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RESEARCH ARTICLE Micron-sized zeolite Beta single crystals featuring intracrystal

interconnected ordered macro-meso-microporosity displaying superior catalytic performance

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Abstract: Serious diffusional limitations are frequently observed for the conversion of bulky molecules over conventional zeolite Beta crystals, which invoke for hierarchical structure to improve the mass transportation property and the accessibility to reactive sites. Zeolite single crystals with intracrystalline hierarchical porosity at macro-, meso- and micro-length scales is of great significance and provides the best solution. However, the construction of large zeolite Beta single crystals with such intracrystalline hierarchical porosity remains a critical challenge. We report here the successful synthesis of hierarchically ordered macro-mesoporous single-crystalline zeolite Beta (OMMS-Beta) with a rare micron-scale crystal size by an in-situ bottom-up confined zeolite crystallization strategy. The fully interconnected intracrystalline macro-meso-microporous hierarchy and the unique micron-sized single crystalline nature of OMMS-Beta lead to highly improved accessibility to active sites and outstanding (hydro)thermal stability, contributing to unprecedentedly high catalytic performances in both gas-phase and liquid-phase acidcatalyzed reactions involving bulky molecules compared to

commercial Beta and nanosized Beta zeolites. All these unprecedented properties of our hierarchically porous micronscale zeolite Beta single crystals with excellent stability can be fully exploited in various catalytic reactions with high catalytic activity, selectivity and reusability. Most importantly, our *in-situ* bottom-up confined crystallization strategy to hierarchically porous zeolite single crystal is highly universal and has been extended to the successful synthesis of other zeolitic materials, including ZSM-5, TS-1 and SAPO-34. Such novel zeolite single crystals with excellent properties can be applied to many other industrial catalytic reactions.

Introduction

Zeolites Beta are widely used as heterogeneous acid catalysts for many applications, especially in petroleum and petrochemical processes related to cracking,¹ alkylation,² isomerization,³ acylation⁴ and as acid adsorbents in the separation of aromatics.⁵

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The remarkable catalytic performances of zeolites Beta are closely related to their well-defined three-dimensional intersecting 12 oxygen-membered ring channels system and strong acidity.⁶ However, these narrow micropores frequently cause diffusional limitations over bulky reactants,7 thus reducing the accessibility of embedded internal catalytic active sites, increasing the coke formation in catalytic reactions⁸ and affecting seriously not only the zeolite activity but also the product selectivity and the catalyst lifetime.9 Fabrication of hierarchically porous zeolites with intra- or intercrystalline mesopores/macropores¹⁰ is a proven strategy to shorten the diffusion path length and to reduce the diffusion constraints.¹¹ Considerable efforts are devoted to construct zeolites with porous hierarchy using different techniques, such as hard/soft-template method and desilication.11d Hierarchically porous zeolites are reported to outperform other microporous zeolites, with higher catalytic activities, longer catalytic lifetimes, lower coke formation, slower deactivation rates and enhanced desirable product selectivity in many acid-catalyzed reactions.¹² Jacobsen et al. performed the pioneering work using commercial carbon nanoparticles¹³ or carbon fibers¹⁴ for preparing mesoporous MFI-type zeolite single crystals (ZSM-5^{13a, 13b, 14} and TS-1^{13c}), which were significantly more active in the catalytic cracking and isomerization of n-hexadecane13a and the epoxidation of cyclohexene^{13c} than their microporous counterparts. Tsapatsis and coworkers demonstrated the ingenious synthesis of size-tunable zeolite nanocrystals (MFI,10c Beta,¹⁵ LTA,¹⁵ FAU¹⁵ and LTL¹⁵) with a wide range of intercrystalline mesoporosities using mesoporous carbon templates through either steam-assisted crystallization^{10c} or hydrothermal synthesis¹⁵ for improved applications in ethanol dehydration.¹⁶ Schwieger and coworkers nicely synthesized a family of MFI-type zeolites (Silicalite-1,11c ZSM-5,17 TS-118) with intracrystalline macropores large by steam-assisted crystallization of mesoporous silica particles. The additional intracrystalline macropores, which were connected to the micropores and the crystal external surface, can drastically enhance the catalyst lifetime of ZSM-5 catalysts in the methanol to olefins (MTO) reaction¹⁷ and increase both the alkene conversion and epoxide selectivity of TS-1 catalysts in the liquid phase epoxidation of 2-octene with hydrogen peroxide.¹⁸ Xiao's group used either a designed cationic amphiphilic copolymer^{12f} or a commercial cationic polymer^{12g} to synthesize zeolite ZSM-5 single crystals with b-axis-aligned mesoporous channels12f or zeolite Beta single crystal with interconnected mesopores.^{12g} The b-axis-aligned mesoporous ZSM-5 showed highly improved catalytic conversions in the condensation reactions of benzaldehyde with hydroxyacetophenone or 1-pentanol compared to ZSM-5 with randomly oriented mesopores and conventional ZSM-5.12f The single-crystalline nature gives mesoporous zeolite Beta crystals better hydrothermal stability and higher catalytic activity than that of conventional zeolite Beta in the condensation of benzaldehyde with glycerol or hydroxyacetophenone and the alkylation of benzene with benzyl alcohol.12g Perez-Ramirez and coworkers made great contributions on the controlled generation of mesoporosity within zeolites by desilication¹⁹ and on the structural analysis to assess the pore connectivity.²⁰

