

# Multiscale defect distribution in Beta zeolite unravelled by the combination of high-resolution electron microscopy and stepwise etching

Guodong Xie<sup>1,§</sup>, Xianchen Gong<sup>2,§</sup>, Lijie Chen<sup>1</sup>, Zhipeng Li<sup>1</sup>, Ye Ma<sup>1</sup>, Shitao Wu<sup>1</sup>, Hao Song<sup>1</sup>, Yuhang Li<sup>1</sup>, Guanqun Zhang<sup>1</sup>✉, Yaqi Fan<sup>1</sup>✉, Peng Wu<sup>2,3</sup>✉, and Yanhang Ma<sup>1</sup>✉

<sup>1</sup>Shanghai Key Laboratory of High-resolution Electron Microscopy & State Key Laboratory of Quantum Functional Materials, School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China

<sup>2</sup>State Key Laboratory of Petroleum Molecular & Process Engineering, Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200062, China

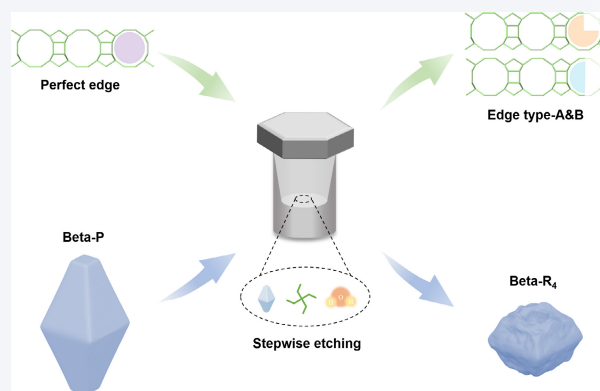
<sup>3</sup>Institute of Eco-Chongming, Shanghai 202162, China

<sup>§</sup>Guodong Xie and Xianchen Gong contributed equally to this work.

 Cite this article: Nano Research, 2026, 19, 94909006. <https://doi.org/10.26599/NR.2026.94909006>

**ABSTRACT:** Zeolites are crystalline microporous materials widely used in industrial applications, and their catalytic and adsorption performances are profoundly influenced by intrinsic defects. However, characterizing the multiscale distribution of such defects remains a major challenge, especially in zeolites with complex stacking faults such as Beta zeolite. Herein, we develop a strategy that integrates high-resolution transmission electron microscope (HRTEM) imaging with controlled stepwise etching to probe the defects distribution in Beta zeolite across multiple length scales. Experimental results suggest that the defective domains in individual Beta zeolite crystals are heterogeneously distributed and preferentially aligned along the *c* axis. HRTEM imaging further reveals a preferential localization of defects at specific T sites within zeolite framework. Moreover, the etching process simultaneously generates a hierarchical Beta zeolite, whose titanosilicate analogue exhibits superior catalytic performance in cyclohexene epoxidation reaction. This work provides new insights into recognizing the multiscale defects distribution in zeolites, which establishes a direct link between the defect engineering and enhanced catalytic performance.

**KEYWORDS:** Beta zeolite, high-resolution imaging, post synthesis method, multiscale structure analysis, defect distribution



## 1 Introduction

Zeolites are crystalline microporous materials formed by tetrahedrally connected T atoms [1–4]. Owing to their unique micropores, high surface area, and outstanding thermal stability, zeolites have been widely used in petrochemical industry as heterogeneous catalysts [5, 6], molecular sieves [7, 8], sorbents [9, 10], and ion exchangers [11, 12]. In practical synthesis, the

idealized perfect zeolite framework is usually disrupted, leading to the formation of local structural defects such as silanols [13], vacancies [14], and framework distortions [15]. These defects can significantly alter the properties of zeolites. In addition to modulating hydrophobicity/hydrophilicity and hydrothermal stability [16], defects also affect the diffusion properties [17] and accessibility of active sites in zeolites [18]. Moreover, they play functional roles in the catalytic application and post-synthetic modification. For example, silanols could improve the product selectivity by enriching reactant molecules [19], or extend the catalytic lifetime through stabilizing metal species [20] and promote desilication process to constructed hierarchical zeolite with enhanced diffusion ability [21, 22]. Likewise, oxygen vacancies are able to incorporate active heteroatoms or generate Lewis acid sites in zeolites to improve selectivity toward target products [23–26].

Received: April 21, 2026; Revised: June 16, 2026

Accepted: July 7, 2026

✉Address correspondence to Guanqun Zhang, [zhanguanqun880318@gmail.com](mailto:zhanguanqun880318@gmail.com); Yaqi Fan, [fanyq@shanghaitech.edu.cn](mailto:fanyq@shanghaitech.edu.cn); Peng Wu, [pwu@chem.ecnu.edu.cn](mailto:pwu@chem.ecnu.edu.cn); Yanhang Ma, [mayh2@shanghaitech.edu.cn](mailto:mayh2@shanghaitech.edu.cn)

Several strategies encompassing both synthetic design and post-synthetic modification have been developed to tailor the defects and thereby fine-tune zeolite properties for specific applications. The incorporation of additional defects could be achieved by increasing the amount of organic structure directing agents (OSDAs) in starting gels or by introducing silylation reagents during synthesis [27]. The design of special OSDAs offers a pathway to control the spatial distribution of defects and generate ordered silanols within zeolite framework [28–30]. Meanwhile, post-synthetic methods such as acid treatment [31, 32], base leaching [33, 34], and steam processing are exploited to modulate the defects content in zeolite [35, 36]. Current defects analysis mainly relies on bulk characterization techniques, including powder X-ray diffraction (PXRD) [37], nuclear magnetic resonance (NMR) [38], Fourier-transform infrared (FTIR) spectroscopy [39], and ultraviolet–visible (UV–Vis) spectroscopy [40]. Atomic-scale structural elucidation is typically limited to zeolites with ordered silanol, which can be accessed through refinement of PXRD patterns [41] or three-dimensional electron diffraction (3D ED) data [42, 43]. Recently, integrated differential phase-contrast scanning transmission electron microscopy (iDPC-STEM) has resolved oxygen vacancies at the intergrown interfaces of MFI-type zeolite [26], and electron ptychography has demonstrated the ability to identify two oxygen vacancies in a specimen with a thickness of 4 nm [44]. Nevertheless, resolving defect distributions across multiple length scale within a single zeolite crystal remains challenging.

