Organotemplate-Free $\beta$ Zeolites: From Zeolite Synthesis to Hierarchical Structure Creation

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Supporting Information

ABSTRACT: Interest in the production of $\beta$ zeolites in the absence of organic structure-directing agent (OSDA) has continued to grow consistently during the past decade. During this time, numerous strategies have been proposed to manipulate the hierarchy of zeolite pore structures in order to facilitate the transport of bulky reactants and to improve the accessibility of active sites in zeolite catalysts. In this work, we describe an organotemplate-free route to produce hierarchical $\beta$ zeolites. Using OSDA-free $\beta$ as the starting zeolites, we explored the applicability of various postsynthetic approaches to create hierarchical structures with mesoporosity, including framework stabilization, dealumination, conventional desilication, and hydrothermal desilication. While framework stabilization and dealumination were not effective in generating mesoporosity, they were necessary as modification steps to determine the efficacy of hierarchical structure creation. Compared to conventional desilication, hydrothermal desilication produces larger mesopores and much better preservation of microporosity and acidity because of the occurrence of recrystallization. The cost-effective, scalable production of organotemplate-free hierarchical $\beta$ zeolites could greatly enhance the adoption of $\beta$ zeolites in oil refining and petrochemical industries, where the advantages of hierarchically structured zeolites can dramatically improve catalytic performances in formulated catalysts.

INTRODUCTION

Zeolite $\beta$ is already a commercially relevant material for oil refining and petrochemical industries, featuring a three-dimensional large-pore and low-Al framework with an intergrowth of two or more polymorphs. $^{1-3}$ $\beta$ zeolite synthesis typically involves the use of organic templates as "structure-directing agent" (OSDA) such as tetraethylammonium cations (‘TEA’) to direct the assembly pathway during zeolite crystallization. When compared to other commercially relevant zeolites (e.g. Y zeolites for fluid catalytic cracking and hydrocracking) that do not require OSDAs, the use of OSDA in $\beta$ zeolite synthesis increases the overall cost of zeolite production and also leads to additional energy expenditure and environmental burden when the OSDA is removed at the end of the synthesis process. For these reasons, the OSDA-free synthesis of $\beta$ zeolite would enable the adoption of this important zeolite to be even more widespread in industries. Although zeolite $\beta$ synthesis was once believed to require organic templates, it was nearly a decade ago that OSDA-free synthesis of $\beta$ zeolite was reported and used zeolite $\beta$ seeds to facilitate crystallization. $^4$ This result generated industrial attention and spurred numerous follow-on studies to understand the crystallization mechanism and product characteristics. $^5$–$^9$ In the past decade, the seed-directed organotemplate-free synthesis has been successfully applied to a series of other types of zeolites and represents a critical achievement in promoting sustainable chemistry for zeolite production. $^{10-12}$

More recently, zeolite-related research has focused on the creation of the hierarchical pore structure. In this usage, hierarchical refers to the presence of at least one additional pore system, typically in the mesopore size range, in addition to the intrinsic zeolite microporosity. $^{13-15}$ This additional mesoporosity is believed to be beneficial for enhancing accessibility to the active sites and reducing transport limitation for bulky reactants that are ubiquitous in oil refining and petrochemical applications. Because zeolite $\beta$ is one of the most important industrial solid-acid catalysts, the creation of hierarchical $\beta$ zeolites has been explored by a variety of synthetic strategies, including both bottom-up and top-down routes. $^{16-20}$ Bottom-up approaches creates hierarchical zeolites by building up microporous and mesoporous segments in the presence of various templating materials or by nanocrystal aggregation. Alternatively, top-down approaches start with
 existed microporous zeolites that are postsynthetically modified to create mesoporosity. Ideally, hierarchical zeolites should possess comparable acidity and crystallinity with respect to their microporous zeolites.