Pioneering work in the development of hierarchically porous zeolite Beta focused most on the nanoparticle assembly²¹ but few on the single crystals.^{12g} Zeolite nanocrystals may to some extent improve the accessibility of catalysts, but their difficult separation

process and poor (hydro)thermal stability in both synthetic and catalytic processes restrict their further application.19b, 22 In addition, most of the conventional synthetic strategies lead to the formation of crystalline size of zeolites Beta in the range of 100-600 nm with relatively poor stability.12g, 23 It is particularly challenging to construct hierarchically porous structure within such one small zeolite Beta crystal. Furthermore, most hierarchically porous zeolite single crystals were designed and synthesized with either mesopores or macropores while the interconnection between different porosity is not quaranteed.^{12a} Simultaneously generated intracrystalline macropores and mesopores within one zeolite single crystal allow for catalytic performance enhancement by providing an unimpeded transport path and enhancing accessibility to more active sites.²⁴ It is thus highly desirable to develop a new strategy to simultaneously construct intracrystalline interconnected macro-mesopores within one zeolite Beta crystal with a particle size at micrometer scale, giving improved diffusion performance and high stability.

Here, we demonstrate the synthesis of micron-sized zeolite Beta single crystals with a highly ordered and fully interconnected intracrystalline macro-mesoporous hierarchy by an in-situ bottomup confined zeolite crystallization process. The single crystalline nature together with the micron-sized crystals endow our hierarchically porous single crystalline zeolite Beta with outstanding (hydro)thermal stability. The highly ordered and fully interconnected intracrystalline porous hierarchy of the resultant micron-sized Beta single crystals contributes to the excellent catalytic performance involving very high catalytic conversion and product selectivity, excellent long-term catalytic stability, low coke formation and significant reusability in both the gas-phase cracking reaction of bulky 1,3,5-triisopropylbenzene (TIPB) and the liquid-phase Friedel-Crafts alkylation of benzene with benzyl alcohol in comparison with benchmark conventional zeolite Beta and nanosized zeolite Beta. In addition, the acid sites poisoning experiments prove that the external active sites are decisive for the catalytic performance for these two reactions with bulky molecules. The introduction of porous hierarchy within Beta single crystal regulates the distribution of acid sites and gives a substantial increase in the number of external active sites, leading to the extraordinary high catalytic activity, long-term stability and low coke formation. More importantly, our in-situ bottom-up confined zeolite crystallization strategy presents as an effective synthetic strategy to fabricate hierarchically porous singlecrystalline catalysts with any kind of zeolite structures and zeotype materials.

Results and Discussion

Hierarchically macro-mesoporous micron-sized Beta single crystals with Si/Al ratio of 28 were synthesized within the confined-space in hierarchically ordered macro-mesoporous carbon (OMMC) template via a steam-assisted crystallization (SAC) process. In a typical synthesis (Figure 1a), the OMMC template prepared using polystyrene spheres of 220 nm (Figure S1 and Experiments), possessing interconnected mesopores and macropores, was impregnated within a zeolite Beta precursor slurry (Experiments). After slow evaporation of water at room temperature, the obtained dry gel completely filled up the mesopores and macropores in the OMMC template and then crystallized through the SAC process (Figure 1a). It is worth

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Figure 1. Steam-assisted crystallization of OMMS-Beta and its structure configuration. (a) Schematic diagram of the synthesis route of OMMS-Beta. (b-h) SEM images of OMMS-Beta(3) as a reference sample (b) and an individual crystal taken from three different directions (c-e) and corresponding schematic illustrations (f-h), Scale bars: b, 2 µm; c-e, 500 nm. (i and j). (i) SEM image of the enlarged area of OMMS-Beta(3), Scale bar: 100 nm. (j) Illustration of hierarchically ordered macro-meso-microporous structure in one single crystal of sample OMMS-Beta. The macropores are stemmed from the octahedral voids (*Oh*, red) and the mesopores from the tetrahedral voids (*Td*, blue).

noting that the mass transport in the dry gel and thus the zeolite crystallization rate within the confined spaces of the OMMC template during the SAC process are much slower than that in the traditional hydrothermal synthesis (HTS). This is a key point for the formation of the rare micron-sized zeolite Beta single crystals with hierarchically porous system. The calcined samples obtained by different crystallization periods (initial, 1 day, 2 days and 3 days) are designed as OMMS-Beta(0), OMMS-Beta(1), OMMS-Beta(2) and OMMS-Beta(3).

