Variation of Aluminum Distribution in Small-sized ZSM-5 Crystals during Desilication

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Abstract: Hollow ZSM-5 zeolites whose size are below 1 micrometer can be produced by desilication of crystals with aluminum-zoning. The parent crystals have a core-shell structure: the core part has nearly no aluminum, whereas the aluminum content in the shell increases when extending to exterior surface. Transmission electron microscopy confirms the preservation of the crystalline shell after base leaching, but cannot identify its subtle change. An increase of the Si/Al ratio of the surface is detected upon leaching the parent material to form the hollow zeolite, using ambient pressure x-ray photoelectron spectroscopy and infrared spectroscopy of substituted alkylpyridines. ²⁷Al MAS NMR exhibits that base leaching results in a reduced percentage of distorted tetrahedrally-coordinated aluminum. The reprecipitation of dissolved species occurs and tetrahedrally-coordinated tin atoms can thus be introduced to the shell framework. Overall, the formation of hollow ZSM-5 zeolites by desilication involves not only the removal of silicon-rich core, but also a reduced percentage of exterior aluminum-related acid sites, which should be considered while using hollow zeolites in acid-catalyzed reactions.

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INTRODUCTION

Materials with hollow structure that can encapsulate particles at the nanometer scale have attracted much attention due to their potential applications in catalysis.¹⁻⁴ The encapsulation isolates nanoparticles from each other and thus prevents their sintering under harsh catalytic conditions. If hollow crystals possess zeolite shells, encapsulated nanoparticles can be protected from external poisoning due to the molecular sieving effect.^{5, 6} Recently, typical strategies of making hollow zeolite crystals have been reviewed.^{7, 8} Hollow crystals produced by the templated-based methods are usually large, in the micrometer range with polycrystalline walls. Moreover, in order to electrostatically adsorb zeolitic species, the property of the template surface sometimes needs to be modified by multistep alternatively coating process which indeed is complicated and time-consuming.^{9, 10} In contrast, by means of controlled dissolution, hollow zeolite crystals can be easily produced.¹¹⁻¹³ The resulted hollow crystals can be as small as few tens of nanometers, which are excellent candidates for nano-reactors and particle hosts.

Recently, we proposed a simple procedure to produce sub-micrometer hollow zeolite crystals by leaching calcined ZSM-5 zeolite crystals in dilute sodium hydroxide solution under mild conditions.^{14, 15} Based on such hollow material, multifunctional catalysts have been prepared by separating different active nanoparticles inside and outside the hollow structure.¹⁶ In many industrial processes of hydrocarbon transformation, multifunctional catalysts that combine the active metallic composition and the acidity are imperative.¹⁷⁻¹⁹ For example, in the Fischer–Tropsch synthesis (FTS), the combination of the active species (cobalt, iron) with zeolite materials can break the classical Anderson–Schulz–Flory (ASF) product distribution in favor of producing short-chain products.²⁰ Considering the potential applications of hollow zeolites in tandem reactions associated with acid-catalyzed reactions,

understanding the nature, the distribution and the accessibility of acid sites in hollow zeolites is important. Regarding the mechanism of formation of hollow zeolite crystals, it has been proposed that the inhomogeneous distribution of aluminum and silicon atoms within crystals leads to a preferential removal of the core.^{21, 22} However, what remains unresolved is whether the shell part of zeolite crystals undergoes (partial) dissolution and/or reprecipitation of the leached species.

Herein, we prepared nanometer-sized hollow zeolite single crystals by desilication and studied their properties associated with aluminum. Energy dispersive X-ray (EDX) analysis was carried out on both parent and hollow crystals, providing the information on spatial distribution of aluminum within one crystal. Depth-profiling of aluminum and silicon was performed by ambient pressure x-rays photoelectron spectroscopy (APXPS), varying the excitation energy of the x-ray from the synchrotron source. The coordination of aluminum was explored by ²⁷Al MAS NMR and ²⁷Al triple quantum (3Q) MAS NMR spectroscopy. Infrared spectroscopy after adsorption of alkylpyridines of different size, namely pyridine, 2,6-lutidine and 2,4,6-collidine, was used to probe the nature and the accessibility of acid sites in the zeolite crystals.

