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Liu, Baoyu; Lu, Weijian; Liu, Yikuan; Feng, Qilong; Huang, Yi; Shang, Jin; Zhu, Yihan; Dong, Jinxiang

**Published in:**  
AIChE Journal

**Published:** 01/11/2023

**Document Version:**  
Post-print, also known as Accepted Author Manuscript, Peer-reviewed or Author Final version

**Publication record in CityU Scholars:**  
[Go to record](#)

**Published version (DOI):**  
[10.1002/aic.18201](https://doi.org/10.1002/aic.18201)

**Publication details:**  
Liu, B., Lu, W., Liu, Y., Feng, Q., Huang, Y., Shang, J., Zhu, Y., & Dong, J. (2023). Synthesis of dodecylbenzene via the alkylation of benzene and 1-dodecene over mesopore Beta zeolites. *AIChE Journal*, 69(11), Article e18201. <https://doi.org/10.1002/aic.18201>

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# Synthesis of dodecylbenzene via the alkylation of benzene and 1-dodecene over mesopore Beta zeolites

Baoyu Liu<sup>\*, a,b</sup>, Weijian Lu<sup>a,b</sup>, Yikuan Liu<sup>c</sup>, Qilong Feng<sup>c</sup>, Yi Huang<sup>d</sup>, Jin Shang<sup>e,f</sup>,  
Yihan Zhu<sup>\*,c</sup>, Jinxiang Dong<sup>a,b</sup>,

<sup>a</sup>School of Chemical Engineering and Light Industry, Guangdong Provincial Key Laboratory of Plant Resources Biorefinery, Guangzhou Key Laboratory of Clean Transportation Energy Chemistry, Guangdong University of Technology, Guangzhou, 510006, P.R. China

<sup>b</sup>Jieyang Branch of Chemistry and Chemical Engineering Guangdong Laboratory (Rongjiang Laboratory), Jieyang 515200, China

<sup>c</sup>Center for Electron Microscopy, Institute for Frontier and Interdisciplinary Sciences, State Key Laboratory Breeding Base of Green Chemistry Synthesis Technology, College of Materials Science and Engineering and College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, Zhejiang, China

<sup>d</sup>School of Engineering, Institute for Materials & Processes, The University of Edinburgh, Robert Stevenson Road, Edinburgh, EH9 3FB, United Kingdom

<sup>e</sup>School of Energy and Environment, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China

<sup>f</sup>City University of Hong Kong Shenzhen Research Institute, 8 Yuexing 1st Road, Shenzhen Hi-Tech Industrial Park, Nanshan District, Shenzhen 518060, China

## Abstract

The alkylation of benzene with long chain  $\alpha$ -olefins is a crucial process in the production of fine chemicals, which requires the upgrading from traditional homogeneous catalysis to heterogeneous catalysis involving zeolites. However, the application of zeolite catalysts has been limited by their fast deactivation due to constrained diffusion resulting from the sole micropores. To address this challenge, a desilication and secondary-crystallization strategy has been employed to fabricate hierarchically structured mesoporous Beta zeolites. The resultant mesoporous Beta zeolites demonstrate excellent catalytic activity and stability in the alkylation of benzene with 1-dodecene, arising from the exposed acid sites and enhanced internal diffusion. Importantly, the internal diffusion

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\* Corresponding author, Email: [baoyu.liu@gdut.edu.cn](mailto:baoyu.liu@gdut.edu.cn) (Baoyu Liu); [yihanzhu@zjut.edu.cn](mailto:yihanzhu@zjut.edu.cn) (Yihan Zhu)

limitations for these mesopore Beta zeolites are negligible, which significantly extends their lifetime and improves their regeneration performance. To achieve these benefits, the degree of mesopores must be deliberately controlled. Overall, this approach provides a promising solution for achieving efficient and environmentally-friendly alkylation processes.

**Keywords:** Beta Zeolite; Diffusion; Alkylation; Linear Alkylbenzene

## **Introduction**

Linear alkylbenzene (LAB), generating normally from alkylation of benzene with  $\alpha$ -olefin ( $C_{10}$ - $C_{14}$ ), is indispensable chemical intermediate in industry for the production of Linear alkylbenzene sulfonate (LAS), which is an essential synthetic surfactant with one of the largest output worldwide and used extensively in household detergents, industrial wetting and detergency.<sup>1-6</sup> However, the reaction process and the products composition of alkylation between benzene with long-chain  $\alpha$ -olefin ( $C_{10}$ - $C_{14}$ ) are extremely complicated.<sup>7</sup> Generally, the desired product LAB has five positional isomers in alkylation of benzene with 1-dodecene, include 2-LAB, 3-LAB, 4-LAB, 5-LAB and 6-LAB, where 2-LAB exhibits the most environmentally favorable features due to its better detergent properties, highest biodegradability and solubility.<sup>8-10</sup> Initially, the homogenous catalysts are adopted to produce the LAB products in industrial process, such as hydrofluoric acid (HF) and aluminum trichloride ( $AlCl_3$ ), which exhibit great activity towards olefins with a variety of thermodynamic mixtures but low selectivity of target 2-LAB, contributing to only 26-33 % in  $AlCl_3$  process and less than 20 % catalyzed by HF.<sup>11-13</sup> On the one hand, the inevitable environmental pollution, seriously equipment corrosion and separation problems are always involved in the homogeneous catalytic process.<sup>14</sup> On the other hand, the increasing demand