As compared to bottom-up methods, top-down desilication is a highly reproducible and scalable approach to create hierarchical zeolite structures. These advantages make top-down desilication a preferred approach for commercial production of hierarchical zeolites.26–32 Pioneering research on desilication in MFI-type zeolites revealed the critical role of framework Al content in determining the efficiency of base leaching. It was demonstrated that only zeolites with appropriate Al contents could be leached in a one-step process that simultaneously created mesopores and preserved micropores.33 With high Al contents in zeolites, very limited mesoporosity was created, while high silica constituents resulted in excessive Si extraction and framework dissolution. For β zeolites, previous studies demonstrated that mesoporosity could be obtained directly by a one-step NaOH leaching process with preservation of microstructure from parent zeolites containing relatively higher Al contents (Si/Al < 20).27–29 These studies also revealed that because the high Si/Al framework (Si/Al > 20) is very sensitive to alkaline solutions, the presence of pore-directing agents (PDAs) is needed to protect the crystallinity and microporosity of the original zeolite framework during mesopore formation. While tetraalkylammonium salts/hydroxides and nonionic organic amines are frequently used as PDAs, the average mesopore size can be manipulated by selecting differently structured PDAs.34 The PDA structure–mesopore property relationship was established between the PDA structure and average mesopore sizes in the resulting hierarchical β zeolites.35

While these results demonstrate the use of top-down approaches to produce hierarchical zeolites, the synthesis of the starting β zeolites themselves usually require organic templates (i.e. TEAOH). To fill this gap, the recently developed seed-directed OSDA-free strategy serves as a promising alternative to provide the starting zeolites for subsequent desilication. To date, there have been no literature reports on the hierarchical structure creation by top-down approaches using OSDA-free β zeolites. OSDA-free β zeolites have Si/Al ratios typically in the range of 4–7 because more aluminosilicate species are needed to balance the electrostatic interactions with the smaller alkaline cations (with high charge densities) during crystallization. Thus, one prominent feature of OSDA-free β zeolites is its high Al content as compared to TEA-β zeolites. The hydrophobic interaction between alkyl-rich organic templates (with low charge density) and silicate species usually results in zeolite crystallization with relatively higher silica contents. Owing to this salient compositional feature, it is an open question whether the Si/Al range for the direct NaOH desilication of TEA-β zeolites (i.e. Si/Al < 20) could be readily extended to the high Al region (e.g. Si/Al < 10).

To drive further improvements in synthesis efficiencies for OSDA-free β synthesis, additional insights can be gleaned by examining the desilication conditions. Conventional top-down desilication creates mesoporosity in NaOH solutions at atmospheric pressures and at low temperatures (e.g. ~65 °C) and avoids framework destruction that usually derives from excessive leaching and dissolution at higher temperatures and/or pressures.26,36–38 Under these conventional conditions, recrystallization does not occur, and the resulting hierarchical zeolites sacrifice some microporosity and crystallinity (with reference to the starting zeolites) due to the destructive nature of desilication. We recently reported an organotemplate-free hydrothermal desilication process for the creation of hierarchical structures in β zeolites by treating microporous β zeolite under hydrothermal conditions that are favorable for crystallization. Under these conditions, we simultaneously create mesoporosity while maintaining high crystallinity and framework integrity without using any OSDAs, PDAs, or mesoporous templates.39 The resulting hierarchical β zeolites featured enlarged mesopores with peak mesopore sizes in the range of 20–30 nm and well-preserved characteristic acidity. The occurrence of recrystallization is evidenced by an

Figure 1. Characterization of OSDA-free β zeolite: (a) XRD (b) argon sorption isotherm (−186 °C) (c) SEM (d) NH3-TPD.
inflection in microporosity during the synthesis process. In this process, an initial decrease in microporosity is due to the dissolution (mesopore creation) but is then followed by an increase in microporosity (recrystallization) under appropriate hydrothermal conditions. On the basis of these results, it is indeed intriguing to explore the applicability of this approach to complete OSDA-free synthesis of hierarchical β zeolites.

In this work, the creation of hierarchical structures of β zeolites is studied by top-down alkaline leaching (desilication) using OSDA-free β zeolites as starting materials. Specifically, the study focuses on designing a complete organotemplate-free synthesis to introduce mesoporosity in β zeolites to enhance scalability, manufacturability, and cost considerations that are important for industry adoption. The understanding of mesopore creation in an organotemplate-free route may further enhance the impact of β zeolites in oil refining and petrochemical industry, where hierarchically structured zeolites can improve catalytic performances in formulated catalysts.