EXPERIMENTAL SECTION

ZSM-5 zeolites crystals were prepared according to our previous report.¹³ 12 g tetrapropylammonium hydroxide solution (25 wt% in water) were added to a teflon reactor containing 12.5 g tetraethyl orthosilicate and water (x g). By varying the amount of water (0 g for synthesizing small crystals and 38.7 g for synthesizing large crystals), crystals of different sizes were obtained. The mixture was heated to 80 °C and stirred for 24 h at 500 rpm. After cooling down to room temperature, a solution of sodium hydroxide (0.24 g), aluminum

nitrate nonahydrate (0.46 g) and deionized water (4 g) was added dropwise to the mixture while stirring vigorously. After homogenization, the mixture was transferred to a stainless steel autoclave equipped with Teflon inlets and heated to 170 °C for 24 h under static conditions. The product was separated by centrifugation for 15 min at 15,000 rpm, washed three times, dried overnight at 100 °C and calcined for 10 h at 550 °C. Base leaching with sodium hydroxide solution (0.15 M, 35 mL/g zeolite) was carried out at 80 °C for 10 h. The reaction was subsequently quenched in an ice/water bath, and the resulting solid product was separated by centrifugation for 15 min at 15,000 rpm, washed three times and dried overnight at 100 °C. For the base leaching with tin source, the concentration of tin tetrachloride was 0.001 M or 0.005 M. HZSM-5 zeolites were prepared by ion exchange to NH_4^+ form first (0.1 M NH_4NO_3 , 25 °C, 3×24 h) followed by drying (100 °C, 10 h) and calcination (550 °C, 10 h) to produce zeolites in H^+ form.

Powder X-ray diffraction patterns were collected on a PANalytical X'Pert PRO MPD diffractometer with Cu K_α radiation at room temperature. Nitrogen physisorption isotherms were measured with a Micromeritics Tristar instrument at 77 K. Zeolite samples were degassed at 300 °C under vacuum for four hours prior to physisorption measurements. The surface area was derived using the BET model. The external surface area and micropore volume were derived from constructed t-plots. Finally, the total pore volume was determined from a single point measured at $p/p_0 = 0.96$. TEM images were obtained with Tecnai F30 microscope operated at 300 kV. HAADF-STEM and EDX measurements were carried out with a Hitachi HD-2700CS microscope operated at 200 kV. Ambient pressure x-ray photoelectron spectroscopy (APXPS) measurements were carried out at the X07DB (In Situ Spectroscopy) beamline of the Swiss Light Source synchrotron. The zeolite powder samples were dispersed in ethanol and drop-casted as a thin film on a gold foil (Sigma-Aldrich, purity 99.99%). The gold foil was mounted to the sample holder of the solid-gas interface endstation,

which allows measurements at precise pressures with a flow conditions of gas/gas mixtures.^{23,}

²⁴ The spectra were recorded at 80 °C and 1 mbar of helium (Messer gas, 99.999% purity) to minimize the charging of the samples. Si 2p and Al 2p photoemission spectra were recorded tuning the excitation energies between 480 to 1210 eV, such that for both elements the photoelectron kinetic energies are 400, 600, 800 and 1100 eV. After subtraction of a Shirley background, the spectra were fitted with Voigt shaped peaks. Integrated intensity of Si 2p and Al 2p was corrected for cross-section as a function of photon energy, flux as function of energy, photo-ionization cross section, asymmetry parameter, and photon flux. For infrared spectroscopy (IR) measurement, the degassing of chamber for dosing was achieved by freeze-pump-thaw cycles. All samples were ion exchanged three times with 1M NH₄NO₃ at room temperature for 24 h, dried at 100 °C and calcined in air at 550 °C for 6h. The samples (HZSM-5) were pressed to self-supporting pellets, placed in the IR cell and annealed at 400 °C for 2 h in vacuum ($\approx 10^{-7}$ mbar). The weight of the pellet was 10 mg for the parent zeolite and 6.2 mg for the hollow zeolite. This allowed us to compare the peak intensity of acid sites directly since the weight yield of the hollow sample was around 60~65 wt % of the parent. After cooling down to 150 °C, alkylpyridines (pyridine or 2,6-lutidine or 2,4,6-collidine) was adsorbed at 10^{-3} mbar by gradually increasing times up to an integral exposure time of 2 hours when the spectrum did not change any more in the following dose. Between the doses weakly bound probe molecule was desorbed by decreasing the pressure to the initial value. After desorption a spectrum with 128 scans was recorded. The background for each spectrum was recorded at 150 °C before the alkylpyridine doses. For the quantification assessment, the molar extinction coefficients were listed in Table S1. Details about calculation can refer to literature.²⁵⁻²⁸ Single quantum solid-state ²⁷Al were performed on a Bruker 400 UltraShield spectrometer at a resonance frequency of 104.29 MHz. The rotor was spun at 10 kHz and the spectra were recorded with a 4 mm MAS probe, with 3,000 scans averaged for each spectrum.