and timeless use of detergents in both industry and household have caused conspicuous environmental pollution in rivers and lakes, which has attracted public attention. Therefore, it's highly desired to develop heterogeneous catalysis process for the production of LAB. Unfortunately, the major technology for global LAB production is still *vis* hydrofluoric acid (HF) catalysis process.<sup>11,15</sup>

Base on the requirement of green chemistry, more and more researches have focused on developing efficient and stable solid catalysts in order to replace the traditional homogeneous catalysis process.<sup>15</sup> Among the variety of heterogeneous catalysts, zeolites have attracted widespread attention since the zeolites possess ordered channels, high surface area and tunable acidity.<sup>16</sup> It was reported that Beta zeolites with 12-membered ring (12-MR) channels exhibited high 2-LAB selectivity in the alkylation of benzene with long chain olefins owing to their prominent shape-selectivity.<sup>2,5</sup> However, the sole micropores in conventional Beta zeolites limited the diffusion of bulk molecules involved in the alkylation between benzene with long chain olefins, impeding its application in the production of LAB.

Generally, hierarchical structure was introduced in the zeolite matrix through shortening the diffusion pathway to improve the transportability of guest molecules.<sup>17-20</sup> So far, numerous strategies have been developed to fabricate hierarchical zeolites,<sup>21-24</sup> such as steaming, leaching by acid or base, hard-/soft-templating route, surfactant-assisted recrystallization method, template-free methods and so on, which strongly enhanced the diffusion properties of zeolite catalysts in the various reaction involved bulk molecules.<sup>25</sup> In present research, a series of mesopore Beta zeolites with exposed acid sites and enhanced

diffusion properties were fabricated by a desilication and secondary-crystallization method, the acidity and mesoporous of obtained Beta zeolites could be systematically modulated by tuning the concentration of TEAOH. The passivation experiment of acid sites revealed that Brønsted acid sites dominated the activity of alkylation, and internal diffusion limitations on the alkylation between benzene with 1-dodecene was negligible. Significantly, the obtained Beta zeolites exhibited superior activity, stability and regenerability in liquid alkylation of benzene with 1-dodecene, which was expected to promote the industrial application in the production of linear alkylbenzene. Besides, further investigation of the deactivation behavior for the spent Beta zeolites demonstrated that the degree of mesoporous for resultant hierarchical Beta zeolites should be delicately optimized in order to maintain the stability of zeolite framework and enhance the transportability of guest molecules simultaneously.

## **Experiments**

### ***Catalyst Preparation***

The statically hydrothermal method was used to prepare pure-silica Beta zeolite. In a typical experiment, fumed silica was fully dissolved into the mixture of TEAOH and deionized water under vigorous stirring. After stirring for desired time, the calculated ethanol (the mass ratio of  $C_2H_5OH/SiO_2 = 1.22$ ) and ammonium fluoride were successively added into the previous gel to obtain homogeneous mixture with a corresponding molar ratio of 37  $NH_4F$ : 100  $SiO_2$ : 48 TEAOH: 732.5  $H_2O$ . After stirring for another 5 h at room temperature, the mixture was transferred into a Teflon-lined stainless-steel autoclave and crystallized at 150 °C for 96 h. The resultant solid product after crystallization was washed,

centrifuged with deionized water repeatedly, and dried at 100 °C for 12 h. At this moment, the obtained sample was denoted as as-prepared Beta-S. Moreover, the final sample calcined in air at 550 °C for 6 h to remove organic templates was named as Beta-S.

