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## A Topotactic Synthetic Methodology for Synthesis of Nanosized MFI Zeolites with Hierarchical Structure

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Abstract: Herculean work has been done for designed synthesis of zeolites with nanosized and hierarchical structure in decades, on account of increasing demands in practical applications, especially catalysis. Here, we demonstrate a new topotactic synthetic strategy to synthesize nanosized and hierarchical zeolites in a one-step procedure. Using silica spheres as the adjustable amorphous precursors and tetrapropylammonium hydroxide (TPAOH) as structure-directing agent, effortless control of both sizes and porosity can be achieved in this system with no extra templates. With a simple hydrothermal process, the hierarchical zeolite spheres can be modified with acid cites (Al species incorporated in framework). Benefited from its mesoporosity, palladium nanoparticles are incorporated into the nanosized hierarchical zeolite, which makes the materials suitable to use in a cascade catalysis reaction of benzimidazole derivatives, including independent acid catalysis and hydrogenation sites. The nanocomposites show exceptional activity and stability in catalysis and recycle reaction. This strategy can be developed into other versatile and practicable scaffold for advanced zeolites catalytic nanoreactor system.

#### Introduction

Zeolites are crystalline microporous aluminosilicates frameworks constituted by  $TO_4$  (T=Si, AI, P, Ge, etc.) tetrahedral structure, owing to their thermal stabilities, high surface areas and adjustable acidities, which are critically important materials for applications in ion-exchange, adsorbents in gas separation, and chemical catalysis.<sup>[1]</sup> Catalytic performance of zeolites is narrowed as pore structure limits the transportation of bulky molecules.<sup>[2]</sup> The most common and conventional way to overcome this problem is utilization of hierarchical zeolites.<sup>[3]</sup> However, complex catalytic processes often include reactions occurring at the external surface of zeolite crystals, which propose more demands in zeolite engineering.<sup>[4]</sup> Despite great efforts for introducing mesoporosity into zeolites, zeolites in practical application are micrometer-sized, which have a negligible external surface to their pore structure inside and

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[b] Dr. X. Wang Faculty of Chemistry and Chemical Engineering Yunnan Normal University, Kunming 650500, P. R. China Supporting information for this article is given via a link at the end of the document. impedance against surface engineering.<sup>[5]</sup> Nanosized zeolites provide enhanced external surface areas, short diffusion path lengths, and customized surface properties, which promise nanosized zeolites in the foreground of future public view during the past decades.<sup>[6]</sup> Recently, Mintova and Valtchev et al. have achieved exhilarating breakthroughs and reported triumphant syntheses of nanosized zeolites, including different types of framework (EMT and FAU) from template-free systems and silanol-free MFI zeolites in a both environmental and economical way.<sup>[7]</sup> A. Corma et al. have synthesized nanosized high-silica beta zeolite (BEA) with large-pore structure, broad Si/Al ratios (15-30) and excellent solid yields (above 95%), which shows its great catalytic performance particularly in oligomerization of 1pentene into liquid fuels.<sup>[8]</sup> M. Tsapatsis et al. have successfully investigated the crystallization process and its key factors in organic-free systems by combining pre- and post-nucleation trajectories.<sup>[9]</sup> Moreover, special attention has been concentrated on colloidal suspensions of zeolites with narrow particle size distributions and particle sizes of less than 200 nm.<sup>[10]</sup> Besides smaller sizes than traditional zeolites, colloidal zeolite suspensions show more advantages in constituting zeolite nanocrystal-built materials.<sup>[11]</sup> Composites and hierarchical structures fabricated by colloidal suspensions of zeolites such as zeolite films or membranes, nanotubes and other 3D framework structures expand the applications of zeolites towards,<sup>[12]</sup> e.g., optoelectronics,<sup>[13]</sup> chemical sensing,<sup>[14]</sup> and nanomedicine.<sup>[10, 15]</sup> It is critical and difficult to control the zeolite nucleation kinetics in order to obtain a desired nanosized colloidal zeolite.<sup>[6]</sup> Up to now, only several types of zeolites can be prepared successfully with nanosized dimensions and stabilized in colloidal suspensions.<sup>[16]</sup>