Using OMMS-Beta(3) as the representative sample (Figures 1b-1i), it can be seen that after the crystallization reaction of three days, crystals of 1.5-2 μ m are obtained (Figures 1b-1i). Each zeolite crystal consists of a number of uniform zeolite spheres with a size of 200 nm, being very similar to the size of polystyrene spheres used for preparing OMMC template (Figure S1), in a highly ordered and closely packed arrangement, as evidenced from the SEM images (Figures 1c-1i). The neighboring spheres,

originally formed in each of adjacent macropores in the OMMC template, are intergrown and tightly interconnected (the green rectangle of Figure 1i) through the windows connecting each cage of the OMMC template (Figure S1). Such highly ordered opaline structure (Figures 1b-1i), in which each spherical element is connected with 12 other adjacent elements, is an exact copy of the highly ordered, interconnected and continuous air voids in the OMMC template (Figure S1). These ordered spherical elements in one individual OMMS-Beta single crystal contribute to the formation of interstitial tetrahedral (T_d) and octahedral (O_h) voids by 4 and 6 spheres from two adjacent layers (Figure 1j), respectively. Such periodically arranged T_d and O_h voids within one zeolite single crystal, which are highly connected each other and are communicated with the micropores present in each spherical element, lead to the creation of two different and interconnected large porosities in addition to the intrinsic microporosity of zeolite Beta, and provide ordered, fully

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Figure 2. Characterization of OMMS-Beta(3). (a) TEM image and ED pattern (inset) of an individual zeolite, Scale bar: 500 nm; the inset: 5 nm-1. (b) TEM image of enlarged area outlined in (a), Scale bar: 200 nm. (c) HRTEM image of enlarged area outlined in (b), Scale bar: 20 nm. (d) XRD pattern, (e) Nitrogen adsorption-desorption isotherms and micropore-size, mesopore-size distribution (inset) and (f) Mercury intrusion and macropore-szie distribution (inset) of OMMS-Beta(3).

interconnected meso- and macroporous structure, precisely replicating the OMMC template (Figure 1j).

Transmission Electron Microscopy (TEM) images (Figures 2a-2c) show the strongly faceted and ordered opal structure constructed by intergrown and highly interconnected zeolite spheres in one individual zeolite crystal of OMMS-Beta(3) as a representative sample (indicated by the circles in Figure 2b), which is in an excellent agreement with the SEM images (Figures 1b-1e and the green rectangle of Figure 1i). The corresponding selected area electron diffraction (SAED) pattern (the inset of Figure 2a) contains discrete diffraction spots, clearly indicating the single crystalline nature of the OMMS-Beta(3) sample. The high-resolution transmission electron microscopy (HRTEM, Figure 2c) image reveals the high degree of crystallization and the same oriented lattice fringes over the entire image region. No grain boundary or interface between two small zeolite spheres are observed, confirming these zeolite spheres are not independent but tightly interconnected into a whole zeolite crystal, being in good accordance with the electron diffraction pattern (inset of Figure 2a) of the whole assembly and SEM images (Figures 1b-1e and the green rectangle of Figure 1i). No amorphous components, planar defects like stacking faults, twins formation or dislocations are found between zeolite spheres, verifying the pristine structure throughout the zeolite crystal and that all the zeolite spheres are crystallized following the structure of the OMMC template in the same orientation and intergrown to give the entire zeolite single crystal.

Sample crystallized after three days evidently show two feature peaks at Bragg angles 2θ of 7.6° and 22.6° in the powder

X-ray diffraction (PXRD) pattern (Figure 2d), corresponding to (101) and (302) reflections of Beta-topology, respectively. No other diffraction peaks but the Beta reflection peaks are observed, confirming that the pure zeolite Beta without any impurity is prepared. The nitrogen adsorption-desorption isotherm has two steep steps in the $p/p_0 < 0.01$ and $p/p_0 < 0.9$ regions, corresponding to the filling of the micropores and the capillary condensation in the mesopores and macropores, respectively (Figure 2e)^{12g}. The micropore diameter of OMMS-Beta(3) determined using non-local density functional theory (NLDFT) is around 0.6 nm (the inset of Figure 2e), which is the same as observed in conventional zeolite Beta.^{23, 25} The micropore surface area and volume of OMMS-Beta(3) are 179 m²·g⁻¹ and 0.10 cm³·g⁻¹, respectively (Table S1), indicating that the fabrication of a hierarchically macro-mesoporous system within the zeolite Beta does not influence its inherent microporous structure. The mesopore size distribution determined using Barret-Joyner-Halenda (BJH) model is centered at 40 nm (the inset of Figure 2e) and the mesoporous surface area and total volume are 120 m² g⁻¹ and 0.28 m²·g⁻¹ (Table S1), respectively. The presence of additional meso- and macropores in OMMS-Beta(3) is further confirmed by the mercury intrusion porosimetry measurement.²⁶ The result shows a narrow mesopores distribution centered at ~32 nm, slightly lower than the value (~40 nm) obtained by the nitrogen adsorption, and a broader macroporous distribution centered at ~95 nm (Figure 2f). These interconnected and periodically ordered mesopores and macropores stem from the tetrahedral (T_d) and octahedral (O_h) voids within the OMMS-Beta(3) sample, respectively (Figure 1j).

