-100°C) and for different periods (6 to 16 hours) showed that experimental parameters did not significantly influence the desilication process. The amount of beta zeolite in the composite, which initially corresponded to 19 wt. %, could not drop below 13 wt. %, corresponding to a maximum rate of dissolution of 30%. Higher dissolution levels could be obtained following a series of three successive treatments of 2 h each in a 1 M Na₂CO₃ solution. Under such conditions, 42% of the original Beta zeolite was dissolved, leading to capsules containing around 90% of Y zeolite. Treatments not only preserved the crystallinity of faujasite, as previously mentioned, but they also considerably reduced the impurities, particularly zeolite P. This zeolite, which is obtained when Al is in excess in the solution, is probably less stable than Y zeolite and its structure collapses upon repeated hydrothermal treatments at 80°C. Despite that, the capsular morphology of the solid was maintained, as evidenced by SEM (Fig. 7). In the absence of impurities, deconvolution of the ²⁹Si MAS NMR spectrum could give direct information on the composition of Y zeolite nanocrystals constituting the shell, in particular the Si/Al framework ratio. Solid-state NMR data confirmed that the solid contained approx. 10 wt. % Beta zeolite, thus supporting XRD estimations of the composition. Moreover, the Si/Al ratio deduced from the signal corresponding to Y zeolite was close to 2.05, which is significantly lower than ratios obtained on solids before alkaline treatments. However, the decomposition of the spectrum into signals corresponding to Beta and Y zeolites was performed using a standard Beta spectrum, without taking into account a possible modification of the NMR line shape due to a change in framework composition of the zeolite during alkaline treatment. Under such conditions, the calculation of the Si/Al ratio is questionable since

the intensity of the NMR line at ca. -103 ppm assigned to $\text{Si}(\text{OSi})_4$ species in the framework of zeolite Y, which overlaps with that of SiOH or Si(1Al) of Beta zeolite, may be doubtful. Indeed, XRD patterns of the composite before and after alkaline treatment perfectly superimposed and did not show any shift that could suggest a substantial change in framework composition. All above characteristics confirm that Beta zeolite could be selectively removed from the composite shells without affecting significantly the composition of faujasite crystals.

4. Conclusion

Beta-Faujasite core-shell structures have been obtained by secondary crystallization of Y zeolite on preformed Beta crystals in their reaction mixture. Since gel compositions for the crystallization of Beta and Y zeolites are very different, the reaction mixture was first enriched with aluminum, the pH was increased and a huge amount of preliminary synthesized Y zeolite seeds was added. Under such conditions, Beta crystals not only served as template for the formation of the core-shell structures but they were also gradually dissolved and provided the necessary Si species for faujasite crystallization. Y zeolite yield was directly related to the amount of Al available in solution and crystallization stopped when all Al species had been consumed. Higher Al concentrations in the gel effectively increased the yield in Y zeolite but greatly favored the formation of by-products, mainly zeolite P. Alternatively, successive additions of moderate Al contents prevented the formation of zeolite P while improving the dissolution of Beta cores and the crystallization of faujasite. However, advanced Beta transformation was inevitably accompanied with a growth of Y zeolite crystals and a loss of hollow characteristics. The best hollow structures possessing a large void volume, a quasi-absence of contaminating

phases and nanometric Y zeolite crystals were obtained after two successive additions of aluminum in the synthesis mixture. Nonetheless, these capsules were not pure and they still contained 20 wt. % of Beta zeolite that could not be removed by addition of Al without severe modification of their morphology. The Beta content could be reduced by selective dissolution of the composites in sodium carbonate solutions, leading to capsules with more than 90 wt. % Y zeolite. Dissolution did not affect the crystallinity of the faujasite framework and had a minor effect on the composition.

In contrast to the state of the art, the present synthesis route, which combines crystallization and controlled dissolution steps, offers the possibility to prepare micrometric Y zeolite capsules made of crystals with a size in the 25-75 nm range and containing a relatively high Si content ($\text{Si/Al} > 2$). Such crystals could be calcined, exchanged and partially dealuminated without significant changes in the crystallinity, making them potentially interesting in acid-catalyzed reactions.

5. References

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Figure captions

Figure 1 XRD and NMR calibration curves obtained on Beta-Y mixtures. (a) XRD pattern of a mixture containing 40 wt. % Y and 60 wt. % Beta (left) and evolution of the ratio of XRD intensities at 6.2° and 7.5° (2-theta) for different compositions (right); (b) ^{29}Si MAS NMR spectrum of a mixture containing 60 wt. % Y and 40 wt. % Beta (left) and evolution of the relative NMR signal corresponding to Y zeolite after deconvolution of the spectrum for different mixtures (right).

Figure 2 Evolution of XRD basal reflection intensities for Beta zeolite at 7.5° (a) and Y zeolite at 6.2° (b) with time during recrystallization. Time arbitrary starts ($t=0$) when the mixture is placed in the oven at 90°C.

Figure 3 XRD patterns of the solid phase recovered at different time intervals during the recrystallization of faujasite shells on Beta crystals. Time (t) arbitrarily starts when the mixture is introduced in the oven at 90°C. Impurities are marked on the pattern recovered after 48 h (○: zeolite A; ●: zeolite P).

Figure 4 SEM pictures of Y zeolite seeds measured at 2 kV (a) and of a Beta-Y composite recovered after 23 hours crystallization measured at 20 kV (b). SEM picture (20 kV) of a group of crystals (c) and corresponding EDX mappings for silicon (d; orange) and oxygen (e; yellow) elements.

Figure 5 TEM pictures of hollow Beta-Y composite aggregates obtained: under standard conditions with a unique addition of Al (a), with 5 wt. % seeds (b), in a higher alkaline medium (c) and by incorporating Al into successive additions of 75% and 60% (d).

Figure 6 Top: ^{29}Si NMR spectra of a hollow Beta-Y composite obtained after 2 additions of Al (75% + 60%). The contribution of Beta zeolite (dotted line) represents 20 % of the total area. Bottom: deconvolution of the signal corresponding to Y zeolite spectrum after subtraction of the dotted curve.

Figure 7 SEM pictures (2 kV) (top) and corresponding XRD pattern (bottom) of polycrystalline Y zeolite capsules obtained by selective desilication of Beta-Y composites synthesized by incorporating Al in two consecutive additions (75% + 60%). XRD reflections 7.5 and 22.3° characteristic of Beta zeolite are indicated by arrows.

Figure(s)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure(s)

Figure 7

Table 1

Characteristics of Beta-Y composites obtained from Beta zeolites with different sizes

Beta zeolite crystals ^a	Si/Al	Crystal shape and size ^b	Beta dissolution (%) ^c		By-products ^d		Y (%) composite ^e	
			1 Al	2 Al	1 Al	2 Al	1 Al	2 Al
Large	9.6	Sphere 1-2 μm	50	80	-	+	45	70
Small	8.6	Ellipse 0.3x0.5 μm^2	45	65	+	+++	55	60

^aMicrometric and nanometric Beta zeolite crystals (see paragraphs 2.1.1 and 2.1.2 of Experimental Section)

^bEstimated from TEM and SEM pictures

^cCalculated from the decrease of the main XRD reflection intensity at 7.5° (2-theta)

^dEstimated from the ratio R between the (311) reflection of Y zeolite at 11.85° (2-theta) and the (101) reflection of zeolite P at 12.45° (2-theta). -: $R < 0.1$; +: $0.1 < R < 0.3$; ++: $0.3 < R < 0.75$; +++: $R > 0.75$.