RESULTS AND DISCUSSION

Seed-assisted OSDA-free β zeolites were successfully synthesized according to a modified procedure reported in the literature. The silica-based yield was significantly increased to 65–70 wt % because of an increase in Al content in the precursor gel, whereas the conventional OSDA-free β synthesis usually led to a silica-based yield below 30 wt %. Figure 1 shows the X-ray diffraction (XRD), Ar physisorption isotherm, scanning electron microscopy (SEM), and NH3-temperature-programmed desorption (NH3-TPD) characterization results. The OSDA-free zeolite exhibits characteristic XRD peaks (for β zeolite) with a Brunauer–Emmett–Teller (BET) surface area and external surface area of 540 and 61 m2/g, respectively. The sorption isotherm exhibits no distinct desorption hysteresis, indicating a lack of mesoporosity within the crystals. The Si/Al ratio of the as-synthesized OSDA-free β is 4.7 as confirmed by both energy-dispersive X-ray (EDX) and inductively coupled plasma (ICP) analysis. From NH3-TPD, the total acidity is 1.31 mmol/g and the maximum desorption temperature is around 319 °C. Intriguingly, the particles of OSDA-free β zeolites are aggregates of nanocrystals in the size range of several hundred nanometers, which are comparable with the size of seeding β crystals. The presence of more Al nutrients in the synthesis gel may facilitate nucleation under the current synthetic conditions that led to the formation of nanoggregates of OSDA-free β zeolites.

For the as-synthesized β zeolites, no additional mesoporosity was created after being treated directly in alkaline solutions. After conventional desilication, the external surface area of the treated β zeolite increased to 79 m2/g, while the micropore volume slightly decreased to 0.26 cm3/g (from 0.28 cm3/g) (Supporting Information: Table S1). When the OSDA-free β zeolites were exposed to hydrothermal desilication conditions, the crystals suffered significant loss in crystallinity and micropore volume (0.11 cm3/g) as well as the occurrence of polymorphism as demonstrated by the XRD characteristic peaks (Supporting Information: Figure S1). Therefore, the high Al content in OSDA-free β zeolites not only retarded the creation of mesoporosity by desilication, but also resulted in a decline in framework stability under hydrothermal conditions.

Our previous study revealed that β zeolites with Si/Al > 20 are not stable in alkaline solutions (0.2 M NaOH, 65 °C) and additional organic PDAs are needed to protect the framework and direct the mesopore formation. Therefore, for an OSDA-free approach, we needed to develop a dealumination procedure to modify the Al content in OSDA-free β zeolites toward a preferable Si/Al ratio <20 (to avoid using any organic PDAs in the following step of mesopore creation). Several reported works in this area demonstrated that the modification on Al content can be achieved by an acid treatment in diluted nitric acid solutions for β zeolites. However, we found that OSDA-free β zeolites are not stable in diluted nitric acid solutions (0.05–0.2 M) and that the crystalline structure deteriorated with significant amorphization after such an acid treatment (80 °C for 2 h). The OSDA-free β zeolites with high Al contents are not stable in acidic (diluted HNO3 solutions at 80 °C under atmospheric pressure) and basic (NaOH at 150 °C under hydrothermal conditions) environments.