Beta zeolite is widely used in industrial production due to its unique 12-membered ring (12-MR) large pores and intersecting three-dimensional channel system [45–48]. Its catalytic and gas adsorption/separation performances are strongly influenced by the internal defects such as silanols [49, 50]. However, the existence of stacking faults in Beta zeolite complicated its framework structure determination, which took over two decades to accomplish [46–48, 51]. Although substantial efforts have been made to resolve the complex stacking faults, the distribution of defects in Beta zeolite across different length scales remains largely unexplored. Therefore, developing a method capable of probing defects distribution at both microstructure and single-crystal levels within individual Beta zeolite crystals is of importance.

Herein, we combine high-resolution transmission electron microscope (HRTEM) imaging with a controlled stepwise etching method to probe the distribution of defects in zeolite Beta. By tracking morphology evolution along different directions at different etching stages, it indicates that the defects are anisotropically distributed and preferentially aligned along the *c* axis within single Beta crystal. HRTEM imaging of crystal edges at different etching stages reveals that the well-defined 12-MR crystal edge progressively transformed into edges with two different structures, suggesting that the defects are probably preferentially localized at specific T-sites. Furthermore, stepwise etching constructs a hierarchical architecture. After converting the Beta zeolite into a titanosilicate analogue, the etched Beta zeolite exhibits superior catalytic activity in the epoxidation of cyclohexene.

## 2 Experimental

### 2.1 Synthesis of parent Beta zeolites (Beta-P)

Parent Beta zeolites were prepared from the synthesis solution with the molar composition of 0.4 tetraethylammonium hydroxide

(TEAOH):1.0 SiO<sub>2</sub>:0.01 Al<sub>2</sub>O<sub>3</sub>:15 H<sub>2</sub>O. In detail, TEOAH solution and tetraethyl orthosilicate (TEOS) were added to deionized water, then Al(OPri)<sub>3</sub> powder was added and stirred at room temperature for 90 min. Afterwards, the mixture was transferred to 60 °C water bath for evaporation of water and ethanol to reach the desired molar ratio. The final solution was then transferred to Teflon-lined stainless-steel autoclave and heated at 140 °C for 7 days. The products were recovered by centrifugation, washed, and dried at 80 °C overnight, then calcined at 550 °C for 5 h to remove the occluded TEA<sup>+</sup> cation (denoted as Beta-P).

### 2.2 Preparation of Beta-R<sub>n</sub> (*n* = 1, 2, 3, 4)

Beta-R<sub>n</sub> zeolite was obtained with stepwise etching. For Beta-R<sub>1</sub>, the Beta-P, TEOAH, and water were mixed in a molar ratio of 0.4 TEOAH:1 Beta-P:15 H<sub>2</sub>O, then the gel was sealed in an autoclave and heated at 140 °C for 3 h. The products were recovered by centrifugation, washed, and dried at 80 °C overnight, then calcined at 550 °C for 5 h (denoted as Beta-R<sub>1</sub>).

For Beta-R<sub>2</sub>, the Beta-R<sub>1</sub>, TEOAH and water were mixed in a molar ratio of 0.4 TEOAH:1 Beta-R<sub>1</sub>:15 H<sub>2</sub>O, then the gel was sealed in an autoclave and heated at 140 °C for 3 h. The products were recovered by centrifugation, washed, and dried at 80 °C overnight, then calcined at 550 °C for 5 h (denoted as Beta-R<sub>2</sub>).

For Beta-R<sub>3</sub>, the Beta-R<sub>2</sub>, TEOAH and water were mixed in a molar ratio of 0.4 TEOAH:1 Beta-R<sub>2</sub>:15 H<sub>2</sub>O, then the gel was sealed in an autoclave and heated at 140 °C for 3 h. The products were recovered by centrifugation, washed, and dried at 80 °C overnight, then calcined at 550 °C for 5 h (denoted as Beta-R<sub>3</sub>).

For Beta-R<sub>4</sub>, the Beta-R<sub>3</sub>, TEOAH, and water were mixed in a molar ratio of 0.4 TEOAH:1 Beta-R<sub>3</sub>:15 H<sub>2</sub>O, then the gel was sealed in an autoclave and heated at 140 °C for 3 h. The products were recovered by centrifugation, washed, and dried at 80 °C overnight, then calcined at 550 °C for 5 h (denoted as Beta-R<sub>4</sub>).