All spectra were normalized to the sample weight. Chemical shifts were referenced to $(\text{NH}_4)\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ for aluminum. The triple quantum (3Q) MAS experiments were conducted on a Bruker Avance 700 spectrometer with a 2.5 mm MAS probe at a spinning speed of 15 kHz. A total of 100 increments with a dwell time of 10 ms in t_1 were acquired with 1536 scans per increment. The isotopic chemical shift (δ_{iso}) and the quadrupole interaction product (P_Q) were calculated according to the following equation²⁹: $\delta_{\text{iso}} = (17\delta_{\text{F1}} + 10\delta_{\text{F2}})/27$, $P_Q = [17/162000\nu_L (\delta_{\text{F1}} + \delta_{\text{F2}})]^{1/2}$, where ν_L is the Larmor frequency. Diffuse reflectance UV-vis spectra of the samples were collected in ambient conditions in the 200–800 nm range using a Cary 4000 spectrometer equipped with a diffuse-reflectance unit (Praying Mantis, Harrick). Spectra are presented in Kubelka-Munk function after subtraction of the spectrum of the bare zeolite.

RESULTS AND DISCUSSIONS

Figure 1 shows TEM images of the parent and hollow zeolites.^{13, 22} Slightly elongated crystals have dimensions of about 60 nm × 80 nm (Figure 1a). Powder X-ray diffraction confirmed the pure phase of MFI-type structure in all samples (Figure S1). Mild base leaching (0.15 M NaOH at 80 °C) dissolved the silicon-rich core, leaving a crystalline shell (Figure 1b). The preservation of a crystalline shell was confirmed by TEM, as well as the appearance of a hysteresis loop in the isotherm with a closure at $p/p_0 = 0.42$ (Figure S2). The parent sample had an external surface area of 94 m² g⁻¹, which further increased to 124 m² g⁻¹ after leaching (Table S1). In the meantime, the total pore volume of the sample increased significantly, from 0.22 cm³ g⁻¹ to 0.35 cm³ g⁻¹. The difference in mesoporosity was also observed by the Barret–Joyner–Halenda (BJH) pore size distribution (PSD) derived from the isotherm, as the leached sample showed additional mesopores whose sizes were between 30

nm and 60 nm (Figure S3). An uneven distribution of aluminum has been confirmed by STEM-EDX in the parent crystals.¹³ Due to the negative charge of the AlO_4^- tetrahedra in the zeolite framework, the Si-O-Al bond is harder to hydrolyze than the Si-O-Si bond in the alkaline solution. This explains why the shell part of crystals retains while the core part is eliminated. The pore evolution process in the core was investigated by cryo-TEM and electron tomography.²² At initial stage of leaching, we observed crystals with multiple voids in the core. Finally, the coalescence of these mesopores resulted in a hollow structure. Large ZSM-5 crystals with a size between 400 and 500 nm also became hollow crystals after base leaching (Figure 1c, d). By using the focused ion beam (FIB) milling, the front and rear ends of a large parent crystal were removed. The remaining middle cross section was analyzed by STEM-EDX (Figure 2).²² The core part of the crystal has nearly no aluminum ($\text{Si}/\text{Al} > 100$), while the shell part is rich in aluminum ($\text{Si}/\text{Al} = 15$).

Next, we further explored the aluminum distribution in the shell part of crystals. To exclude the possible effect of the core on the accuracy of analysis, large hollow zeolite crystals were investigated. A non-homogeneous distribution of aluminum in the shell was clear from the EDX mapping (Figure 3). According to the intensities of the aluminum signal, we can roughly divide the shell into two parts. An outer shell presents a higher aluminum content than the inner shell. However, due to the sensitivity of zeolite materials to the electron beam, we cannot expose the crystal to the beam for a long time and thus the resolution of signal was insufficient to quantify the Si/Al ratio as a function of distance from the surface. By changing the leaching conditions, our recent results show that the shell tends to be thinner with an increase in post-treatment time (Figure S4).