In order to improve structural stability, the OSDA-free β zeolites were ion–exchanged to NH4-form and then calcined at 750 °C in air for 15 h. This step was demonstrated to be very effective in improving framework stability of the OSDA-free β zeolites against acid treatments. At such temperatures, the zeolite crystals experience minor framework dealumination induced by steaming as well as a condensation at defect sites. The characteristic XRD peaks (Supporting Information: Figure S2) shifted to slightly higher angles after calcination (the corresponding d spacing values decreased) because the average Si–O bond length is shorter than that of Al–O when Al atoms are extracted from the framework during the calcination process. Note that the static calcination does not change the bulk Si/Al ratio in zeolites but creates more extra framework Al species (EFAL) (Supporting Information: Figure S3). 29Si NMR characterization demonstrates a reduction in Q3 Si species in the calcined zeolites, which is due to the condensation of silanol groups (generation of Si–O–Si bonds) during calcination (Supporting Information: Figure S4). Because the Si–O bond energy is much higher than that of the Al–O bond, the calcined samples are anticipated to have much improved stability. Indeed, the calcined β zeolites have well-preserved crystallinity and are stable in diluted nitric acid solutions for dealumination (Supporting Information: Figure SS). The slight dealumination led to an increase in the external surface area for the stabilized β zeolite [but no observable additional mesoporosity in the Barrett–Joyner–Halenda (BJH) or nonlocal density functional theory (NLDFT) pore size distribution (PSD)], which is likely due to the creation of smaller pores at or smaller than 2 nm. The total pore volume increased slightly from 0.33 cm3/g (for OSDA-free β) to 0.35 cm3/g.

Meanwhile, introduction of mesoporosity directly in the stabilized zeolite by desilication is still not feasible. Neither conventional nor hydrothermal desilication creates discernable additional external surface areas due to the high Al contents within stabilized β zeolites. However, unlike the as-synthesized zeolites, the stabilized OSDA-free β can be readily dealuminated by an acid treatment with well-preserved crystallinity (Supporting Information: Figure SS), and the Si/Al ratios can be continuously manipulated by changing the concentrations of the nitric acid solutions (Figure 2). Similar to the stabilization, dealumination by acid treatment resulted in the creation of additional micropores (with a corresponding increase in micropore volume) and external surface areas but with no remarkable generation of porosity in the mesopore range. The Ar sorption isotherms do not show distinct desorption hysteresis loops (Supporting Information: Figure S6). Therefore, even though acid treatment is effective in...
For two reasons, namely: (i) this Si/Al ratio is in the identical alkalinity and the preservation of microporosity. In conventional desilication or hydrothermal desilication under conditions, the leaching temperature is not sufficiently high to induce recrystallization, so the resulting hierarchical zeolites possess notably larger mesopores and greater total pore volumes when compared to hierarchical zeolites created by conventional desilication. Upon contacting the alkaline solution during the heating process, desilication accompanies mesopore creation. Meanwhile, the hydrothermal desilication can be completed in an organotemplate-free environment with the partially dissolved starting zeolites serving as seeds for local recrystallization. Thus, the hydrothermal desilication actually serves as a hybrid top-down and bottom-up approach to obtain hierarchically structured zeolites possessing notably larger mesopores and greater total pore volumes when compared to hierarchical zeolites created by conventional desilication. 

Table 1 summarized the Si/Al ratios and porous properties of the representative β zeolites used in this study. Figure 3 shows the XRD patterns, Ar physisorption isotherms, NLDFT PSD, and NH3-TPD results for the two hierarchical β zeolites via conventional and hydrothermal desilication. As shown, both samples exhibited characteristic β crystalline structures, but the conventionally desilicated zeolite has relatively lower crystallinity with weaker peak intensity (Figure 3a). Ar sorption isotherms (Figure 3b) and NLDFT PSD (Figure 3c) revealed the significant differences in porous properties between these two mesoporous zeolites. Hierarchical β zeolite by conventional desilication shows a much higher external surface area (393 m²/g) with smaller mesopores, but suffers from a discernable (~25%) decrease in the micropore volume (to 0.21 cm³/g). In comparison, the hydrothermally desilicated hierarchical β zeolite exhibits larger mesopores with ideal preservation of the micropore volume (0.28 cm³/g). These features are consistent with those of hierarchical β zeolites using TEA-β as parent zeolites. A sequential desilication and recrystallization mechanism was proposed to elucidate the creation of larger mesopores and the ideal preservation of microporosity (in hierarchical β zeolite after hydrothermal desilication). Upon contacting the alkaline solution during the heating process, desilication accompanies mesopore formation. For hydrothermal desilication (150 °C), the destructive effect is more severe on the parent β framework leading to the creation of larger mesopores (and/or macropores) during the initial stage of synthesis. When the synthesis proceeds for an extended time under hydrothermal conditions, the environment becomes favorable for zeolite crystallization. Partially dissolved hierarchically structured zeolites serve as seeds for local recrystallization, similar to the seed-directed OSDA-free synthesis of β zeolites. The occurrence of (re)crystallization is constrained locally without discernable changes in acidity and porous properties.