Hierarchical Beta zeolites were prepared via a desilication and secondary-crystallization process by further treating the obtained sample in alkaline conditions. Generally, the selective extraction of framework Si by treatment in alkaline solutions due to hydrolysis in the presence of OH<sup>-</sup>, referred to as desilication or base leaching, was a widely used top-down method to introduce the mesopores in the matrix of zeolites.<sup>26</sup> As a result of the negatively charged [AlO<sub>4</sub>]<sup>-</sup> tetrahedra, hydrolysis of the Si-O-Al bond in the presence of OH<sup>-</sup> was hindered compared to the relatively easy cleavage of the Si-O-Si bond in the absence of neighboring Al tetrahedra,<sup>27</sup> thus the pure silica Beta zeolite was chosen as the parent to finish the desilication process in present research. Typically, the specific amount of aluminum isopropoxide (3 g/L in the final solution) was dissolved in TEAOH solution to obtain the mixture, where the concentration of TEAOH was adjusted to 0.1, 0.2, 0.3 and 0.4 mol/L, respectively. Subsequently, the as-prepared Beta-S was mixed with the solutions composed of aluminum isopropoxide and TEAOH, where the amount of the mixture solution was 30 mL/g of as-prepared Beta-S. After crystallization under 170 °C for 72 h in static condition, the final solid was centrifuged, washed with deionized water, dried at 100 °C overnight and calcined in air at 550 °C for 6 h. The resultant samples were denoted as Beta-0.1, Beta-0.2, Beta-0.3 and Beta-0.4 depending on the concentration of TEAOH in the mixture, respectively.

### ***Catalyst Test***

The catalytic performances of the resultant Beta zeolites were evaluated in a fixed-bed reactor with a 10 mm inner diameter reaction tube. Typical, Beta zeolite catalyst (250 mg, 20-30 mesh) was uniformly diluted with quartz sands (20-30 mesh) in a volume ratio of 1:1, then the catalyst was loaded in the center of reaction tube with 10 mm filling height and degassed at 200 °C for 6 h. After cooled down to a desire temperature of 80 °C, the reactant mixture (benzene and 1-dodecene with a molar ratio of 8.75 : 1) was fed into the reactor at a rate of 0.2 ml/min. The reaction was kept at 80 °C with atmospheric pressure and a weight hourly space velocity (WHSV) of 42.2 h<sup>-1</sup>. The effluent product was collected periodically and analyzed by a gas chromatograph (Agilent 7820A) equipped with a HP-5 column (Agilent, 30 m × 0.320 mm, 0.25 micron) and a flame ionization detector (FID).

## **Results and discussion**

### ***Characterization of zeolite catalysts***

Figure 1 showed the high angle XRD patterns of the resultant Beta zeolites. All the samples exhibited the characteristic peaks of \*BEA-type zeolite (the black columnar at the bottom of the figure was standard XRD pattern),<sup>28-30</sup> indicating that Beta zeolite crystal structure was still maintained after the desilication and secondary-crystallization treatment. However, the intensity of diffraction peaks for Beta-0.1, Beta-0.2, Beta-0.3 and Beta-0.4 were obviously lower than Beta-S, which demonstrated that the framework of Beta zeolite could be destroyed on a certain degree during the alkaline treatment process.<sup>22,31</sup>

N<sub>2</sub> adsorption-desorption isotherms were carried out to investigate the porosity of the obtained Beta zeolites. As shown in Figure 2, all the zeolite samples showed a steep uptake in the low relative pressure region ( $P/P_0 < 0.01$ ), which revealed that the intrinsic micropore



was filled with nitrogen.<sup>32,33</sup> Furthermore, it could be clearly seen that Beta-0.1, Beta-0.2, Beta-0.3 and Beta-0.4 exhibited a type-IV N<sub>2</sub> isotherms with a hysteresis loop compared with Beta-S, demonstrating that the mesopores were successfully introduced into the framework of alkaline treated zeolites by organic base desilication and secondary-crystallization process.<sup>34-36</sup> However, the Beta-0.1 and Beta-0.2 exhibited a type H2 hysteresis loop, which can be attributed to a condensation and evaporation processes occurring in pores with narrow necks and wide bodies (often referred to as 'ink bottle' pores), while the Beta-0.3 and Beta-0.4 showed a type H3 hysteresis loop that was reasonably assigned to the slit-shaped pore.

The textual properties of the resultant Beta zeolites were listed in Table 1. Obviously, the total BET surface ( $S_{BET}$ ), external surface area ( $S_{ext}$ ) and total volume ( $V_{tol}$ ) of resultant zeolites gradually increased in the order of Beta-0.1 < Beta-0.2 < Beta-0.3 < Beta-0.4, respectively, which was significantly higher than Beta-S, and the  $V_{tol}$  of Beta-0.4 was more than twice as much as Beta-S. Furthermore, it was worth noting that the mesoporous volume ( $V_{meso}$ ) and  $V_{meso}/V_{tol}$  for Beta-0.1, Beta-0.2, Beta-0.3 and Beta-0.4 were also conspicuously improved at the same time. These results confirmed that the additional mesopores were successfully introduced into the framework of Beta zeolites, and the mesopore degree in the matrix of Beta zeolites can be modulated by tuning the TEAOH concentration during the desilication and secondary-crystallization process.