### 2.3 Preparation of Ti-Beta-P and Ti-Beta-R<sub>n</sub>

The Ti-containing Beta zeolite was prepared with a post-synthetic modification of aluminosilicate Beta zeolite according to the following procedure. Typically, Beta-P zeolite (Si/Al = 21) was dealuminated by treatment with 13 M HNO<sub>3</sub> at 413 K for 24 h. The solid product was collected by filtration, thoroughly washed, dried, and subsequently calcined at 823 K for 6 h. This dealumination and calcination process cycle was repeated twice to obtain the final sample, designated as DeAl-Beta-P (Si/Al > 1000). The DeAl-Beta-P zeolite was then added into H<sub>2</sub>TiF<sub>6</sub> aqueous solution to form a mixture with the composition of 1.0 SiO<sub>2</sub>:0.1 H<sub>2</sub>TiF<sub>6</sub>:66.7 H<sub>2</sub>O. The mixture was stirred at 308 K for 5 h, allowing Ti incorporation into the framework of Beta zeolite. After cooling, the sample, denoted as Ti-Beta-P, was recovered by filtration, washing, drying and air calcination at 823 K for 6 h. Ti-Beta-R<sub>n</sub> was prepared using a similar procedure, by using Beta-R<sub>n</sub> employed as the parent zeolite.

Details about the materials, characterization methods, statistical analysis methods, and catalytic performance were listed in the Electronic Supplementary Material (ESM).

## 3 Results and discussion

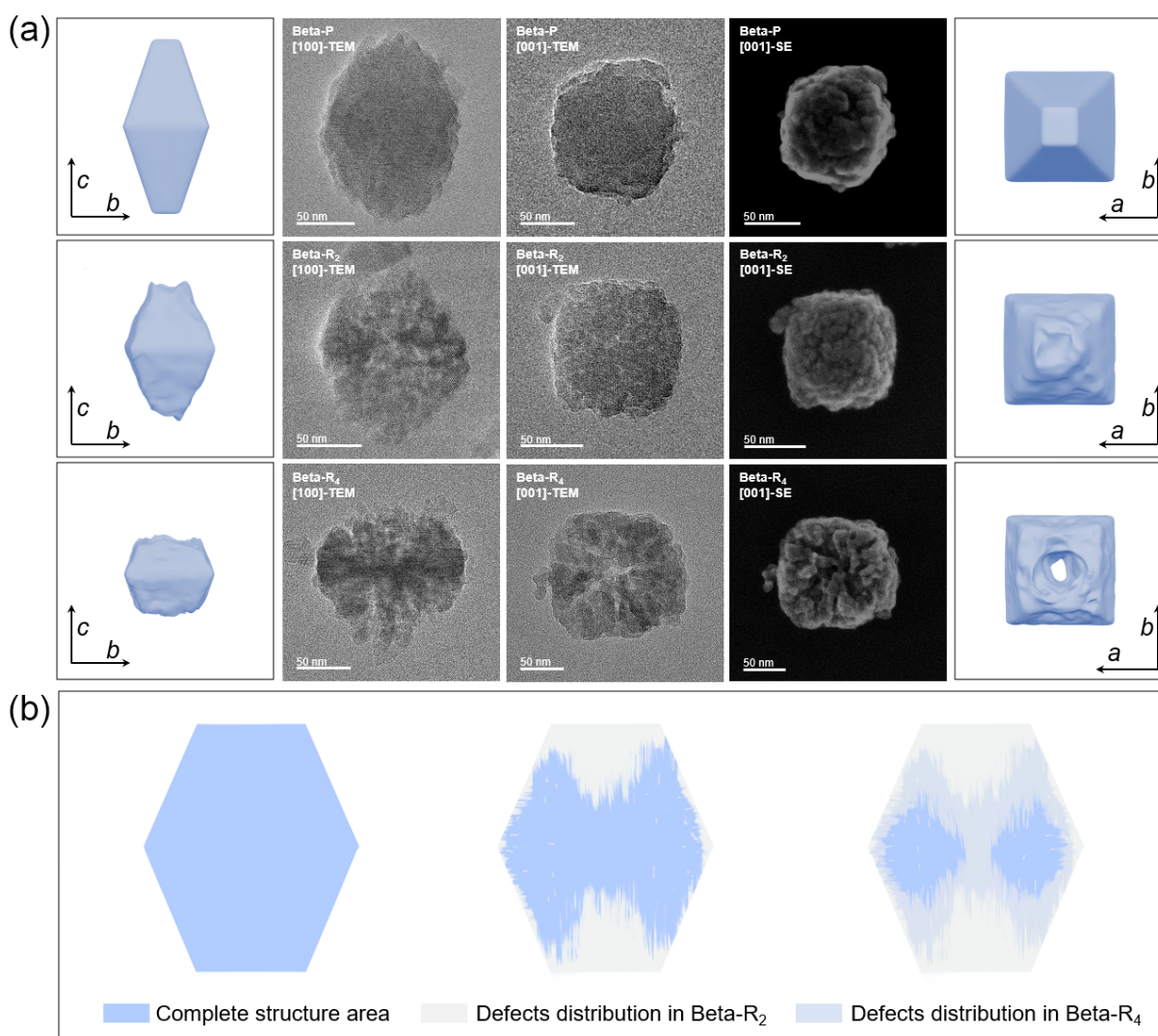
Beta-P was synthesized following a previous report with modifications [52], and its PXRD patterns confirmed high crystallinity (Fig. S1 in the ESM). Secondary electron (SE) and transmission electron microscope (TEM) images (Fig. S2 in the

ESM) showed that the Beta-P possessed a typical truncated bipyramidal morphology with a size of  $\sim 150$  nm. Thereafter, the stepwise etching process of Beta zeolite was carried out using TEOAH solution as the etching agent, and a series of products denoted as Beta- $R_n$  ( $n = 1-4$ ) were prepared (Figs. S3 and S4 in the ESM).