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Figure 3. Crystallization process of OMMS-Beta. SEM images and corresponding of schematic illustrations inset of (a) OMMS-Beta(0), (b) OMMS-Beta(1), (c) OMMS-Beta(2) and (d) OMMS-Beta(3), Scale bars: a, b 100nm; c, d, 500nm.(e) XRD patterns, (f) 29Si NMR spectra, (g) 27AI NMR spectra and (h) nitrogen adsorption isotherms of (I) OMMS-Beta(0), (II) OMMS-Beta(1), (III) OMMS-Beta(2) and (IV) OMMS-Beta(3).

Samples at different crystallization times were collected and characterized by SEM, XRD, ²⁷AI MAS NMR, ²⁹Si MAS NMR and nitrogen adsorption-desorption analysis to gain deeper insights into the transformation process (Figure 3). Initially, all the air voids in the OMMC template were filled with the precursor gel. After drying the gel and removing the OMMC template, it is very interesting to see that all the amorphous spheres of about 200 nm are tightly packed and continuously connected together into a highly ordered arrangement, which precisely replicated the

inverse opalline structure of the OMMC template (Figure 3a). It is worth stressing that after filling up the air voids within the OMMC template by the dried precursor gel, all the amorphous spheres formed due to the confined space of the OMMC template are already interconnected to form a continuous gel structure throughout the entire OMMC template. These confined amorphous spheres then gradually crystallize within the OMMC template under the SAC condition. With a crystallization time of one day, OMMS-Beta(1) mainly consists of spheres (~200 nm)

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with rough surface and already visible crystallinity but without the tight interconnection between the spheres as observed in OMMS-Beta(0) (Figure 3b). It is intriguing that these spheres, originally formed within the macropores of the OMMC template, all have a small fraction of spheres attached on the surface (indicated by arrows in Figure 3b and also observed on the out layer spheres in Figure 3a). This means that the spheres in opalline structure formed by amorphous dried gel are partially dissociated due to the partial crystallization. This dissociation leads to the presence of the small fraction of spheres attached to each sphere. The first OMMS-Beta single crystals with a typical Beta-type zeolite cubelike shape and a crystal size close to 1 µm are obtained after a crystallization time of two days (Figure 3c). Each crystal is constructed by several zeolite spheres (~200 nm) and all these zeolite spheres are tightly bonded with each other. The crystallinity is gradually increased as the crystallization time proceeds. After a crystallization of 3 days, OMMS-Beta(3) sample shows well shaped crystals (Figure 3d). Each crystal is assembled by more spheres and the crystal size increases to 1.5 μm-2 μm (Figure 3d) as previously analyzed in Figure 1 and 2. It is clearly observed that the crystalline degree of the resultant OMMS-Beta samples increases with the prolonged crystallization (Figure 3e). The crystallinity is largely improved, suggesting the very well crystallization after three days. The coordination and environment of the Si species in all the samples are further studied by ²⁹Si MAS NMR technique (Figure 3f). The OMMS-Beta(0) features a small shoulder at δ =-96 ppm [Q² groups Si(OSi)₂(OH)₂], a broad signals at δ =-103 ppm [Q³ groups, Si(OSi)₃(OH)] and two other broad signals at δ =-109 nm and δ =-116 ppm [Q⁴ groups, Si(OSi)₄].²⁷ As the crystallinity of the samples increases, the shoulders at both δ =-96 nm [Q² groups] and δ =-103 nm [Q³ groups] disappear. A small shift of the Q⁴ groups towards higher magnetic field is observed while these Q⁴ signals become much narrower, suggesting that the coordination states of the Si species transformed from an amorphous to a crystalline framework. Moreover, three overlapping signals exist in OMMS-Beta(1)-(3) samples at δ = -110, -112, -115 ppm, all assigned to Q⁴ groups at different crystallographic non-equivalent tetrahedral sites in the Beta structure.27 The fact that the resonance peaks in OMMS-Beta become narrower is due to the homogeneity of the Si environment as the crystallization proceeds, indicating that the crystallinity of resultant Beta zeolitic framework increases gradually with increasing reaction time.²⁸ It is clearly observed from the ²⁷AI MAS NMR spectra (Figure 3g) that the sharp and symmetrical signal at δ=55 ppm, assigned to the tetrahedrally coordinated framework aluminum, is gradually enhanced with increased crystallization time while the resonance at δ =0 ppm, corresponding to the octahedrally coordinated extraframework aluminum, is absent for all the samples except for OMMS-Beta(0).12g These results indicate that the amorphous aluminum atoms have been successfully incorporated into the zeolite Beta single crystalline framework in tetrahedral position during the in-situ bottom-up confined zeolite crystallization process. The N₂ adsorption-desorption isotherms of the calcined samples over various crystallization periods change from a type II to a type I with two uptakes at $p/p_0 < 0.01$ and $p/p_0 > 0.9$, respectively with increasing crystallization time (Figure 3h), also indicating the gradual generation of microporosity, mesoporosity and macroporosity in the products. The sharp uptake at $p/p_0 <$