Table 1. Summary of Si/Al Ratios and Porous Properties of Representative OSDA-Free β Zeolites

| entry | OSDA-free zeolite β samples | Si/Al * | peak/(average) d_{meso} (nm) $^{b}$ | S_{BET} (m²/g) | S_{mic} (m²/g) | V_{mic} (cm³/g) | V_{total} (cm³/g) |
|-------|-----------------------------|---------|-------------------------------------|----------------|---------------|----------------|------------------|
| 1     | as-synthesized              | 4.7     | 2/(5.3)                             | 540            | 64            | 0.28           | 0.33             |
| 2     | stabilized (NH₄-form)       | 4.6     | 2/(4.8)                             | 567            | 122           | 0.27           | 0.35             |
| 3     | dealuminated (0.13 M HNO₃)  | 13.8    | 2/(3.8)                             | 691            | 216           | 0.32           | 0.40             |
| 4     | hierarchical β (hydrothermal) | 10.0   | 20–30 (7.0)                         | 588            | 118           | 0.28           | 0.44             |
| 5     | hierarchical β (conventional desilication) | 10.5 | 3.0–3.5 (4.7) | 570            | 393           | 0.21           | 0.52             |

*For the as-synthesized sample, its Si/Al ratio is confirmed by both ICP and EDX. The Si/Al ratios of other samples are characterized by EDX.

$^{b}$Peak d_{meso} is the peak mesopore size according to PSDs from the BJH method (adsorption branch). For the first three samples (entry 1–3) in the table, no additional PSD peaks in the mesopore region were observed, and the main size distributions are around 2 nm. The numbers in parentheses are the average mesopore sizes.
crystal growth because there are no additional aluminosilicate sources, and the recrystallization may only rely on the limited dissolved aluminosilicate species from the starting zeolites. The differences in the preservation of microporosity and crystallinity resulted in strikingly different acidity in the resulting hierarchical zeolites, as demonstrated in the weight-normalized NH3-TPD curves. Hydrothermal desilication leads to the creation of hierarchical β zeolite with much higher total amounts of acid sites (a total acidity of 0.76 mmol/g according to NH3-TPD). The maximum desorption temperature ($T_{d,max}$) is around 345 °C, which is higher than that of OSDA-free β (319 °C, Figure 1) because of the greater separation of Al sites after dealumination as well as well-preserved microporosity after introduction of mesoporosity. In comparison, the conventionally desilicated β zeolite shows a $T_{d,max}$ around 286 °C due to the partial amorphization upon base leaching.

Upon hydrothermal desilication, both TEA-β and dealuminated OSDA-free β undergo the creation of hierarchical structures with peak mesopore sizes of 20–30 nm. However, hierarchical β zeolite from OSDA-free β shows smaller average mesopore sizes (~7.0 nm) than that from TEA-β (~10.0 nm), which is due to the larger contribution of smaller mesopores within the dealuminated OSDA-free β zeolite. As discussed previously, the OSDA-free β needs to be stabilized and then acid-treated before mesopore creation in alkaline solutions. These treatments resulted in framework dealumination with the formation of EFAL species and additional porosity in the small mesopore range (~2 nm) that reduced the overall average mesopore sizes. Such pretreatments are not necessary for TEA-β zeolite because of its relatively lower initial framework Al content. On the other hand, the stabilization and dealumination seem to weaken the framework resistance to base leaching under conventional desilication conditions. The hierarchical β zeolite from the dealuminated OSDA-free β zeolite possessed much higher external surface area than hierarchical zeolite from TEA-β as well as lower crystallinity and microporosity (after conventional desilication). 29