Various methods have been developed to integrate mesoporosity into zeolites, including surfactant templating,[17] hard-templating,<sup>[18]</sup> fabrication of interparticle mesopore with nano zeolites,<sup>[19]</sup> post-synthetic chemical etching and so forth.<sup>[20]</sup> However, the burdensome multistep procedure and costly templates hinder the industrial application for large-scale production. Furthermore, it will benefit admirably for achieving the combination of reduction of zeolite size and integration of intracrystalline hierarchical structure into zeolites.[4-6] In spite of very demanding applications, successful works that can prepare nanosized colloidal zeolites with hierarchical structure are rarely reported. It is arduous to combine the advantages because assembly between traditional templates directing mesoporosity and zeolite material units requires a totally different chemical kinetics process with reduction of zeolite size. Hence, developing a general and elegant strategy for the synthesis of nanosized hierarchical zeolites is indeed difficult and remains a grand challenge.

Herein, we demonstrate a facile and effortless approach to prepare nanosized zeolites with hierarchical porous structure by in situ crystallization strategy. Choosing silica spheres as silica precursor and in situ crystallization framework and tetrapropylammonium hydroxide (TPAOH) as structure directing agent (SDA), synthesis system is added with a high base density and very low content of water. As shown in Scheme 1, TPAOH can ionize into TPA<sup>+</sup> and OH<sup>-</sup> readily in aqueous solution, and high density of OH<sup>-</sup> can promote desilication in the silica spheres, which causes generation of mesoporosity. A very small amount of water in the synthesis system makes silicates polymerizing around TPA<sup>+</sup> process in situ happen in the framework of mesopores during the crystallization process, thus forming the hierarchical zeolite spheres. The morphology and pore structure of the products can be adjusted by controlling reaction time and the ratio of Si: TPAOH: H<sub>2</sub>O in sol-gel crystallization process. With further crystallization, the hierarchical zeolite spheres grow into faultless zeolite nanoparticles with a uniform size and high crystallinity. The sizes of hierarchical zeolite and zeolite nanoparticles can be controlled by adjusting the diameters of amorphous silica spheres. The assynthetized zeolites own a narrow particle size distribution and can be easily dispersed in water to form steady colloidal suspensions and constitute nanozeolite membranes. The assynthetized hierarchical zeolite spheres can be further modified by adding acid sites in aluminium solution by a hydrothermal process and packaged with noble metal particles within the mesopores. The obtained nanocomposites show high catalysis performance, reliable stability and recyclability in cascade twostep catalyzing synthesis of benzimidazole derivatives.

#### **Results and Discussion**

In Scheme 1, the schematic graph clearly illustrates the whole synthetic process of nanosized zeolites with different pore structures by the in situ crystallization strategy. Initially, the solid silica spheres with a uniform diameter of 220 nm are prepared by Stöber method,<sup>[21]</sup> as revealed by transmission electron microscopic (TEM) image (Figure 1a). Then, accompanied with the depolymerization of amorphous solid silica spheres, the diameter of the silica spheres shrinks to 160 nm, and a large number of mesopores can be clearly observed from the exposed porous spheres (Figure 1b). As the reaction proceeds, the dis-



**Scheme 1.** Schematics illustration for the synthesis of hierarchical zeolite sphere and nanosized zeolite particle by in situ crystallization.

solved silica and TPA<sup>+</sup> hydrated cation species rebond into the defective interface of porous intermediates to form hierarchical MFI type zeolites (Hier-S-1). The Hier-S-1 grow into angular zeolites with high crystallinity after further reaction with remaking of bonds around SDA (Figure 1c and the insert). The open mesopores disappear and clear lattice fringes can be observed. Those nanosized zeolite nanoparticles (nano S-1) have a uniform size of 140 nm and all the particle size observations are confirmed by dynamic light scattering (DLS) measurements in Figure S1. In the whole synthetic process, there are no separated smaller zeolites forming from nucleation of dissolved silica species in all samples. Both nanosized Hier-S-1 and nano S-1 can form colloidal suspensions with Tyndall effect and be paint as zeolite thin films on a glass piece, as shown in Figure 1d and Figure 1h. Such a colloid solution can be steady for at least a week without any precipitation. Moreover, by using the solid silica spheres of 320 nm as precursor, both larger Hier-S-1 and nano S-1 with sizes of 280 nm and 260 nm are successfully obtained, and TEM images and DLS curves of these samples are showed in Figure 1e-g and Figure S2.