0.01 reveals the presence of micropores in all OMMS-Beta(1-3) samples. The micropore size calculated by the NLDFT method is around 0.6 nm, which is in good agreement with the pore size of zeolite Beta.23 The surface area and pore volume of micropores increase gradually with the increased crystallization time (Table S1), which means that the amorphous domain has been gradually transformed into microporous zeolitic phases. OMMS-Beta(1-3) samples all exhibit type I isotherms with a steep increase and a large hysteresis at $p/p_0 > 0.9$, suggesting the presence of large mesoporosity and macroporosity (Figure 3h). It is worth noting that the mesopore size distribution centered at 40 nm can be observed for all OMMS-Beta samples (Figure S2), indicating that the in-situ bottom-up confined zeolite crystallization process can be carried on within the OMMC template and precisely replicated the inverse opal structure. It can thus be concluded that our insitu bottom-up confined zeolite crystallization process is a successful strategy to create highly ordered and fully interconnected intracrystalline porous hierarchy within one zeolite Beta single crystal with a rare micron-sized crystal size and high crystallinity.

The excellent thermal and hydrothermal stability of our OMMS-Beta(3) single crystals have been evidenced through a series of high-temperature treatment (1000°C for 1h) and high-temperature treatment in vapor stream (780°C for 2h). The detailed N2 isotherms, XRD and SEM characterizations clearly show that these thermally and hydrothermally treated samples maintain intact the well-defined ordered hierarchically macro-mesomicroporous framework with a high crystallinity (Figures S3-S6). The crystallinity before and after (hydro)thermal treatment is verified using Eq (1) (Experiments). Therefore, the hydrothermally and thermally treated OMMS-Beta(3) samples practically maintain the same crystallinity as the as-synthesized OMMS-Beta(3) sample. The surface area and pore volume equally remain practically the same (Table S2). Such excellent thermal and hydrothermal stability should be attributed to the single crystalline nature of the rare micron-scale sized zeolite. The outstanding (hydro)thermal stability under very severe conditions is of great importance for their catalytic stability. All the above observations clearly demonstrate that micron-sized zeolite Beta single crystals with a high crystallinity, highly ordered and fully interconnected macro-mesoporous structure, excellent thermal/hydrothermal stability are obtained.

To illustrate the extraordinary accessibility to active sites of OMMS-Beta single crystals, the acidic properties and the distribution of active sites are determined by the ammonia temperature programmed desorption (NH₃-TPD) analysis²⁹ and the organic base (triphenylphosphine, TPP) adsorption method ³⁰ (Experiments), respectively. The ammonia molecule with a kinetic diameter of 0.44 nm can penetrate into micropores and will give the total acidity of zeolites while the basic TPP molecule is sterically bulky with a kinetic diameter of 0.94 nm and can access only the acid sites on the external surface out of micropores.³¹ For comparison, the benchmark conventional zeolite Beta (designated as C-Beta) and nanosized zeolite Beta (designated as Nano-Beta) are used as reference catalysts. Both C-Beta and Nano-Beta contain multimodal porosities confirmed from the detailed adsorption-desorption characterizations (Figures S7-S9). The C-Beta with a crystal size of 300-600 nm has mesopores at 3.2 nm and the Nano-Beta has interparticular mesopores at

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Figure 4. Catalytic performance of various zeolite Beta catalysts in the gas-phase cracking reaction of 1,3,5-TIPB the liquid-phase benzylation of benzene with benzyl alcohol. (a) catalytic activities (1,3,5-TIPB conversions) at different temperatures and (b) deactivation behavior at 500 °C in the 1,3,5-TIPB cracking reaction. (c) Benzyl alcohol (BA) conversions and (d) diphenylmethane (DPM) selectivities over OMMS-Beta, Nano-Beta and C-Beta. (e) Benzyl alcohol (BA) conversions and (f) diphenylmethane (DPM) selectivities over OMMS-Beta, micropore-poisoned OMMS-Beta and TPP-poisoned OMMS-Beta.