Systematic electron microscopic analysis was performed to track the structural evolution of individual Beta zeolite crystals (Fig. 1(a) and Fig. S5 in the ESM). TEM, STEM, and SE images of series were acquired along [100] and [001] directions to monitor the morphology changes of Beta zeolite during etching. Compared with Beta-P, Beta- $R_1$  retains the truncated bipyramidal morphology, while the smooth crystal surface became slightly rough with the emergence of small mesopores and voids inside the crystal (Figs. S4 and S5 in the ESM). In Beta- $R_2$ , dissolution begins at the two truncated ends while the overall bipyramidal morphology is largely preserved. The bright contrast observed in the TEM image along [100], indicates the generation of larger mesopores together with increased surface roughness. For Beta- $R_3$ , the continued dissolution of the two truncated ends led to a pronounced reduction in the

crystal dimension along [001] and the truncated bipyramidal morphology was nearly lost. The intracrystalline mesopores further enlarged and connected to the external surfaces, which could be observed based on the contrast difference in TEM image and surface details in SE image. For Beta- $R_4$ , the crystal size along [001] further decreased with the formation of mesopores that penetrate the entire crystal along the  $c$  axis. SE image showed that the surface became rougher with the further enlargement of intracrystalline mesopores. Schematic models were constructed to show the spatially oriented structural evolution of Beta zeolite samples. These observations indicated that the dissolution process was anisotropic in single Beta crystal, leading to a  $c$ -axis dependent degradation rather than random or spatially uniform etching. Moreover, the dissolution process generated a hierarchical architecture with abundant intracrystalline mesopores, which could efficiently improve molecular diffusion in Beta zeolite.

The powder Beta samples acquired at different etching stages were analyzed by multiple characterizations techniques. All Beta samples exhibited strong characteristic reflection peaks at  $7.89^\circ$  and  $22.60^\circ$  in PXRD patterns (Fig. 2(a)), indicating the \*BEA

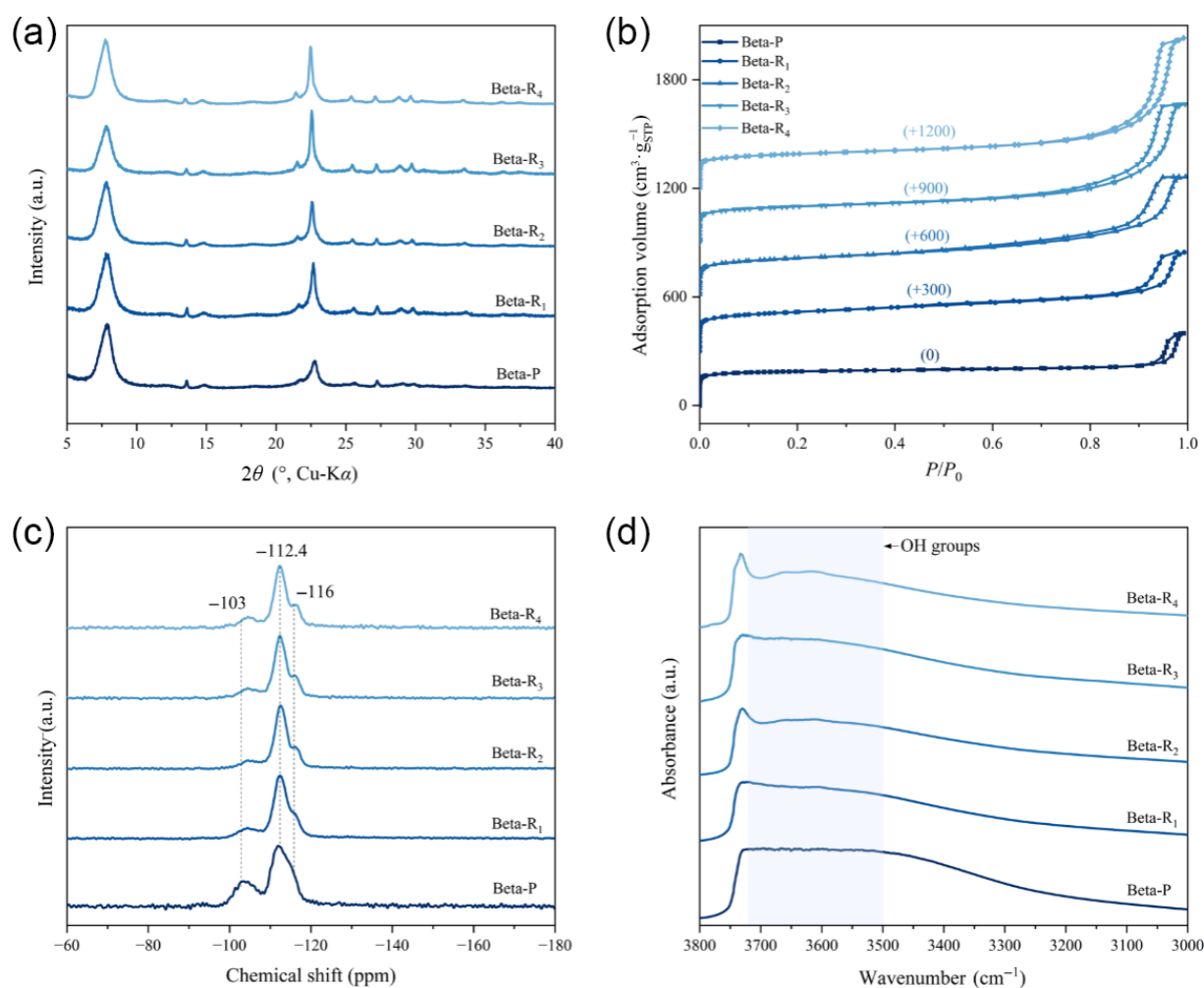


**Figure 1** (a) Schematic models of Beta-P, Beta- $R_2$ , Beta- $R_4$  (from top to bottom) along  $a$ -axis (first column from left) and  $c$ -axis (first column from right). TEM images of Beta-P, Beta- $R_2$ , Beta- $R_4$  single crystal along  $a$ -axis (second column from left). TEM images of Beta-P, Beta- $R_2$ , Beta- $R_4$  single crystal along  $c$ -axis (middle column). SE images of Beta-P, Beta- $R_2$ , Beta- $R_4$  single crystal along  $c$ -axis (second column from right). (b) Schematic diagrams of the defects distribution in crystals at different etching stages, Beta-P (left), Beta- $R_2$  (middle) and Beta- $R_4$  (right).