A non-destructive depth profile of silicon and aluminum in the shell of zeolite crystals was performed by ambient pressure x-ray photoelectron spectroscopy (APXPS) employing a variation in excitation energy of the x-rays from the synchrotron source. Zeolites are

insulating samples and thus potentially suffer from severe charging during XPS measurements under high vacuum conditions. This generally leads to positive shifts of the binding energy and to the broadening of photoelectron spectral lines because of differential charging effects.³⁰ It is well known that during the APXPS measurements, ionized gas created by the incident x-rays can help to reduce sample charging.³¹ In a previous work, the uneven distribution of aluminum within the integral crystals has been confirmed by XPS.³² In this work, an excitation energy range between 480 to 1210 eV was selected to enhance the signal sensitivity to the top-most surface layers (< 10 nm) and to try to observe if the composition of the material is constant along the probed depth.³³ Figure 4 shows the spectra of Al 2p and Si 2p as a function of the photoelectron kinetic energy. The gradual increase in the Si 2p line width is because the spherical monochromator available at the beamline has not an even resolving power. Specifically, high resolving power is achieved at low photon energies (400 to 700 eV), then it tends to decrease. Smaller resolving power means lower resolution and in turn larger full width at half maximum, which is a technical feature of the beamline. Being the core-level peaks of Al and Si quite close, we can assume that the resolving power of the monochromator affects the line-shape of the spectra in the same way. Because the attenuation length (AL) of photoelectrons generated from the sample increases with their kinetic energy, the difference in the relative intensity between the Si 2p and Al 2p signals acquired at different excitation energies indicates that the chemical composition varies with the probed depth. Estimation of the Si/Al ratios was carried out after subtraction of a Shirley background and fitting the Si 2p and Al 2p peaks with Voigt profiles. Figure 5 shows the Si/Al ratios from both parent and hollow zeolites with probing depth. Inelastic mean free path (IMFP) values were estimated for silica using QUASES software (QUASES-IMFP-TPP2M ver 3.0).³⁴ An increase in the aluminum content was obvious when extending to the shell exterior, which is consistent with the EDX results (Figure 3). At the lowest

probed depth, both the hollow and the parent zeolite show the lowest Si/Al ratios of 10 and 8, respectively. The Si/Al ratio increases and stabilizes around 32 and 27, respectively in the hollow and parent zeolite at all the other probed depths, in good agreement with EDX results. This indicates that, within the information depth achieved by means of XPS (95% of the signal comes from 3xAL, therefore approximately 8 nm), a large surface enrichment of aluminum is observed in the topmost layers, while the composition of the rest of the shell is relatively constant, showing a lower Al atomic percentage. Furthermore, for the same probing depth, the hollow zeolite crystals exhibited a higher Si/Al ratio than the parent zeolite crystals (Figure 5). Note that the derived Si/Al ratios from XPS measurements provide semi-quantitative proof to show the alteration trend.

The fact that aluminum is concentrated in the shell, especially the top most layers of crystals, is important since it influences acid-catalyzed reactions.³⁵ During base leaching, desilication plays a major role in forming new pores and as such the Si/Al ratio of zeolite decreases from 58 to 32. The previous studies demonstrate that aluminum atoms that concern zeolite acidity were usually affected during base leaching and the redistribution of aluminum atoms lead to a decreased percentage of Brønsted over Lewis acid sites.³⁶ In this study, we employed infrared spectroscopy after adsorption of alkylpyridines of different size (pyridine: 0.57 nm, 2,6-lutidine: 0.67 nm, and 2,4,6-collidine: 0.74 nm) to probe the accessibility of the acid sites.²⁸ Figure 6 shows that pyridine adsorption on acid sites distinguishes Brønsted sites (1545 cm⁻¹) with Lewis sites (1455 cm⁻¹).²⁵ In contrast, only Brønsted sites are probed by lutidine and collidine, with characteristic lutidinium and collidinium ion bands centered at 1627 cm⁻¹.²⁸ Given the larger molecular sizes of lutidine and collidine relative to that of **MFI** zeolite pore system (0.56 nm), limited access of probe molecules to sterically hindered sites was expected. Therefore, for the parent and hollow zeolites, which preserved perfect microporous channels in the shell, only the acid sites located on the exterior surface and/or