10.6 nm and large macropores. Consequently, these two samples with multi modal porous structure are thus excellent references for comparison. The distribution of active sites is one of the most important factors to determine the catalytic performance. The introduction of intracrystalline interconnected porous hierarchy within the zeolites not only improves their diffusion performance, but also changes the distribution of active sites. For the sake of

clarity, the acid sites embedded within the micropores are labelled as internal acid sites and all the acid sites out of micropores are named as external acid sites. These three samples with the similar Si/Al ratios exhibit almost the same total acidity shown by the NH₃-TPD analysis (Figure S10 and Table S3). It is worth noting that a greater accessibility of the bulky TPP molecules related to the external sites is achieved upon the fabrication of intracrystalline interconnected meso-/macropores within the zeolites. Due to its higher external surface area compared to that of C-Beta, Nano-Beta has a higher adsorption capacity for TPP (21 µmol·TPP·g⁻¹ cat) than that of C-Beta (13 µmol·TPP·g⁻¹ cat) while OMMS-Beta(3) sample contains much higher external surface acidity (28 µmol·TPP·g⁻¹ cat), which is 2 times higher than that of C-Beta and 33% higher than Nano-Beta, respectively. These increased external catalytic sites within the OMMS-Beta(3) catalysts are widely-open, indicating that more active sites are exposed and accessible, being of great importance for the catalytic performance.

The combination of the fully interconnected porous hierarchy, the high (hydro)thermal stability, single crystalline nature and the abundant external acid sites makes OMMS-Beta(3) an extraordinary solid acid catalyst, especially for converting bulky reactants. The catalytic activities of OMMS-Beta were firstly evaluated in the gas-phase cracking reaction of bulky 1,3,5-TIPB (Scheme S1). It is clearly observed that our OMMS-Beta(3) catalyst exhibits a very high catalytic conversion of 49.0% even at a low reaction temperature at 250°C, which is 5 and 2.2 times higher than that of the C-Beta (9.8%) and the Nano-Beta (21.4%), respectively (Figure 4a). The 1,3,5-TIPB conversion increases slowly for both C-Beta and Nano-Beta as the reaction temperature increases from 250°C to 500°C. In contrast, the 1,3,5-TIPB conversion increases rapidly for OMMS-Beta(3) sample as the temperature increases and can achieve an unprecedentedly high value of 86.4% at 500°C, which is 4.0 and 2.0 times higher than that of C-Beta (22.6%) and Nano-Beta (43.4%), respectively. Such excellent catalytic activity of OMMS-Beta(3) is directly related to its open, interconnected and ordered intracrystalline hierarchically micro-meso-macroporous architecture and high external surface acidity, which enhances the accessibility of bulky 1,3,5-TIPB molecules (with a kinetic molecular dimension of 0.95 nm) to the larger amount of external active sites. The high stability of intracrystalline hierarchically porous structure and abundant external acid sites are also of great importance for their long-term catalytic stability and cycle stability in reactions involving bulky reactants. C-Beta and Nano-Beta samples suffer from serious deactivations in which about 70% of their catalytic activities are lost after 30 pulse injections at 500 °C. In contract, OMMS-Beta(3) shows unchanged activity and the catalytic conversion stabilizes at 86.0 % in the given 30 injections (Figure 4b). Generally, the deep cracking of 1,3,5-TIPB usually takes three successive steps, which are the first dealkylation of 1,3,5-TIPB to form diisopropylbenzene (DIPB) and propylene, the second dealkylation of DIPB to give isopropylbenzene (IPB) and propylene and the third dealkylation of IPB to give benzene and propylene (Figure S11). The propylene from deep cracking of 1,3,5-TIPB is a chemical urgently needed by the industry. Consequently, it is highly desirable to realize the deep cracking by developing novel catalysts. The main products catalyzed by C-Beta are DIPB and propylene accompanied by few IPB and benzene, indicating the low cracking degree of 1,3,5-TIPB. As the