Powder X-ray diffraction (XRD) patterns of different products are shown in Figure 2a, indicating the crystalizing process of the samples. The initial solid silica spheres are amorphous. For the Hier-S-1 samples, the XRD patterns show the characteristic peaks of MFI structure, suggesting the existence and crystallization of MFI framework in the samples. After calcination, the diffraction intensity of feature peaks before 10° (20) increase visibly, due to removal of organic SDA (red line of Hier-S-1 (c)) in Figure 2a. Stronger peaks can be observed in the patterns of nano S-1, which declare their higher crystallinity, as compared to Hier-S-1. The evolution of the crystallinity are further proven by Ultraviolet ray resonance Raman spectroscopy (UV Raman) in Figure 2b and Fourier transform infrared spectroscopy (FT-IR) in Figure 2c. The occurrence of zeolite frameworks can be distinguished characteristically in the UV resonance Raman spectra. The wide absorption peaks around 300-500 cm<sup>-1</sup> are attributed to fluorescent effect of nanosized silica spheres in Raman spectra. For Hier-S-1 samples, decreasing of these wide adsorption peaks shows the changes in the frameworks of different chemical conditions. The detected Raman absorption peaks at 310  $\mbox{cm}^{-1},$  380  $\mbox{cm}^{-1},$  1035  $\mbox{cm}^{-1}$  and 1100  $\mbox{cm}^{-1}$  in the spectrogram of Hier-S-1 further confirm the formation of MFI frameworks (Figure 2b).<sup>[22]</sup> Furthermore, these bands strengthened in the pattern of nano S-1 for its higher crystallinity. In FT-IR spectrum, it is obviously that the as-synthesized both Hier-S-1 and nano S-1 show band at 550 cm<sup>-1</sup> specifically assigning to five-ring (pentasil) structures in MFI zeolites, while there is no this adsorption band in that of the initial silica spheres (Figure 2c), which further conform the formation of MFI structures.[23]

The N<sub>2</sub> adsorption-desorption isotherms can exhibit the characteristics of pore structures of as-synthesized samples (Figure 2d). For Hier-S-1, a slight hysteresis loop at relative pressures (0.5–0.85) indicates the existence of mesopores in this sample. Brunauer-Emmett-Teller (BET) surface areas vary from 9 m<sup>2</sup> g<sup>-1</sup> (solid silica spheres) to 102 m<sup>2</sup> g<sup>-1</sup> (Hier-S-1), which

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Figure 1. TEM images of solid silica sphere (a), Hier-S-1 (b) and nano S-1 (c), HRTEM image of nano S-1 (inset); (d) photographs of colloidal solution Hier-S-1 (left) and nano S-1 (right) with Tyndall effect; TEM images of solid silica sphere (e), Hier-S-1 (f) and nano S-1 (g) with larger sizes; (h) photographs of zeolite membrane prepared by nano S-1 colloidal suspension on a glass piece.



Figure 2. XRD patterns (a), UV Raman (b) and IR (c) spectra of different samples obtained with different crystallization periods. XRD peaks reflecting of (011) and (200) crystallographic plane strengthen after calcination (red line). (d-e) N<sub>2</sub> adsorption-desorption isotherms of silica spheres, Hier-S-1, Hier-S-1(c) and nano S-1 at 77 K. (f) (f) Pore size distribution curves for Hier-S-1 (right) and nano S-1 (left). These results are according to Horvath-Kawazoe model (nano S-1 and microporous part of Hier-S-1) and NLDFT model (mesoporous part of Hier-S-1).

further indicates the open mesoporosity aroused by desilication. On the other hand, after calcination, the surface area of Hier-S-1 (c) increase to 301 m<sup>2</sup> g<sup>-1</sup> and mircopore volumes alter from 0 cm<sup>3</sup> g<sup>-1</sup> (Hier-S-1) to 0.08 cm<sup>3</sup> g<sup>-1</sup>, which suggests the existence

of a large number of micropores in the hierarchical zeolite nanospheres after the organic SDA being removed. The pore size distribution curves of these samples in Figure 2f (right) obtained by using the non-local density functional theory