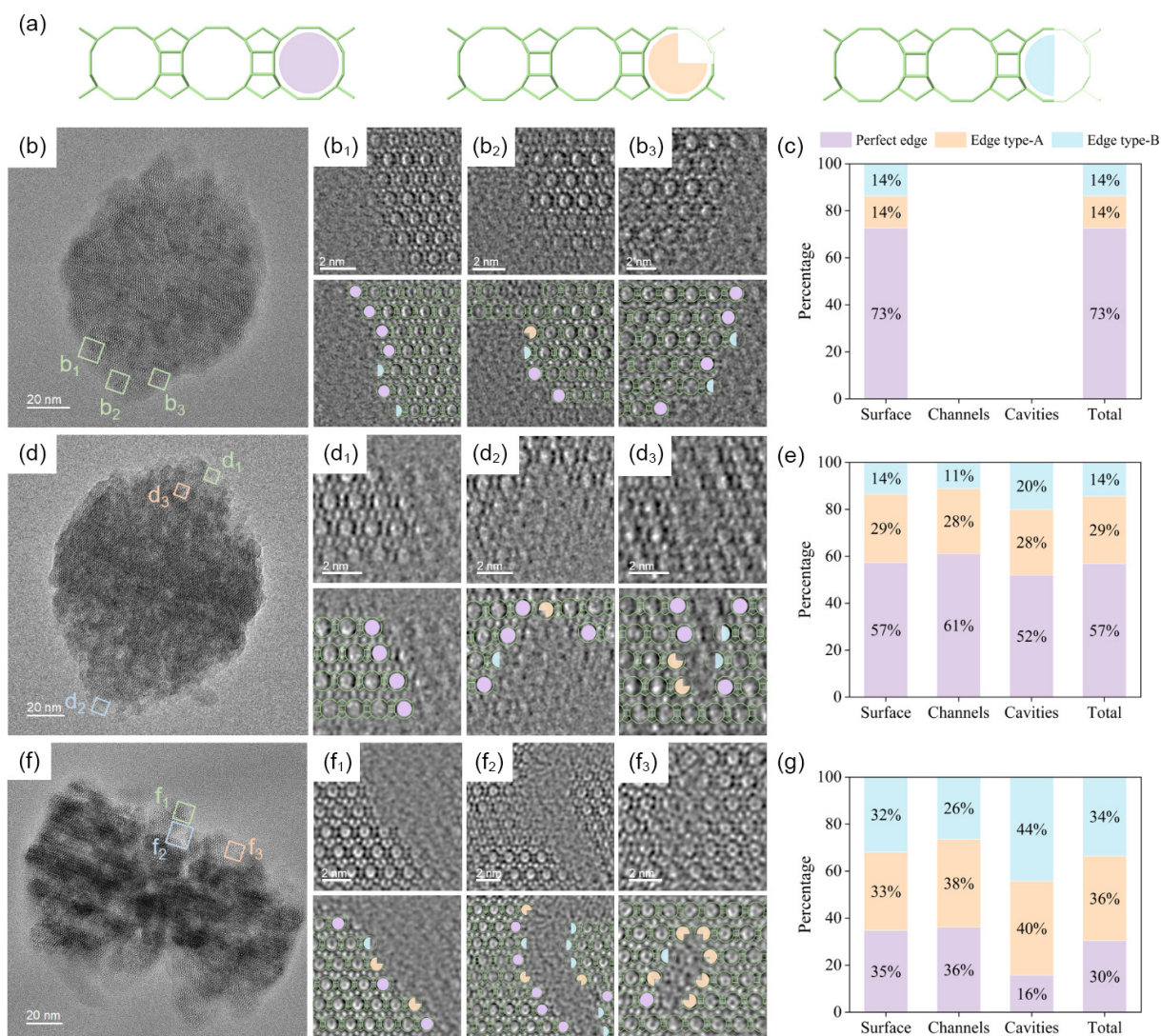
framework was well-maintained at each etching step. The relative intensity of peak at  $22.60^\circ$  gradually increased with the stepwise etching, suggesting there might be an enhancement of structural ordering or removal of disordered species.  $N_2$  sorption isotherms were demonstrated in Fig. 2(b). All samples showed type IV isotherms, where a pronounced enhancement in mesopore uptake ( $P/P_0 = 0.4\text{--}0.7$ ) could be observed with the hysteresis loop gradually enlarged upon the stepwise etching. The corresponding textural properties were summarized in Table S1 in the ESM. All Beta samples showed a well-preserved micropore volume of  $\sim 0.20\text{--}0.22\text{ cm}^3\text{g}^{-1}$ . Consistently, both mesopore volume ( $V_{\text{meso}}$ ) and total pore volume ( $V_{\text{total}}$ ) exhibited a progressive increase, with  $V_{\text{meso}}$  rising from  $0.39$  to  $1.09\text{ cm}^3\text{g}^{-1}$ , and  $V_{\text{total}}$  from  $0.61$  to  $1.28\text{ cm}^3\text{g}^{-1}$ . This continuous increase of the pore volume value directly corroborates the formation of intracrystalline mesopores observed in Fig. 1(a). The  $^{29}\text{Si}$  MAS NMR spectra of Beta zeolite samples showed signals at  $-103$ ,  $-112.4$ , and  $-116$  ppm (Fig. 2(c)). The signals at  $-112.4$  and  $-116$  ppm are attributed to framework  $\text{Si}(\text{OSi})_4$  species ( $Q^4$ ) at two different crystallographic sites, while the peak at  $-103$  ppm could be assigned to the framework  $\text{Si}(\text{OSi})_3(\text{OH})$  species ( $Q^3$ , SiOH groups) [53]. As the etching progressed, the peak intensity at  $-103$  ppm decreased indicating the reduction of SiOH defects in the Beta zeolites. Consistently, the FTIR spectra in the region of hydroxyl stretching (Fig. 2(d)) show that the bands at  $3500\text{--}3720\text{ cm}^{-1}$ , attributed to internal silanol