The morphology and frameworks of the synthesized zeolites were investigated by Scanning electron microscopy (SEM) and Transmission electron microscopy (TEM), respectively. The typical SEM images of Beta-S, Beta-0.1, Beta-0.2, Beta-0.3 and Beta-

0.4 were shown in Figure 3. It was observed that all the Beta zeolites exhibited a sugar-like quadrilateral shape with uniform sizes. Clearly, Beta-S (Figure 3a) exhibited a smoother and flatter surface compared with the other, while the modified catalysts Beta-0.1, Beta-0.2, Beta-0.3 and Beta-0.4 (Figure 3b-e) showed a more rough surface, which was closely related to the concentration of TEAOH during the desilication and secondary-crystallization process, it's known that TEAOH could not only act as an organic base to etch and dissolve the silicon species in the zeolite lattice, but also serve as template to guide the crystallization of Beta zeolite under the suitable crystallization conditions.

TEM imaging was carried out to study the structure of zeolite frameworks, with different samples analyzed in Figure 4. Beta-S had a dense framework (Figure 4a), while the modified samples (Beta-0.1, Beta-0.2, Beta-0.3, and Beta-0.4) had an unconsolidated structure (Figure 4b-e). The quantity of voided nanodomains increased with the concentration of TEAOH, indicating that more mesopores or cavities were created in the interior of the zeolite framework with a higher amount of organic base. Scheme 1 listed the regulatory process for the mesopore Beta zeolites with various concentrations of TEAOH. These results were in agreement with the textural properties analysis in Table 1, which confirmed that the present desilication and secondary-crystallization treatment was an excellent method to introduce intra-mesopores in Beta zeolites. We conducted further investigations to examine the zeolite structures of the samples using our low-dose HRTEM method. Our HRTEM images in Figures 5 were acquired at a very low dose of electrons ( $\sim 10 \text{ e}^- \text{ \AA}^{-2}$ ), and corrected for the contrast transfer function (CTF) of the objective lens to enhance interpretability. Firstly, we aimed to investigate the zeolite structure using HRTEM

to assess the achievable image resolution and the safety of our low-dose imaging conditions in preserving the original crystal structure. Figure 5a presented a typical HRTEM image of Beta-0.4, which was acquired along the  $\langle 001 \rangle$  zone axis. The inset of Figure 5a displayed a fast Fourier transform (FFT) of this image, revealing information transfer as high as 1.3 Å. This high-resolution attested to the intact structure of mesopore walls towards typical Beta-0.4 under our imaging conditions, suggesting that substantial structural details can be extracted from the image. The enlarged image contrast in Figure 5b clearly identified the main structural features, which matched perfectly with the projected structural model and the simulated electrostatic potential map (Figure 5c-d). The pore structure was further characterized by integrated differential phase-contrast scanning transmission electron microscopy (iDPC-STEM) in Figure 6. The Fourier transform of the corresponding electron microscope images reached a resolution of 1.77 Å, which satisfied the observation of the pore structure of Beta-0.4 zeolite. The connectivity of the inner wall of some pore channels of zeolite arising from the desilication process was shown in the enlarged image in the red box in Figure 6c, where the area marked by the blue circle had two or even three channels connected, and the color pore distribution map clearly exhibited these results. The mesopores located in the interior of zeolites were produced through destroying the zeolitic framework with desilication, which was confirmed by the structural model of the zeolite in the  $\langle 011 \rangle$  direction shown in Figure 6d.

Based on the aforementioned analyses, the proposed formation mechanism of mesoporous Beta zeolites by the desilication and secondary-crystallization strategy was presented in Scheme 2. It was observed from Scheme 2 that the desilication and secondary-

crystallization strategy was like the tunnel boring machine, the TEOH played two roles simultaneously. On the one hand,  $\text{OH}^-$  species could attack the framework of pure-silica Beta zeolite, which led to the depolymerization of  $\equiv \text{Si} - \text{O} - \text{Si} \equiv$  through the  $\equiv \text{Si} - \text{O} - \text{Si} \equiv + \text{OH}^- \rightleftharpoons \equiv \text{Si} - \text{OH} + \equiv \text{Si} - \text{O}^-$  mechanism,<sup>37</sup> and the silicate oligomers were extracted from the interior of Beta zeolites, resulting in the formation of defects located in the interior of zeolites, which was similar to the role of drill in the tunnel boring machine. On the other hand, the  $\text{TEA}^+$  were inclined to adsorb on the surface of Beta zeolites with  $\equiv \text{Si} - \text{O}^-$  species through the electrostatic interactions, inhibiting the attack by  $\text{OH}^-$ , and the continued secondary-crystallization was finished *via* extracted silicate oligomers and additional aluminum species combined with  $\text{TEA}^+$ , which ensured the mesopore walls were zeolitic crystalline framework rather than amorphous structure, leading to enhanced acidity and superior stability, which was similar to the role of segment erector in the tunnel boring machine.