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(NLDFT) further confirm the existence of open mesopores (with a peak at 6 nm) and micropores in this sample after calcination, which are aroused by desilication and zeolite crystalizing, respectively.<sup>[24]</sup> The N<sub>2</sub> adsorption analysis results are consistent with the TEM observations. Nano S-1 possess a type-I isotherm and a surface area of 452 m<sup>2</sup> g<sup>-1</sup> after removal of template in 550 °C. All sharp adsorption increasement is before 0.05 and after 0.95 in adsorption branch, declaring that nanosized zeolites are identically microporous. Compared with the pore volume of Hier-S-1 (c) (0.21 cm<sup>3</sup> g<sup>-1</sup>), the reducing of pore volume in nano S-1 (0.16 cm<sup>3</sup> g<sup>-1</sup>) can be attributed to the disappearance of mesopores and the development of micropores. Pore size analysis results of these particles in Figure 2f (left) match the exactly with data known from works reported.<sup>[25]</sup>

On the basis of above results, we propose an in situ crystallization process for the formation of Hier-S-1 and nano S-1 from silica spheres. In the above synthesis process, it is worth to notice the dual functions of TPAOH. Firstly, TPAOH can ionize into TPA<sup>+</sup> and OH<sup>-</sup> readily in aqueous solution. Unlike traditional method, water in our synthesis system is scanty and OH<sup>-</sup> in the reaction mixture is rather high in water with a theoretical concentration of 8.4 M. The high density of OH<sup>-</sup> can promote desilication in the silica spheres, which causes generation of mesoporosity.<sup>[26a, b]</sup> Then, such a high level of hydroxides can amplify the interaction between TPA<sup>+</sup> and amorphous solid interface,[26c] and the Si-O-TPA units can further react with dissolved SiO42-. The obtained structures are charge-balanced and hydrophilicity-steady, hindering the further OH<sup>-</sup> etching in the crystalline surface of as-formed mesopore.<sup>[26d,</sup> <sup>27]</sup> Here we obtain the Hier-S-1. The classic model of zeolites formation reported by M. Tsapatsis et al. indicates that the nucleation happens selectively in the liquid phase interface between the hierarchical aluminosilicates and silicates gels.<sup>[23, 28]</sup> As the reaction proceeds, the dissolved SiO42- species in the reaction mixture grow into the surface of Hier-S-1. The spherical morphology has been changed into angular particle with solid surface, and porous structure can be still observed inside. (Figure S4) With further repolymerization and rebonding of dissolved silica species, the mesoporous structures in the sample disappear and then well-ordered zeolitic MFI structure are finally formed (Figure 1c and 1d). Since the high concentration of gel causing the nucleating individually in the liquid phase need more activity energy, the repolymerization of dissolved SiO<sub>4</sub><sup>2-</sup> around the hydrated cation TPA<sup>+</sup> happens in the original amorphous silica spheres in situ. Moreover, both Hier-S-1 and nano S-1 may be effectively prepared by controlling the balance of TPAOH density and reaction time (Table S1, S2&S3 in Supplementary Information). Under a higher density of TPAOH or a longer reaction synthesis system, the in situ crystallization reaction occurs much more promptly and profoundly, indicating that base density and reaction time play significant roles in the synthesis process.

With the further hydrothermal treatment of additional TPAOH, a silicon-recrystallized process occurs in the crystallized wall of Hier-S-1 and aluminium can be simultaneously incorporated into these as-prepared zeolites during this process. Presence of aluminium species in zeolites framework may provide active acid