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injections increased, the increased DIPB content and the decreased propylene content (Figure S12a) suggest the decreased catalytic capacity and the deactivation of C-Beta. The larger interparticlar mesoporous structure present in Nano-Beta offers better accessible external active sites and facilitates the diffusion of the bulky 1,3,5-TIPB as compared with C-Beta as indicated by TPP adsorption experiment (Table S3). However, the same deactivation trend is observed for Nano-Beta catalyst although less DIPB but more Benzene and propylene in content are obtained (Figure S12b), indicating that the same reduced capacity of Nano-Beta and the catalyst is deactivated with increasing the number of injections. Significantly, the average selectivity of propylene from deep cracking of TIPB over OMMS-Beta(3) catalyst can reach at a very high value of 58% (Figure S12c), which is 2.0 and 1.5 times higher than that of C-Beta (29%) and Nano-Beta (38%), respectively. The main products are benzene and propylene with small content of IPB but without DIPB, indicating the much deeper cracking degree of 1,3,5-TIPB over OMMS-Beta(3) catalyst. Furthermore, the products selectivity over OMMS-Beta(3) catalyst remains practically constant up to 30 injections, indicating the high catalytic stability of OMMS-Beta(3) catalyst. The much deeper cracking process and excellent catalytic stability achieved on OMMS-Beta(3) catalyst compared to C-Beta and Nano-Beta should be attributed to their significant intracrystalline diffusion performance of guest molecules and the low amount of coke deposition. The coke deposition on the reacted samples was analysed by the thermogravimetric analysis (TGA). OMMS-Beta(3) used in cracking of 1,3,5-TIPB for 30 injections showed two times less coke deposition (3.0 %) than C-Beta (7.3 %) and Nano-Beta (6.0 %). It can be concluded that the presence of excellent hierarchically porous diffusion system, strong accessible external surface acidity together with high (hydro)thermal stability provides a highly efficient catalyst, exhibiting enhanced catalytic activity, significant selectivity of light olefins, excellent catalytic stability as well as higher resistance to coke formation during the 1,3,5-TIPB catalytic cracking.

The highly improved catalytic performance is further evidenced in the liquid-phase Friedel-Crafts (F-C) alkylation of benzene with benzyl alcohol (Scheme S2). The F-C benzylation of benzene can produce value-added diphenylmethane (DPM), which is important intermediate product widely used in pharmaceuticals, petrochemicals, fine chemicals, dyes and many other chemicals. Hierarchically porous zeolites are the ideal liquid phase reaction catalysts due to their structural superiorities.² It can be clearly seen that the catalytic conversion of benzyl alcohol over C-Beta and Nano-Beta at a reaction temperature of 80 °C can only reach a maximum value of 19.8% and 50.4%, respectively (Figure 4c and Table S2), while OMMS-Beta(3) gives much higher conversion of 85.2%, which is 4.0 and 1.7 times higher than that of C-Beta and Nano-Beta, respectively. The initial DPM selectivities over C-Beta and Nano-Beta are 72.4 % and 80.0 % and decrease to 61.2% and 72.4% after 120 h reaction, respectively (Figure 4d). The highest selectivity value towards DPM of 88.1% is observed for OMMS-Beta(3) (Figure 4d). More importantly, such high DPM selectivity remains unchanged over OMMS-Beta(3) during the long-term reaction for 120 h. The liquidphase catalytic reactions of bulky molecules mainly take place on the external surface of microporous zeolites. Such remarkable catalytic activity and long-term catalytic stability are mainly ascribed to the abundant external surface acid sites and outstanding mass transport properties of OMMS-Beta(3), which can be further evidenced by the detailed catalytic evaluations of the thermally/hydrothermally treated samples and the recycling test of the regenerated catalysts (Tables S2 and S4). There is only a very slight decrease in benzyl alcohol conversion and DPM selectivity over both the thermally and the hydrothermally treated OMMS-Beta(3) catalysts after 120 h reaction at 80°C (Table S2). Significantly, the catalytic performance in terms of the benzyl alcohol conversion and DPM selectivity of the regenerated OMMS-Beta(3) catalysts after first, second and third cycles of 120 h reaction in benzene alkylation by benzyl alcohol remains practically unchanged (Table S4). The OMMS-Beta(3) catalysts discharged after first, second and third reaction cycles of 120 hours are further characterized by the detailed N2 adsorptiondesorption isotherms, XRD and SEM techniques, confirming that the OMMS-Beta(3) catalyst has excellent reusability without any pore structure modification after three reaction cycles and high temperature multiple oxidative regeneration processes (Figures S13-S14).