### ***Acidity of Beta zeolites***

To further investigate the acidity of resultant Beta zeolites, fourier transform infrared (FT-IR) spectroscopy was carried out with pyridine (Py) and 2,6-ditert-butylpyridine (DTBPy) as probe molecules. It was worth noting that the IR spectra of pyridine adsorption was used to detect the total acidity (including Brønsted acid and Lewis acid) since the probe molecule pyridine (a kinetic diameter around 0.5 nm)<sup>38</sup> could enter the interior channel of Beta zeolite.<sup>39</sup> Figure 7a exhibited the IR spectra of adsorbed pyridine over the synthesized Beta zeolites, where the peaks at around  $1455 \text{ cm}^{-1}$  and  $1545 \text{ cm}^{-1}$  were generally assigned to Lewis acid sites and Brønsted acid sites, respectively.<sup>40,41</sup> The quantified results of Beta

zeolites were summarized in Table S1, it was noted obviously from Table S1 that Beta-S didn't show any Brønsted acid sites, however, after the desilication and secondary-crystallization process, the obtained Beta-0.1 to Beta-0.2, Beta-0.3 and Beta-0.4 exhibited different concentration of Brønsted acid sites and Lewis acid sites, and the content of Brønsted acid sites in these hierarchical Beta zeolites gradually increased with the increasing amount of TEAOH during the modified treatment.

Moreover, the IR spectra of DTBPy adsorption was adopted to investigate the external Brønsted acid sites of Beta zeolites, DTBPy probe molecule could only detect the external Brønsted acid sites owing to the large size (a kinetic diameter around 0.8 nm)<sup>42</sup>. As shown in Figure 7b, all the samples exhibited a peak at about 1616 cm<sup>-1</sup> except Beta-S, which was the characteristic peak of external Brønsted acid sites.<sup>38</sup> Clearly, it was observed from Table S1 that the concentration of external Brønsted acid sites decreased in the order of Beta-0.4 > Beta-0.3 > Beta-0.2 > Beta-0.1, which showed the same trend as total Brønsted acid measured by pyridine infrared, demonstrating that the acidity of Beta zeolites could be systematically tailored by tuning the concentration of TEAOH in the desilication and secondary-crystallization process. In addition, the <sup>27</sup>Al MAS NMR spectra was further carried out to detect the coordination state of Al species in Beta zeolites. Figure 8 presented the <sup>27</sup>Al MAS NMR spectra of typical Beta-0.1 and Beta-0.4. It was noted that both the catalysts exhibited a single peak at ~1 ppm, which was assigned to the octahedral coordinated aluminum, corresponding to the non-framework aluminum species.<sup>43</sup> Besides, the signal at ~56 ppm was attributed to tetrahedral coordinated aluminum,<sup>44</sup> which was the source of Brønsted acid sites that the cations located on the bridging oxygen between Si

and Al in the zeolite lattice were replaced by H<sup>+</sup>.<sup>45</sup> Obviously, both the spectrum of Beta-0.1 and Beta-0.4 showed another broad peak at ~56 ppm, which was further deconvoluted into three resonance peaks at ~54 ppm, ~55 ppm and ~58 ppm, respectively, as shown in Figure S1. According to the previous research,<sup>43</sup> the peak at ~54 ppm was assigned to aluminum atoms on T1 and T2 position in a four-membered ring of Beta zeolite framework, where the peaks at ~55 and ~58 ppm were attributed to aluminum atoms on the positions T7 and T3, respectively. It was reported that the Al species located on the T5-T9 were easily transformed into Brønsted acid sites owing to the high substitution energy of proton H,<sup>46</sup> however, most of Al in the Beta-0.1 and Beta-0.4 located in the T1-T3, because the secondary-crystallization process and Na<sup>+</sup> free system can definitely influence the distribution of Al species in the framework of Beta zeolites. Nevertheless, the Beta-0.4 exhibited a larger fraction of T7 compared with Beta-0.1 (31.2 % vs 21.9 %), indicating that excessive TEA<sup>+</sup> was beneficial for the formation of Brønsted acid sites due to its structure directing ability.

### ***Catalytic performance***

The catalytic performances of resultant Beta zeolites were evaluated by liquid alkylation between benzene and 1-dodecene under the accelerated deactivation reaction condition (low molar ratio of benzene with 1-dodecene, high WHSV), and the reaction was carried out in a fixed-bed reactor, as shown in Figure 9. The conversion of 1-dodecene and selectivity of 2-LAB as a function of time on stream over resultant Beta zeolite catalysts was presented in Figure 10. It was observed from Figure 10 that all the Beta zeolites exhibited a superior selectivity of 2-LAB, which was generally more than 88 % since the

topological structure of Beta zeolite was suitable for the formation of 2-LAB according to previous research.<sup>15</sup>