nest, are progressively weakened in the Beta- $R_n$  samples, further confirming the decline of SiOH-related defects [54]. Both the NMR and FTIR results demonstrate that the stepwise etching process gradually decreases the concentration of SiOH defects in Beta zeolite. Combined with the observations in Fig. 1(a) and the fact that etching preferentially removes low-crystalline (defect-rich) domains [55], these results further suggest that the dissolved regions possibly are defect-enriched domains, supporting that defects in Beta zeolite are distributed anisotropically, preferentially along the  $c$  axis and in the crystal interior, as schematically depicted in Fig. 1(b). In addition, ICP analysis shows a clear decrease in the Si/Al ratio during treatment (Table S1 in the ESM), indicating that the etching process was dominated by desilication.

HRTEM imaging was further applied to Beta single crystals at different etching stages to reveal the microstructural transformation process. HRTEM image of Beta-P along  $[100]$  revealed the characteristic 12-MR channels of the  $^*\text{BEA}$  topology (Fig. 3(b)). Examination of different regions in Figs. 3(b)<sub>1</sub>–3(b)<sub>3</sub> reveals three types of edges that can be classified according to the extent of edge truncation. As shown in Fig. 3(a), these correspond to perfect edges (purple), edges missing one-quarter of the 12-MR (orange), and edges missing one-half of the 12-MR framework (blue). As the stepwise etching generated mesoporous channels and intracrystalline cavities in Beta zeolites, structural analysis of Beta- $R_n$  samples was also conducted in these regions. For Beta- $R_2$  (Fig. 3(d)),



**Figure 2** (a) PXRD patterns, (b)  $N_2$  adsorption/desorption isotherms, (c)  $^{29}\text{Si}$  MAS NMR spectra, and (d) FTIR spectra of Beta-P and Beta- $R_n$  ( $n = 1, 2, 3, 4$ ).



**Figure 3** (a) Schematic diagrams of three different edge types in Beta zeolite, perfect edge (left), edge type-A (middle), and edge type-B (right). (b), (d), and (f) TEM images of Beta-P, Beta-R<sub>2</sub>, and Beta-R<sub>4</sub> single crystal. (b<sub>1</sub>)–(b<sub>3</sub>) HRTEM images of Beta-P acquired from the different external surface (green rectangle-marked) areas in (b) (top) and images overlaid with the different edge types (below). (d<sub>1</sub>) and (f<sub>1</sub>) HRTEM images of Beta-R<sub>2</sub> and Beta-R<sub>4</sub> acquired from the external surface (green rectangle-marked) areas in ((d) and (f)) (top) and images overlaid with the different edge types (below). (d<sub>2</sub>) and (f<sub>2</sub>) HRTEM images of Beta-R<sub>2</sub> and Beta-R<sub>4</sub> acquired from the mesoporous channels (blue rectangle-marked) areas in ((d) and (f)) (top) and images overlaid with the different edge types (below). (d<sub>3</sub>) and (f<sub>3</sub>) HRTEM images of Beta-R<sub>2</sub> and Beta-R<sub>4</sub> acquired from the intracrystalline cavities (orange rectangle-marked) areas in ((d) and (f)) (top) and images overlaid with the different edge types (below). (c), (e), and (g) Bar charts of the statistical results of the proportion of different structure states in different microenvironment regions.

HRTEM imaging analysis were focused on external surface (Fig. 3(d<sub>1</sub>)), mesoporous channels (Fig. 3(d<sub>2</sub>)), and intracrystalline cavities (Fig. 3(d<sub>3</sub>)). Structure model fitting results suggested that three different edges existed on the external surfaces, but also in the newly generated mesopores. A similar situation was also observed in Beta-R<sub>4</sub> sample (Fig. 3(f)), in which three different regions were analyzed and three edge states could be identified (Figs. 3(f<sub>1</sub>)–3(f<sub>3</sub>)).