Figure 4 shows SEM and transmission electron microscopy (TEM) images of hydrothermally desilicated hierarchical β zeolite. SEM shows apparent grooves and cracks on the crystalline surfaces that contribute to the hierarchical structure. TEM demonstrates the existence of additional mesoporosity within well-defined β zeolite crystals. Cumene sorption uptake curves were measured on hierarchical β zeolite (after hydrothermal desilication, H-form) and microporous OSDA-free β (Figure 5). It is clear that the sorption proceeds much faster toward equilibrium for hierarchical β zeolite than the microporous β. The solution for the transient diffusion equation for a spherical particle is expressed as 45

$$\frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D t}{r_c^2}\right)$$

A simplified solution for short times (fractional uptake $m_t/m_\infty$ up to 0.25) is

$$\frac{m_t}{m_\infty} = \frac{6}{\sqrt{\pi}} \frac{D t}{r_c^2}$$

Figure 4. SEM (a) and TEM (b) images of hierarchical β zeolite after hydrothermal desilication.
From the uptake curves in Figure 5, the transport diffusivity can be calculated by assuming identical spherical crystals for both hierarchical and microporous \( \beta \) zeolites. The differences in the uptake curves translate into more than 1 order of magnitude improvement in transport diffusivity for the hierarchical \( \beta \) zeolite at 35 °C (1.4 × 10^{-18} \text{ m}^2/\text{s}). Therefore, both microscopic characterization and sorption rate measurements corroborated the existence of open and accessible mesopores, which is in stark contrast with the enclosed mesoporosity within dealuminated zeolite Y crystals that may not provide preferable diffusional improvements for bulky molecules.46

**CONCLUSIONS**

In this work, we have demonstrated an organotemplate-free route to synthesize hierarchical \( \beta \) zeolites from OSDA-free \( \beta \) zeolites. The as-synthesized OSDA-free \( \beta \) zeolite suffered stability drawbacks in both acidic and basic environments because of the exceptionally high Al contents. Framework stabilization was achieved by static calcination (on the NH\(_4\)-form zeolites) in air at 750 °C, during which a slight dealumination and condensation occurred with the formation of more stable Si–O–Si bonds. In order to introduce mesoporosity, the stabilized \( \beta \) zeolites were dealuminated in diluted nitric acid solutions because the static stabilization did not alter the bulk Si/Al ratio of OSDA-free \( \beta \) zeolites. The Al content modification by such an acid treatment is highly controllable and the Si/Al ratios of the resulting zeolites can be continuously manipulated. The creation of the hierarchical structure was achieved on appropriately dealuminated \( \beta \) zeolites in alkaline solutions under atmospheric or hydrothermal conditions. While mesoporosity can be introduced by both approaches, the resulting hierarchical zeolites exhibited strikingly different properties. Conventional desilication resulted in the generation of smaller mesopores and much larger external surface areas but suffered a loss in crystallinity, microporosity, acid site strength, and total acidity. In comparison, the hierarchical \( \beta \) zeolites by hydrothermal desilication possess much larger mesopores with ideally preserved microporosity and acidity due to the occurrence of recrystallization. Because the hydrothermal synthetic step does not involve any organic templates, this work demonstrates the feasibility of producing hierarchical \( \beta \) zeolites via an organo-template-free route without sacrificing intrinsic microporosity and acidity of \( \beta \) zeolites.

**EXPERIMENTAL SECTION**

**Synthesis of OSDA-Free \( \beta \) Zeolites.** OSDA-free \( \beta \) zeolite was synthesized using colloidal silica according to a modified procedure reported in the literature.40 To prepare the starting synthesis gel, 1.92 g Al\(_2\)O\(_3\) was dissolved in 24.8 g H\(_2\)O. The solution was then mixed with 0.89 g Al(OH)\(_3\) and stirred for 30 min at room temperature. Then, 16 g 30% Ludox colloidal silica was added. The mixture was stirred for another 3 h. Once a uniform synthesis gel was obtained, 15 wt % zeolite \( \beta \) seeds (0.72 g, Si/Al = 14, wt % based on silica) was added into the gel and the mixture was stirred for 30 min to produce a uniform dispersion of seeding crystals in the gel. The molar composition of the starting synthesis gel was: 1SiO\(_2\):0.142Al\(_2\)O\(_3\):0.6NaOH:25H\(_2\)O. Finally, the hydrothermal synthesis was completed at 140 °C for 4 days.