Nevertheless, the activity and stability of these Beta zeolites were quite difference, the Beta-0.1 and Beta-0.2 showed a similarly short lifetime with a low conversion of 1-dodecene (< 10%), and the activity of Beta-0.1 and Beta-0.2 was dropped below 5 % (under the yellow dotted line) at only 3 h and completely lost activity after 5 h. On the one hand, the low activity was attributed to their poor Brønsted acid sites (Table S1), because the Brønsted acid dominated the activity in present research (Figure S2 and Figure S3), in which the typical H-form Beta-0.1 and Beta-0.4 were ion exchanged with Na<sup>+</sup> to shield the Brønsted acid sites while maintain the Lewis acid sites, it was observed from Figure S2 that both Na-Beta-0.1 and Na-Beta-0.4 catalysts showed ignorable absorption peaks at ~1545 cm<sup>-1</sup>, indicating that the content of Brønsted acid sites were negligible. However, an obvious characteristic absorption peak at ~1455 cm<sup>-1</sup> was still observed, demonstrating the existence of Lewis acids in these catalysts. The catalytic performance of Na-Beta-0.1 and Na-Beta-0.4 in alkylation between benzene with 1-dodecene were shown in Figure S3. It was found that both Na-Beta-0.1 and Na-Beta-0.4 showed negligible activity (< 3 %) in 8 h. These experimental results verified that the Lewis acid sites in Beta zeolite contributed ignorable activity in alkylation of benzene and 1-dodecene, while the Brønsted acid sites were the main active sites, and the interior and external Brønsted acid sites of Beta zeolites were responsible for the activity in the alkylation between benzene with 1-dodecene (Figure S4 and S5). On the other hand, the repaid deactivation of Beta-0.1 and Beta-0.2 could be reasonably attributed to their constrained porosity as aforementioned results (Table 1).

Conversely, Beta-0.3 and Beta-0.4 showed superior activity with a high conversion and their stability was significantly improved. Moreover, the activity of Beta-0.4 was prolonged to ~ 30 h with a stable conversion (> 8 %), exhibiting the best durability and stability among these zeolites, it was reasonably attributed to the opened porosity and higher concentration of exposed Brønsted acid sites for Beta-0.4, which can effectively improve the activity of Beta zeolites and enhance the transport properties of guest molecules, resulting in high conversion of 1-dodecene and long lifetime. In addition, these resultant Beta zeolites exhibited comparable selectivity of 2-LAB due to the extraordinary shape-selectivity of Beta zeolitic topology<sup>47</sup>. Moreover, the diffusion properties of the typical Beta-0.1 and Beta-0.4 were further investigated by adsorption kinetic experiment, it was showed that the effective diffusional time constants ( $D_{eff}/h^2$ ) determined from adsorption kinetics curves (Figure S6) for Beta-0.1 and Beta-0.4 was  $7.52 \times 10^{-5}$  and  $2.21 \times 10^{-4} \text{ s}^{-1}$  (Table S2), respectively, indicating that the diffusion process in Beta zeolites was dominated by intracrystalline diffusion<sup>48</sup>. Notably, the corresponding effective diffusion coefficient ( $D_{eff}$ ) of Beta-0.4 was up to  $4.48 \times 10^{-17} \text{ m}^2 \text{ s}^{-1}$  (Table S2), which was 2.7 times higher than Beta-0.1 ( $1.66 \times 10^{-17} \text{ m}^2 \text{ s}^{-1}$ ), suggesting that Beta-0.4 possessed a superior diffusion property compared with Beta-0.1. Therefore, the Beta-0.4 exhibited prolonged lifetime than Beta-0.1.

To further evaluate the utilization degree of resultant Beta zeolites, Thiele modulus and the effectiveness factor of typical Beta-0.1 and Beta-0.4 in the alkylation between benzene with 1-dodecene were calculated, and the corresponding data was shown in Figure 11. Obviously, both the effectiveness factor ( $\eta$ ) of Beta-0.1 and Beta-0.4 was close to 1, but



Beta-0.4 exhibited a high degree of utilization compared with Beta-0.1 due to the highly opened mesoporous.