To quantify the evolution of edge structures, we further conducted an edge structure classification and statistical analysis on other additional Beta-P and Beta-R<sub>n</sub> crystals in different regions (Figs. S6–S14 in the ESM). In Beta-P, perfect edges dominate (~73%), whereas edge type-A (~14%) and edge type-B (~14%) are present in similar proportions (Fig. 3(c)). When the stage came to Beta-R<sub>2</sub>, the distribution changes significantly: The proportion of perfect edge decreased to 57%, edge type-A increased to 29% and edge type-B remains unchanged (~14%) (Fig. 3(e)). In Beta-R<sub>4</sub>

samples, the proportions of perfect edge, edge type-A, and edge type-B are 30%, 36%, and 34%, respectively (Fig. 3(g)). Thus, the fraction of perfect edge steadily declined during stepwise etching, accompanied by an increase of defective edge structures. Moreover, the relative proportions of edge type-A and edge type-B followed a characteristic evolution, changing from an approximately equal ratio in Beta-P, to a nearly 2:1 ratio in Beta-R<sub>2</sub>, and then returning to near equality in Beta-R<sub>4</sub>. A similar trend was also observed at the external surface regions, where the ratio between edge type-A and edge type-B changes from 1:1 in Beta-P, to about 2:1 in Beta-R<sub>2</sub>, and back to nearly 1:1 in Beta-R<sub>4</sub>. In mesoporous channels and intracrystalline cavities regions, although no strict quantitative ratio is maintained, the relative abundances of edge type-A and edge type-B also vary systematically from Beta-R<sub>2</sub> to Beta-R<sub>4</sub> with the decrease of perfect edge. These results suggest that the evolution of defective edge states follows a region-dependent yet nonrandom pathway.

This consistent proportional evolution suggests local defects sites are preferentially located at specific T-sites (or site ensembles) rather than being randomly distributed within the framework (Fig. S15 in the ESM).

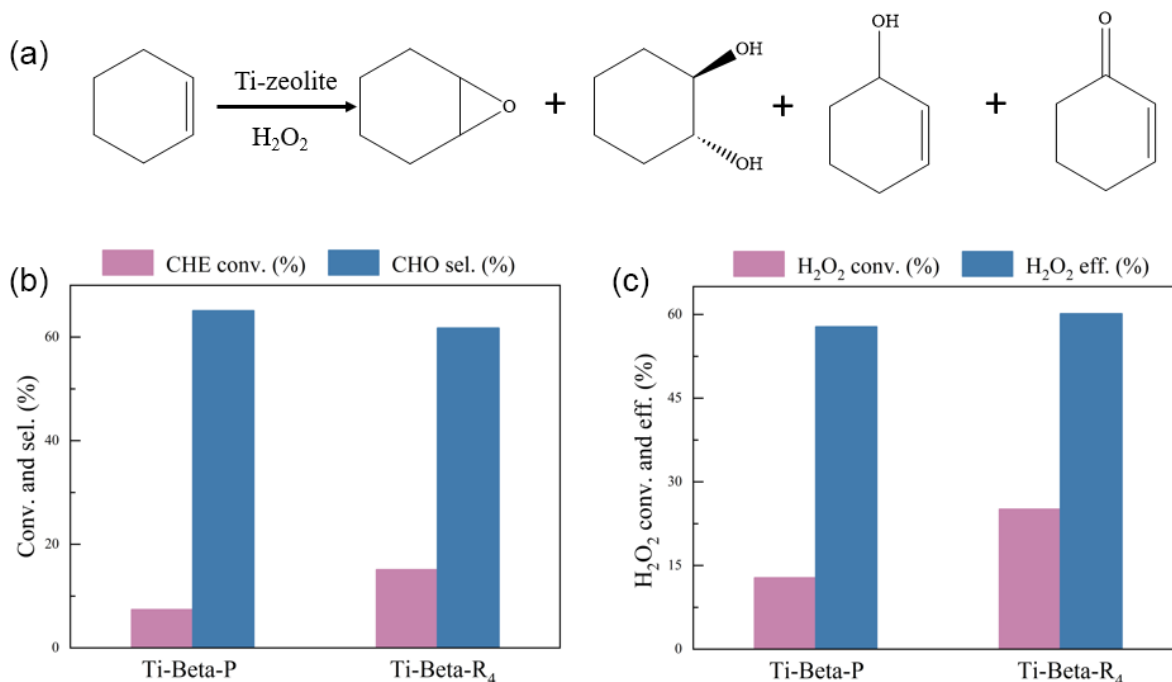
Furthermore, we also applied the stepwise etching method to demonstrate the universality on other Beta zeolites, such as commercial Beta (Beta-NKC) and template-free synthesized Beta (Beta-TPF) as well as mesoporous Beta (Beta-meso). TEM images (Figs. S16–S18 in the ESM) showed a similar structure evolution phenomenon with preferential etching along the central region of the *c*-axis. Moreover, HRTEM images and local structural analysis (Figs. S19 and S20 in the ESM) of commercial Beta zeolites at different etching stages also indicated the existence of three different edge states. The corresponding statistical results of edge type proportion (Fig. S21 in the ESM) suggested that the decreasing perfect edge and increasing type-A and B edges were present in commercial Beta zeolites as well.

Previous studies have proved that hierarchical zeolites could efficiently alleviate the diffusion limitations of microporous structure [56]. As the Beta- $R_4$  samples exhibited a hierarchical architecture with well-maintained microporous structure, it might serve as a promising catalyst with superior diffusion ability. Three-dimensional electron tomography was employed to verify the connectivity and accessibility of the mesopores. The reconstructed results (Video S1 and Fig. S22(a) in the ESM) and SE images (Figs. S22(b) and S22(c) in the ESM) further confirmed that, the abundant mesopores were connected to the external crystal surface, which could effectively enhance the diffusion ability. Thereafter, cyclohexene was selected as a probe molecule to evaluate the diffusion properties of Beta-P and Beta- $R_4$  zeolites. The  $q(t)/q(\infty)$  and  $t^{0.5}$  plots showed excellent linearity, with the slope of the curves representing the diffusion rate of zeolites. As summarized in Table S2 in the ESM, the diffusion rates increased from  $2.27 \times 10^{-5}$  for Beta-P to  $2.55 \times 10^{-5}$  for Beta- $R_4$ , corresponding to an enhancement of 12%. These results further demonstrate that stepwise etching

could introduce accessible mesopores into Beta zeolite while preserving its crystallinity, thereby effectively improving its diffusion for cyclohexene molecules.