catalytic sites. The pore structures of Hier-S-1 are changed after hydrothermal treatment with AICI<sub>3</sub> (AI-Hier-S-1). Sizes of mesopores in the Al-Hier-S-1 samples increase obviously as shown in Figure 3a. After calcination, the Al-Hier-S-1 has a BET surface area of 305 m<sup>2</sup> g<sup>-1</sup> and a pore volume of 0.41 cm<sup>3</sup> g<sup>-1</sup>. The pore size distribution owns two peaks; a microporous one is before 2 nm and another has an average pore size of 7 nm, respectively (Figure 3d). The increasement of pore volume can be attributed to the magnifying of pore size. Without any Al ions introduced into the system, the nanoparticles recrystallize and form a big crystal after hydrothermal treatment (Figure S5-a). The N<sub>2</sub> adsorption-desorption curves in Figure S6 reveal that the non-aluminium sample is totally microporous, which agrees with the TEM observation. In the depolymerization of crystallized wall and rebonding of silica species and TPA<sup>+</sup> process, hydrolytic aluminium ions can slow down the condensation reaction by decreasing the pH value, thus maintain the hierarchical structures and dispersibility of the samples during the hydrothermal treatment. Other aluminium species (NaAlO<sub>2</sub> and Al(OPr<sup>i</sup>)<sub>3</sub>) and different ratios of TPA/Al can also be introduced into the hydrothermal process, and the results are investigated and discussed in ESI (Figure S7 and S8). The X-ray photoelectron spectroscopies (XPS) results of different Al-Hier-S-1 samples are shown in Figure 3b and Figure S9. The AI 2p XPS presents a single peak between 72 eV to 76 eV for each sample, however, the binding energies are different, attributing to different chemical conditions of Al in samples.



Figure 3. (a) TEM images of Al-Hier-S-1 (treated with AlCl<sub>3</sub>). (b) Al 2p XPS spectra of Al-Hier-S-1. (c) N<sub>2</sub> adsorption–desorption isotherms of Al-Hier-S-1 after calcination at 77 K. (d) Pore size distribution curve for Al-Hier-S-1. The result is according to NLDFT model.

Such Al-Hier-S-1 can be used to encapsulate Pd nanoparticles for its mesoporosity, which makes it (Pd/Al-Hier-S-1) a great candidate for multifunctional catalyst for either cooperative or independent acidic catalysis or hydrogenation.<sup>[29]</sup> Benzimidazole derivatives have been a popular kind of attractive

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compounds for its vital medical and biological applications.<sup>[30]</sup> The synthesis of a biologically active compound, 2-(4aminophenyl)-1H-benzimidazole can be selected as a model reaction to demonstrate the functionalized Pd/Al-Hier-S-1 can work as a bifunctional catalyst in the synthesis of benzimidazole derivatives including a catalytic acid reaction and hydrogenation. XRD patterns of Pd/Al-Hier-S-1 sample shows a weak peak in 40° (20) in Figure 4b indicating existence of small-sized Pd nanoparticles. Calculated from Scherrer Equation, Pd nanoparticles have an average size of 6 nm, which is matched with the TEM observation in Figure 4a and Pd nanoparticle size distribution in Figure S12. The lattice fringes could be clearly observed, suggesting that the high crystallinity of Pd particles. The interplanar distances are measured to be 0.228 nm and assigned to the (111) reflection of the cubic (fcc) metal nanoparticle. The Pd 3d XPS spectra in Figure 4d consists a doublet corresponding to Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub>. The peaks around 335.7 and 340.9 eV are attributed to metallic Pd<sup>0</sup>, and those around 337.1 and 342.7 eV correspond to Pd<sup>2+</sup> species. From Energy Dispersive X-Ray Spectroscopy (TEM-EDAX) analyses in Figure 4c, Pd/Al-Hier-S-1 is loaded with 0.76 wt% palladium and 5.4 wt% aluminium.



**Figure 4.** (a) TEM image of Pd/Al-Hier-S-1 and HRTEM image of Pd nanoparticles inset. (b) XRD patterns of Pd/Al-Hier-S1. Amplified patterns (35° to 45°) is amplifying inset. (c) EDAX analysis of Al-Hier-S-1, peaks without labels are Cu and C that come from Cupper grid. (d) Pd 3d XPS spectra of Pd/Al-Hier-S-1.