To further investigate the deactivation behavior of spent catalysts, the spent Beta zeolites after reaction were denoted as Beta- $x$ -S ( $x = 0.1, 0.2, 0.3$  and  $0.4$ , respectively). Figure 12 showed the pyridine infrared spectra of calcined Beta- $x$ -S zeolites, and the corresponding quantified acidity of zeolites was summarized in Table S3. It was observed that the concentration of Brønsted acid sites for spent Beta-0.1-S, Beta-0.2-S, Beta-0.3-S and Beta-0.4-S was dropped by 70.6 %, 66.9 %, 45.3 % and 44.6% compared with their individual fresh samples, respectively. Besides, the N<sub>2</sub> adsorption-desorption isotherms of Beta- $x$ -S zeolites were also presented in Figure S7. Obviously, the adsorption capacity of these catalysts was found to decrease on a certain degree, especially, Beta-0.1-S and Beta-0.2-S showed a significant decrease. Table S4 listed the textural properties of the spent zeolite samples, it was observed that the value of  $S_{BET}$ ,  $S_{ext}$ ,  $V_{tot}$  and  $V_{meso}$  of spent samples gradually increased in the order of Beta-0.1-S < Beta-0.2-S < Beta-0.3-S < Beta-0.4-S, which exhibited the similar trend with previous fresh samples (Table 1). However, it was found that there was a sharp decline in the value of  $S_{BET}$  and  $S_{ext}$  for Beta-0.1-S (dropped by ~56.6 % in  $S_{BET}$  and ~60.0 % in  $S_{ext}$ ) and Beta-0.2-S (dropped by ~41.5 % in  $S_{BET}$  and ~42.2 % in  $S_{ext}$ ), while Beta-0.3-S (dropped by ~18.3 % in  $S_{BET}$  and ~2.6 % in  $S_{ext}$ ) and Beta-0.4-S (dropped by ~14.2 % in  $S_{BET}$  and ~5.8 % in  $S_{ext}$ ) presented a slight decrease. These results indicated that the channels of the Beta-0.1 and Beta-0.2 were more easily blocked owing to the inferior diffusion properties, resulting in the shortened lifetime compared with Beta-0.3 and Beta-0.4 (Figure 10).

The XRD patterns of Beta-*x*-S zeolites were shown in Figure S8. It was observed that the spent Beta zeolites still maintained \*BEA-topology after accelerated deactivation reaction, but the crystallinity of individual spent zeolites was significantly decreased compared with fresh sample, indicating that the structure of Beta zeolites was destroyed on a certain degree. It was found that the relative crystallinity of Beta-0.1-S, Beta-0.2-S, Beta-0.3-S and Beta-0.4-S was dropped by 68.8 %, 78.1 %, 57.1 % and 46.6 %, respectively, suggesting that Beta-0.3 and Beta-0.4 showed the robust stability even though they were fed in the reaction for more than five times as long as Beta-0.1 and Beta-0.2, which was attributed to the fact that additional TEA<sup>+</sup> can effectively guide the crystallization during the hydrothermal treatment and improve the structure stability of mesopore zeolites.

Furthermore, a part of the uncalcined Beta-*x*-S samples was taken for thermogravimetric (TG) analysis to further study the cokes formed in zeolites, and the weight loss curve was showed in Figure S9. It could be seen from Figure S9 that the soft coke content of Beta-0.3-S and Beta-0.4-S was about 1.5 times higher than Beta-0.1-S and Beta-0.2-S, and the hard coke content of Beta-0.3-S and Beta-0.4-S was about 2.5 times higher than Beta-0.1-S and Beta-0.2-S, which was attributed to the more opened porosity of Beta-0.3 and Beta-0.4 that was beneficial for accumulation of organic species during the reaction. Assuming that the total coke was the sum of the soft coke and hard coke in the thermogravimetric diagram, the proportion of hard coke for Beta-0.1-S, Beta-0.2-S, Beta-0.3-S and Beta-0.4-S was 34.5 %, 33.8 %, 41.7 % and 49.4 %, respectively, indicating that the main coke in resultant mesopore Beta zeolites was soft coke, and Beta-0.3-S and Beta-0.4-S possessed more hard coke than Beta-0.1-S and Beta-0.2-S simply because Beta-0.3-

S and Beta-0.4-S have rich voids and long feeding time.

To further investigate the composition of soft cokes occluded in zeolites during the alkylation, the typically deactivated Beta-0.4-S was treated with 40 % hydrofluoric acid solution to liberate the inner cokes. The soluble coke in the spent zeolite was extracted with methylene chloride and analyzed by GC-MS, as shown in Figure 13. It was observed that the deposited compounds were very complex, such as reactants, linear alkylbenzene, cracking products of 1-dodecene, olefins oligomer, isomers and over alkylated bulk molecules, indicating that 1-dodecene underwent a series of complex processes and linear alkylbenzene could be further transformed into the bulk polyalkylbenzenes. These soft coke species gradually accumulated in the channels of zeolites, which eventually became the hard coke and blocked the pores of zeolites, resulting in the deactivation of catalysts.

Based on the above analysis, it was reasonably proved that the deactivation of catalysts in the alkylation between benzene with 1-dodecene was attributed to the structural collapse and accumulated coke, and the degree of mesoporous for hierarchical Beta zeolites should be delicately optimized in order to maintain the stability of zeolite framework and enhance the transportability of guest molecules simultaneously. In addition, the Beta-0.4 also exhibited excellent regenerability compared with Beta-0.1 (Figure S10) since Beta-0.4 had optimized mesoporous that can balance the requirements of structure stability and diffusion reinforcement, which pave the way for the practical application of zeolites in the production of linear alkylbenzene.