subsurface can be detected. The percentage of exterior acid sites was quantified by comparing the number of acid sites detected by adsorption of large probe molecules with the amount of acid sites detected by adsorption of pyridine (B_{lu}/B_{py} , B_{coll}/B_{py}) using the molar extinction coefficients given in the literature (Table S1).²⁸ Table 1 shows that the ratio between the amount of Brønsted sites and that of Lewis sites did not change significantly after leaching. However, a lower percentage of exterior acid sites was observed for the hollow zeolite, as both the B_{lu}/B_{py} and B_{coll}/B_{py} ratios decreased after leaching. A decreased percentage of Brønsted acid sites on the exterior surface of hollow zeolite crystals indicates that aluminum redistribution occurs in the shell during leaching.

The aluminum coordination was examined by solid-state ^{27}Al magic angle spinning (MAS) NMR spectroscopy on hydrated samples. Both the parent and hollow zeolites exhibited a prominent resonance at 54 ppm, which corresponded to framework four-coordinated aluminum, and no five- or six-coordinated aluminum was detected (Figure 7). However, some distorted tetrahedrally-coordinated aluminum in the parent zeolite, although as a minority, was observed in the region of 30-40 ppm. Triple quantum (3Q) MAS NMR experiment was performed on the above samples as well, which provided better resolution (Figure 8).²⁹ The width of the line in the F1 projection was caused by the distribution of aluminum within the zeolite framework. In the present case, we observed a slight heterogeneity in the four-coordinated aluminum peak, which was attributed to an uneven distribution of aluminum atoms over different T-sites (Figure 8a).^{37, 38} With the introduction of a hollow structure, a more uniform chemical environment for aluminum was observed, as the small cross-peaks inherent in the parent zeolite were eliminated (Figure 8b). The signals were narrow in the F2 projection, indicating a small quadrupolar interaction of aluminum.³⁶ Table 2 summarizes the results of isotropic chemical shift (δ_{iso}) and the quadrupolar interaction product (P_Q). Both the parent and hollow zeolites have similar chemical shift

values in the F1 and F2 projections. The elimination of the distorted aluminum does not result in the considerable variation in quadrupolar parameters (P_Q) considering their lower percentage in content. The relative intensity of peaks attributing to different T-sites in the framework might change as the resonance shape of the hollow zeolites is different from that of the parent zeolites. This suggests that some aluminum had leached out or had been relocated during the base treatment.

Hollow zeolite crystals have a more silicon-rich external surface (a higher Si/Al ratio), as observed by means of IR and XPS. From NMR, we also concluded that part of aluminum species were leached out. These aluminum atoms had a distorted tetrahedral coordination. The above observations indicate that the aluminum atoms on the exterior surface of the shell were partially removed during base leaching. The redistribution of silicon species has been observed in the tetrapropylammonium hydroxide (TPAOH) leaching system since the TPAOH can promote the recrystallization of leached species on the crystal external surface.³⁹ However, this phenomenon is never observed in the sodium hydroxide leaching system that is more economical to produce hollow zeolite crystals. During base leaching, most silicon species are extracted from the framework, dissolved in the solution, but still part of them have the possibility to re-precipitate. Considering the similarity of tin and silicon atoms in forming a tetrahedral structure within the zeolite framework, a base solution containing a fraction of tin was used to leach crystals. After leaching hollow crystals were obtained as well, and a peak below 220 nm was observed in the UV-VIS spectrum of the resulted hollow zeolites (Figure 9). This peak was generally assigned to an electronic transition of isolated tin (IV) species coordinated to four oxygen atoms in the zeolite framework.⁴⁰⁻⁴² However, the existence of well-dispersed tin clusters cannot be excluded. An increase of the concentration of tin species in the base solution led to the formation of tin clusters or nanoparticles apart from isolated tin atoms, suggesting that there was a limit for the incorporation of tin atoms

(Figure S5). The enrichment of tin in the shell exterior of hollow crystals was also observed, which was consistent with a previous report.⁴³ Based on the above observation, we think that during base leaching, both dissolution and reprecipitation took place in the crystal shell, removing the distorted aluminum atoms from its outermost surface as well as incorporating the leached species into the framework. As a consequence, the remaining external shell of hollow zeolite crystals had a higher Si/Al ratio.