**Postsynthetic Treatments of OSDA-Free \( \beta \) Zeolites.** The as-synthesized OSDA-free \( \beta \) zeolites underwent different postsynthetic treatments to modify framework content, to create mesoporosity, and to enhance framework stability. The OSDA-free zeolites (NH\(_4\)-form) were stabilized by a calcination step at 750 °C in air for 15 h. The NH\(_4\)-form zeolites were obtained by triple ammonium exchange in 0.8 M NH\(_4\)NO\(_3\) at 80 °C for 2 h. Framework dealumination was then achieved by acid treatment in diluted HNO\(_3\) solutions at 80 °C for 2 h with a weight to solution volume ratio of 1 g zeolite in 50 mL HNO\(_3\) solution.

Two base leaching treatments were pursued using different approaches in 0.2 M NaOH solutions, referred to as conventional desilication (65 °C for 30 min) and hydrothermal desilication (150 °C for 21 h) in this article. In all desilication treatments, starting zeolites were added into the NaOH solutions to make a suspension with a NaOH/Si ratio of 0.35 and a resulting H\(_2\)O/Si ratio of 97. The alkaline-treated zeolites were retrieved by quenching, centrifuging, washing with distilled water, and drying in an oven at 110 °C. For protonic form \( \beta \) zeolites, the ammonium-exchanged zeolites were calcined at 550 °C for 5 h at a heating rate of 10 °C/min. Note that the applied hydrothermal desilication conditions are the most favorable conditions (in the temperature range of 100–220 °C and mediated alkalinity range of 0.05–0.55 for hydrothermal desilication) in terms of preserving microporosity and generating mesoporosity by this approach using the same starting \( \beta \) zeolite.

**Characterization.** A Bruker D8 Discover diffractometer was used for powder XRD characterization (a copper tube and a VANTEC-500 2-D detector) in the 2θ range of 5°–40°. SEM images were analyzed by a JEOL JSM-7100F with an Oxford EDX spectroscopy system. TEM characterization was completed by a JEOL 2010F TEM/scanning TEM with a Gatan OneView 4k × 4k camera (200 kV). TEM samples were prepared by casting sample suspensions in ethanol on a carbon-coated copper grid. Argon (Ar) physisorption isotherms were obtained at −186 °C on a Micromeritics ASAP 2460. All samples were degassed at 350 °C overnight under vacuum with Micromeritics Smart VacPrep. The surface areas were estimated by the BET approach in the \( P/P_0 \) range of 0.02–0.10. The mesopore size distribution was obtained by the NLDFT method. The same method is also applied to obtain...
micropore volume ($V_{\text{mic}}$) and total pore volume ($V_{\text{tot}}$) by converting original sorption data in the Quantachrome data reduction software (based on the model of Ar at $-186$ °C on a zeolite with cylindrical pores). NH$_3$-TPD analysis was performed by Micromeritics AutoChem II equipped with a flow-through reactor connected to a thermal conductivity detector. The samples were degassed at $580$ °C for 1 h followed by the adsorption of ammonia at $180$ °C. The NH$_3$-adsorbed zeolites were purged in helium flow for another $5$ h at $180$ °C to minimize NH$_3$ physisorption. Then, the TPD signals were recorded by heating the samples from $180$ °C at a rate of $15$ °C/min in a helium flow to the target temperature. The cumene vapor adsorption experiments were performed on an IGA-100 sorption analyzer at $35$ °C (relative pressure of 0.10). The vapor relative pressure was controlled automatically by mixing the wet vapor feed with a dry N$_2$ line that serves as a carrier gas for the vapors. The “dry mass” of the samples was weighted under N$_2$ atmosphere before feeding vapors to the sample chamber.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02762.

Additional XRD characterization, $^{27}$Al NMR, $^{29}$Si NMR, Ar physisorption, and summary of content and porous properties of some OSDA-free $\beta$ zeolites (PDF)

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**Notes**
The authors declare no competing financial interest.

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