Cyclohexene oxide (CHO) is an important oxygen-containing intermediate widely used in the production of surfactants, resins, adhesives, and other industrial products [57]. Epoxidation of cyclohexene using hydrogen peroxide ( $H_2O_2$ ) as the oxidant and titanasilicates as the catalyst offers a cost-effective and environmentally benign route, aligning with the principles of green and sustainable chemistry. However, the large molecular size of cyclohexene imposes diffusion limitations within the micropores, thereby restricting reaction activity. Therefore, Beta- $R_4$ , featuring a hierarchical architecture, is anticipated to exhibit superior performance in this reaction.

Ti-Beta zeolites were successfully prepared via a two-step post-synthesis strategy [58], which consists of dealumination in nitric acid solution and subsequent titanium incorporation with hexafluorotitanic acid solution. As shown in Figs. S23 and S24 in the ESM, Ti-Beta-P and Ti-Beta- $R_4$  samples retained the \*BEA type framework with good crystallinity as well as the crystal morphology after dealumination and titanium incorporation. The two samples show similar titanium contents (Table S3 in the ESM) and uniform titanium distribution (Fig. S25 in the ESM). Moreover, the signal at  $960\text{ cm}^{-1}$  in FTIR spectra and the signal at 210 nm in UV-Vis spectra confirmed the presence of tetracoordinated titanium species for both Ti-Beta-P and Ti-Beta- $R_4$ . No obvious evidence for extra-framework hexacoordinated titanium and anatase phases was observed due to the absence of signals at 260 and 330 nm in UV-Vis spectra (Fig. S26 in the ESM) [53]. As shown in Fig. 4(a), the main product of the cyclohexene epoxidation reaction is 1,2-epoxycyclohexane, with by-products including 1,2-cyclohexanediol, cyclohexanol, and cyclohexanone. Ti-Beta- $R_4$  exhibited significantly superior catalytic performance compared to Ti-Beta-P, with approximately twofold higher conversions of both cyclohexene and  $H_2O_2$ . Specifically, the cyclohexene conversion increased from 7.4%



**Figure 4** (a) Epoxidation reaction routes in Ti-zeolite, (b) cyclohexene conversion and cyclohexene oxide selectivity over Ti-Beta-P and Ti-Beta- $R_4$ , and (c)  $H_2O_2$  conversion and efficiency over Ti-Beta-P and Ti-Beta- $R_4$ .

to 15.1% and the  $\text{H}_2\text{O}_2$  conversion increased from 12.8% to 25.1% (Figs. 4(b) and 4(c) and Table S3 in the ESM). Considering that the two catalysts contain similar Ti contents and Ti coordination states, the enhancement of catalytic performance can be primarily attributed to the hierarchical structure of Ti-Beta- $\text{R}_4$ , which effectively mitigates diffusion limitations for the bulky cyclohexene molecule.

## 4 Conclusion

In summary, we have established a strategy that combines HRTEM imaging with stepwise etching to resolve the distribution of defects within individual Beta zeolite crystals across multiple length scales. Analysis at single-crystal level reveals an anisotropic defect distribution preferentially aligned along the  $c$  axis in the central region of the crystal. Microstructure analysis using HRTEM images identifies the progressive evolution of well-defined 12-MR crystal edges into two defective edges, suggesting a preferential defect localization at specific T-sites. Meanwhile, the Beta- $\text{R}_4$  zeolite produced via stepwise etching exhibited enhanced large molecules diffusion compared with the parent zeolite, and its titanosilicate analogue showed superior catalytic activity in cyclohexene epoxidation. This work provides new insight into the multiscale defect distribution in zeolites and highlights the relationship between defect engineering and catalytic performance.

**Electronic Supplementary Material:** Supplementary material (PXRD patterns, SE images, TEM images, STEM images, EDS mappings, statistical analysis details, FTIR spectra, UV-Vis spectra, textual properties, catalytic performance, and 3D reconstruction of Beta- $\text{R}_4$ ) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909006>.

## Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

## Acknowledgements

This work was supported by the Major State Basic Research Development Program of China (No. 2022YFA1506000), the Science and Technology Commission of Shanghai Municipality (No. YDZX20253100001002), and the National Natural Science Foundation of China (No. 22302124). The authors also thank Prof. Osamu Terasaki and ChEM SPST, ShanghaiTech University (No. EM02161943), for scientific and characterization support. G. D. X. thanks Hui Guo (Hebei University) for her assistance with the schematic diagrams of defects distribution.

## Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

## Author contribution statement

G. D. X.: Data curation, project administration, validation, writing manuscript, experimental design. X. C. G.: Data curation, project

administration, validation, writing manuscript, experimental design. L. J. C.: Data curation, project administration, validation. Z. P. L.: Data curation, validation. Y. M.: Project administration, validation, funding acquisition. S. T. W.: Project administration, validation. H. S.: Data curation, project administration. Y. H. L.: Data curation, project administration. G. Q. Z.: Data curation, project administration, experimental design, writing manuscript. Y. Q. F.: Data curation, project administration, writing manuscript, experimental design. P. W.: Project administration, writing manuscript, experimental design. Y. H. M.: Data curation, project administration, funding acquisition, writing manuscript. All authors discussed the results and commented on the manuscript.

## Use of AI statement

None.

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Nano Research, 2026, 19, 94909006