The as-prepared Pd/Al-Hier-S-1 is then used as the dualfunctional catalyst for the one-pot cascade synthesis of 2-(4aminophenyl)-1H-benzimidazole. The reaction route is depicted in Figure 5a. The substrate 4-nitro-benzaldehyde and 1,2phenylenediamine diffuse through our catalyst and convert into the intermediate 2-(4-nitrophenyl)-1H-benzimidazole. With further reaction, the intermediate molecule is reduced by hydrogen under catalysis of Pd nanoparticles and then the target molecule 2-(4-aminophenyl)-1H-benzimidazole can be obtained. The final product are characterized by mass spectrometry and 1H NMR spectroscopy respectively. Both the characterization data are presented in the ESI. The conversion of products are characterized by High-resolution liquid chromatography (HPLC) with a UV detector. Nearly 100 % conversion of the substrate 4nitro-benzaldehyde and 87 % yield in average of the targeted compound 2-(4-aminophenyl)-1H-benzimidazole are obtained after 5 cascade catalysis. The Pd/Al-Hier-S-1 can maintain high catalytic activity and great chemical stability during five successive cycles. Steady conversions of target molecule are shown in Figure 5c, which suggests that there is no evident activity change. The high catalytic activity of the Pd/Al-hier-S-1 may be attributed to the two separate active sites, widelydistributed aluminium species in the crystallized porous framework and high crystallinity of small-sized Pd particles in this nanoreactor. The hierarchical structure can immobilize noble metal particles, shorten reaction pathways and allow the fast diffusion of the reactants and products. The excellent performance in this cascade catalysis, stable and recyclable properties confirm that the designed Pd/Al-hier-S-1 can be an effective and powerful catalyst for the cascade reaction of synthesizing benzimidazole derivatives.



**Figure 5.** (a) Schematic illustration of the multistep reaction sequence involving an acid catalysis and subsequent catalytic hydrogenation for the synthesis of 2-(4-aminophenyl)-1H-benzimidazole. (b) Synthesis yields of cascade catalysis and table for the recycle ability of Pd/Al-Hier-S-1 (c) in five successive reactions.

#### Conclusions

In summary, we have demonstrated a novel and elegant in situ crystallization route to prepare nanosized hierarchical zeolites. Through the dual functions of TPAOH (both resulting in alkaline desilication and directing MFI zeolite structure), hierarchical zeolite nanoparticles are facilely obtained by silicates polymerizing around TPA<sup>+</sup> process in situ in the framework of mesopore during the crystallization process. These hierarchical zeolites can further proceed post-synthesis, with aluminium species incorporated among the crystallized frameworks and then anchoring noble metal nanoparticles. On the basis of the available acidity and encapsulated palladium species that offers hydrogenation activity, the as-synthesized materials are used as

a cascade catalyst to synthesize benzimidazole derivatives. The nanocatalysts show remarkable catalytic performance, representing chemical stable and recyclable properties. It is not hard to envisage that this in situ strategy reported in this work can be applied into the design of other sophisticated zeolite platform or nanoreactors.

#### **Experimental Section**

Chemical and materials. Tetrapropyl ammonium hydroxide (TPAOH, 25 wt% in H<sub>2</sub>O) and L-ascorbic acid were obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). Tetraethylor-thosilicate (TEOS), potassium tetrachloropalladate (K<sub>2</sub>PdCl<sub>4</sub>), 4-nitro-benzaldehyde and 1,2-phenylenediamine were obtained from Aladdin chemical reagent Co. (3-Aminopropyl) triethoxysilane (APTES), (3-mercaptopropyl) trimethoxysilane (MPTMS) and (4-aminophenyl)-1Hbenzimidazole standard were pur-chased from Sigma-Aldrich. Ammonia solution (27 wt%), aluminium chloride (AlCl<sub>3</sub>), sodium aluminate (NaAIO<sub>2</sub>), Aluminium isopropoxide (AI(OPr<sup>i</sup>)<sub>3</sub>, 99.5 wt%), ethanol, isopropanol and methanol were purchased from Beijing Chemical Works. Deionized water was used for the current experiments. All the chemicals were used without further purification.

Synthesis of silica sphere. Silica spheres were synthesized via a modified Stöber reaction.<sup>[21]</sup> Firstly, 50 mL of islpropanol, 40 mL of distilled water and 10 mL of ammonia (27 wt%, aqueous solution) were mixed and stirred in 40 °C water bath for 10 mins. Then 0.561 g TEOS (0.6 mL, 0.04 mol) was added into the reaction solution dropwisely and stirred vigorously for 30 mins to form the silica seeds. After that, 2.244 g (2.4 mL, 0.16 mol) of TEOS was added into the mixture and kept for 2 h at 40 °C for further silica sphere growth. The silica spheres were collected by centrifugation with a condition of 10000 r per minute. Different organic groups can be doped by introducing mixing different organosilane into later TEOS in the last step. For example, amino-group can be introduced by mixing 5 wt. % APTES in the later TEOS addition for silica growth. The products isolated by centrifugation were washed with ethanol and water repeatedly, and finally dried at 65 °C in oven overnight.