### **Data Availability and Reproducibility Statement**

The numerical data from Figures 1, 2, 7, 8, 10, 11 and 12 are available as a .zip file in the Supplementary

Material, this .zip file includes a compilation of input files that are described in Figures 1, 2, 7, 8, 10, 11 and 12.

## **Conclusions**

In summary, a series of mesopore Beta zeolites were fabricated by a desilication and secondary-crystallization strategy, and the degree of mesoporous for the resultant Beta zeolites could be systematically modulated by tuning the concentration of TEOH in the desilication and secondary-crystallization process. The obtained mesoporous Beta zeolites greatly enhanced catalytic activity and exhibited excellent stability toward alkylation between benzene with 1-dodecene by improving diffusion properties. In addition, our research based on the investigation of deactivation process revealed that the mesopores of Beta zeolites can be optimized by simply tuning the concentration of organic base to balance the requirements of structure stability and diffusion intensification, and the resultant mesoporous Beta zeolites also presented robust regeneration performances, which promoted the industrial application of Beta zeolites in the production of linear alkylbenzene.

## **Associated content**

### **Supporting Information**

Experimental contents for synthesis and characterization of Beta zeolites; details for acid sites passivation experiment and the study of catalytic and diffusion performance of Beta zeolites; additional XRD, FTIR, N<sub>2</sub> isotherm, TG, <sup>27</sup>Al MAS NMR and Acidity analysis.

### **Declaration of Competing Interest**

The authors declare no competing financial interest.

### **Acknowledgment**

This work was supported by the National Natural Science Foundation of China (No. 21978055, 22278090, 22075250 and 22122505) and National Key Research and Development Program of China (No. 2022YFE0113800), Natural Science Foundation of Guangdong Province, China (No. 2022A1515012088), the Science and Technology Planning Project of Guangdong Province, China (No. 2022A0505050073 and 2022A0505030013), “High-level Talents Program” of Pearl River, China (No. 2017GC010080).

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## Figure and Table Captions

**Figure 1.** XRD patterns of resultant Beta zeolites.

**Figure 2.** N<sub>2</sub> adsorption-desorption isotherms of obtained Beta zeolites.

**Figure 3.** SEM images of (a) Beta-S, (b) Beta-0.1, (c) Beta-0.2, (d) Beta-0.3 and (e) Beta-0.4, respectively.

**Figure 4.** TEM images of (a) Beta-S, (b) Beta-0.1, (c) Beta-0.2, (d) Beta-0.3 and (e) Beta-0.4, respectively.

**Figure 5.** Real space high resolution structural visualization of typical Beta-0.4 zeolite, (a) cryogenic low-dose denoised HRTEM images of zeolite taken along the [001] directions. Insets show raw images (upper left) and the FFT patterns (upper right), (b) the enlarged images after correcting the contrast inversion effects due to the objective lens CTF for zeolite, (c) simulated projected electrostatic potential maps with point-spread-function (PSF) widths of 2.0 Å, (d) the corresponding projected crystal structural models embedded.

**Figure 6.** (a) iDPC-STEM image of the typical Beta-0.4 zeolite, (b) fourier transform corresponding to (a) with a resolution of 1.77 Å, (c) the enlarged image in the red box in Figure a (top) and the corresponding color-drawn channel distribution map (bottom). The blue circle mark is the area where there is channel connectivity, (d) the <011> crystal orientation projection structure of zeolite, (e) the simulated iDPC-STEM image, the parameter settings are consistent with the actual experimental parameter settings, (f) the magnified image in the purple box in Figure c, can clearly distinguish the independent zeolite channels.

**Figure 7.** FTIR spectra of pyridine (a) and 2,6-di-tert-butyl pyridine (b) adsorption over resultant Beta zeolites.



**Figure 8.**  $^{27}\text{Al}$  MAS NMR spectra of Beta-0.1 and Beta-0.4 catalysts.

**Figure 9.** Schematic of the fixed bed used for alkylation of benzene with 1-dodecene.

**Figure 10.** Catalytic performance of resultant Beta zeolites in alkylation of benzene with 1-dodecene.

Reaction conditions: molar ratio of benzene/1-dodecene = 8.75,  $T = 80\text{ }^{\circ}\text{C}$ , atmospheric pressure,  $\text{WHSV} = 42.2\text{ h}^{-1}$ .

**Figure 11.** Effectiveness factor as a function of Thiele modulus for different Beta zeolites.

**Figure 12.** FTIR spectra of pyridine adsorption of calcined Beta-x-S zeolites.

**Figure 13.** GC–MS analysis of the soluble coke on spent of Beta-0.4-S.

**Scheme 1.** Proposed regulatory process of mesoporous Beta zeolites via organic base desilication and secondary-crystallization strategy.

**Scheme 2.** Proposed formation mechanism of mesoporous Beta zeolites via organic base desilication and secondary-crystallization method.

**Table 1.** Textural property of the resultant Beta zeolites.