CONCLUSIONS

Using tetrapropylammonium hydroxide as structure-directing agent, we have synthesized ZSM-5 zeolite crystals that, upon base leaching, convert into hollow zeolite crystals. The parent ZSM-5 crystal has a dramatic difference in the aluminum concentration between the core and the shell parts, with aluminum being virtually completely concentrated in the shell. A gradual increase of the aluminum content is observed in the shell when extending to its exterior surface. Hollow ZSM-5 crystals with a crystalline shell are produced by desilication. During base leaching, besides the dissolution of silicon atoms in the core, the reprecipitation of the leached species in the shell framework takes place, as shown by incorporation of tin atoms into the zeolite framework. The dissolution and reprecipitation processes result in an increase in the Si/Al ratio of the external surface of hollow zeolite crystals, which might have an influence on acid-catalyzed reactions.

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Conflict of Interest

The authors declare no conflict of interest.

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Figure 1 TEM images of (a, c) the parent zeolite crystals and (b, d) the hollow zeolite crystals. Images of (c, d) are reproduced from ref 22 with permission. Copyright 2019 Royal Chemistry Society.

Figure 2 EDX map of the cross section of a large parent ZSM-5 crystal. The green and the red line represent the outer boundary of the core and the shell, respectively. Reproduced from ref 22 with permission. Copyright 2019 Royal Chemistry Society.

Figure 3 HAADF-STEM images of the larger hollow zeolite crystals and EDX mapping.

Figure 4 Measured (a) Si 2p and (b) Al 2p intensities for the parent zeolite crystals (p) and the hollow zeolite crystals (h) with the photon kinetic energy in the region of 400-1100 eV. The low excitation energy was used to ensure a more surface-sensitive analysis of the aluminum-rich shell. The noisy signal of aluminum is due to its low content and charging effect.

Figure 5 Depth profile of the Si/Al ratios as determined from variable kinetic energy APXPS.

Figure 6 IR spectra after adsorption and desorption of the alkylpyridines at 423 K on (a) parent zeolite and (b) hollow zeolite. The spectrum of the zeolite before any introduction of probe molecule was used as the reference.

Figure 7 The ^{27}Al MAS NMR spectra of the parent and hollow zeolites.

Figure 8 ^{27}Al 3QMAS NMR spectra and the corresponding projections of (a) the parent zeolite and (b) the hollow zeolite.

Figure 9 (a) UV-VIS spectrum and (b) TEM image of hollow crystals leaching in the sodium hydroxide solution with tin source. The concentration of tin tetrachloride was 0.001 M. The loading of tin was 0.66 wt %. The sharp peak below 220 nm can be assigned to an electronic transition of isolated tin (IV) species coordinated to four oxygen atoms in the zeolite framework. No obvious tin clusters or nanoparticles were observed from TEM.

Table 1 The quantified infrared results with the substituted pyridines.

Sample	B/L ^a	B _{lu} /B _{py} ^b	B _{coll} /B _{py} ^c
Parent	5.2	0.48	0.17
Hollow	5.7	0.34	0.12

^a Ratio between the amount of Brønsted (B) and Lewis (L) sites by IR of pyridine adsorption.

^b Ratio between the amount of Brønsted (B) sites by lutidine (lu) and pyridine (py) adsorption.

^c Ratio between the amount of Brønsted (B) sites by collidine (coll) and pyridine (py) adsorption.

Table 2 Properties of the ^{27}Al 3Q MAS NMR of zeolites.

Sample	Site	δ_{F1}	δ_{F2}	δ_{iso}	P_{Q}
		[ppm]	[ppm]	[ppm]	[MHz]
Parent	Al^{IV}	57.9	56.5	57.4	1.80
Hollow	Al^{IV}	57.7	56.3	57.2	1.80

Table of Contents

The formation of hollow ZSM-5 zeolite crystals by desilication involves not only the removal of silicon-rich core, but also a reduced percentage of exterior aluminum-related acid sites.