In order to further illustrate the catalyst performance superiority of the interconnected and ordered micro-mesomacroporous hierarchy of our micron-sized Beta single crystals, the selective poisoning of the internal and the external acid sites on all the C-Beta, Nano-Beta and OMMS-Beta(3) has been realized, whose catalytic behaviors are again evaluated in the liquid-phase alkylation of benzene with benzyl alcohol. The internal acid sites within the micropores can be selectively poisoned by completely blocking the micropores with carbon species formed during the benzene isopropylation process (designated as Micropore-poisoned sample, Experiments)³² and the external acid sites located within the meso/macropores can be poisoned by the chemisorption of triphenylphosphine (TPP) as TPP molecules cannot penetrate into the micropores (designated as TPP-poisoned sample, Experiments).^{2, 31} Figure 4e shows that the benzyl alcohol conversion over the TPP-poisoned OMMS-Beta(3) is very low with a value of 25% after reaction for 120 h. In contrast, the Micropore-poisoned OMMS-Beta(3) still exhibits very high conversion (71%, Figure 4e). More importantly, the Micropore-poisoned OMMS-Beta(3) shows the same high DMP selectivity as the pristine OMMS-Beta(3). The high DPM selectivity of both the micropore-poisoned and the TPP-poisoned OMMS-Beta(3) remain almost constant during the long-term reaction for 120 h (Figure 4f). It can be inferred that the external active sites of catalysts are decisive for both the catalytic conversion and product selectivity in the alkylation of benzene with benzyl alcohol, which is also evidenced by the catalytic results obtained on both selective-poisoned C-Beta and Nano-Beta (Figure S15). Both the micropore-poisoned Nano-Beta and the TPP-poisoned Nano-Beta (Figures S15a-S15b) exhibit lower catalytic conversion of benzyl alcohol than pristine Nano-Beta. However, the catalytic activity loss and DPM selectivity loss on the TPP-poisoning Nano-Beta are much higher than those on Micropore-poisoned one, indicating clearly that external accessible acid sites out of micropores contribute much more in the benzene alkylation by benzyl alcohol than acid sites located in their intrinsic micropores. In regards to C-Beta, in addition to the intrinsic micropores, there is an additional small mesopores of 3.2 nm with low quantity, meaning that there exist less external acid sites in the catalyst. The micropore-poisoned C-Beta thus shows a much higher catalytic conversion loss and DPM selectivity loss than that of TPP-poisoned C-Beta (Figures S15c-

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S15d). All the above results suggest that the alkylation reactions continue on the abundant external active sites even after the internal sites are deactivated. The OMMS-Beta(3) has much higher external surface acidity contributed from the intracrystalline interconnected hierarchically porosity (Table S3). As a result, OMMS-Beta(3) exhibits much higher catalytic conversion and product selectivity in comparison with C-Beta and Nano-Beta. A large amount of accessible external active sites and superior diffusion performance give our hierarchically meso-macroporous Beta single crystalline catalyst an extraordinary performance in comparison with benchmark conventional microporous Beta and zeolite Beta nanocrystals. All these results clearly demonstrate that the micron-sized zeolite Beta single crystals with fully interconnected intracrystalline porous hierarchy exhibit extraordinary catalytic performance involving high catalytic conversion, high product selectivity, long-term catalytic stability and superior reusability in both gas-phase and liquid-phase catalytic reactions involving bulky molecules, which will be expected to be extended to other catalytic reactions.

Conclusion

In summary, the rare micron-sized Beta zeolite single crystals with a highly ordered and fully interconnected intracrystalline macro-meso-microporous hierarchy have been successfully synthesized by an in-situ bottom-up confined crystallization process. The highly ordered and fully interconnected hierarchically porous structure provides more efficient masstransport system and highly improved accessiblility to active sites, which greatly reduces the degree of coke deposition. In addition, such unique intracrystalline porous hierarchy contributes to the regulation of the spatial distribution of active acid-sites and gives a substantial increase in the number of accessible external active sites, thus leading to superior catalytic performance in comparison with conventional microporous Beta and zeolite Beta nanocrystals. The catalytic conversions over our OMMS-Beta(3) are nearly 4.0 and 2.0 times higher than that of C-Beta and Nano-Beta both in the gas-phase cracking reaction of bulky 1,3,5triisopropylbenzene (TIPB) and the liquid-phase Friedel-Crafts alkylation of benzene with benzyl alcohol, respectively. Unprecedentedly high deep cracking degree, high selectivity of propylene and much lower coke formation in the cracking of bulky 1,3,5-TIPB can be achieved over OMMS-Beta(3). More importantly, the rare micron-sized single crystalline nature endows OMMS-Beta(3) with outstanding (hydro)thermal stability, which in turn provides excellent catalytic stability involving the long-term stability and excellent reusability in bulky molecules reactions. The catalytic conversion of our Beta single crystals in bulky 1,3,5-triisopropylbenzene cracking reaction can stabilize continuously at a very high constant value in the given 30 injections. OMMS-Beta(3) exhibits an unchanged DPM selectivity during the long-term reaction for 120 h and very high catalytic activity after three reaction cycles in the liquid-phase Friedel-Crafts alkylation of benzene with benzyl alcohol. All these unprecedented properties of our hierarchically porous micronscale zeolite Beta single crystals with excellent stability can be fully exploited in various catalytic reactions with high catalytic activity, selectivity and reusability. Most importantly, our in-situ bottom-up confined crystallization strategy to hierarchically porous zeolite single crystal is highly universal and has been extended to the successful synthesis of other zeolitic materials, including ZSM-5, TS-1 and SAPO-34. Such novel zeolite single crystals with excellent properties can be applied to many other industrial catalytic reactions.

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An *in-situ* bottom-up confined zeolite crystallization strategy is developed to construct micron-sized hierarchically ordered macromesoporous single-crystalline zeolite Beta with improved accessibility to active sites and outstanding (hydro)thermal stability for both gas-phase and liquid-phase acid-catalyzed reactions of bulky molecules.