Synthesis of nanosized and hierarchical zeolites. Typically, 0.60 g (0.05 mol) of silica spheres and a matching amount of TPAOH solution were added into auto-clave. Extra water was added to keep the ratio of Si: TPAOH:  $H_2O$  into x: 1: 10x. The obtained sol was dispersed via sonication for 10 mins to make sure the mixture is homogeneous. Then the Teflon-lined autoclave was sealed and heated in an oven of 140 °C for 2-144 h. After reaction, the products were washed with distilled water and obtained by centrifugation and dried at 65 °C. To remove organic template, the samples were heated at 550 °C in air for 6 h. Detailed reaction conditions and crystallization results of the samples were depicted in Table S1 with different silica sources and ratios of Si: TPAOH:  $H_2O$ . Nanosized hierarchical zeolite

spheres and faultless nano zeolite particles were denoted as Hier-S-1 and nano S-1, respectively.

Al-riching decoration of hierarchical zeolites sphere and incorporating Pd nanoparticles in mesopores. Al-doped hierarchical zeolites (Al-Hier-S-1) were synthesized by a TPAOH and aluminium species treatment method. Typically, 0.12 g asprepared hierarchical zeolites was treated with 10 mL solution of 0.1 M TPAOH in the Teflon-lined autoclave. Different amounts of aluminium species were added into TPAOH solutions, with amount to keeping the ratio of Si: Al= 4. Al was incorporated into the framework of the crystallized wall of Hier-S-1 with the presence of TPAOH.<sup>[20]</sup> The autoclave was heated to 170 °C in an oven and the hydrothermal process went through 72 h. The products were collected by centrifugation, washed with deionized water three times, and then dried overnight at 65 °C. To incorporate Pd nanoparticles, 40 mg of Al-Hier-S-1 and 140 mg of L-ascorbic acid were mixed in 9 mL of deionized water. 0.064 mL (10 g L<sup>-1</sup>) of K<sub>2</sub>PdCl<sub>4</sub> aqueous solution was then added to the mixed suspension and stirred at room temperature for 10 min. The resulting solid were collected by centrifugation, washed with deionized water, and then dried at room temperature under vacuum overnight. The obtain samples were denoted as Pd/Al-Hier-S-1.

**Cascade catalysis of 2-(4-aminophenyl)-1H-benzimidazole.** 50 mg of Pd/Al-Hier-S-1 was dispersed in 10 mL of methanol via sonication, followed by the addition of 66 mg (0.4 mmol) 4-nitrobenzaldehyde and 54 mg (0.5 mmol) 1,2-phenylenediamine. The resulting mixture was stirred at reflux temperature under an air atmosphere for 4 h and then transferred into a steel pressure vessel without any separation. The vessel was then charged with H<sub>2</sub> to 2 bar and left to react for 8 h. After the reaction was complete, the reaction mixture was diluted with methanol and the catalyst was separated by centrifugation. After washing with methanol for three times, the catalyst were dried at 65 °C in oven overnight.

Characterization. TEM (Field Emission Transmission Electron Microscopy) analysis was conducted on FEI Tecnai G<sup>2</sup> F20 stwin D573 field emission transmission electron microscope operated at 200 KV. SEM (Scanning Electron Microscopy) analysis was conducted on JEOL JSM-6700F field-emission scanning electron microscope. The particle size and zeta potential were measured by photon correlation spectroscopy employing a Nano ZS90 laser particle analyzer (Malvern Instruments, UK) at 25 °C (The refractive index and absorbtivity parameters were used as below: SiO<sub>2</sub> 1.450, 0.010). Powder Xray diffraction (XRD) patterns were obtained by using a Rigaku 2550 diffractometer with CuK $\alpha$  radiation ( $\lambda$  = 1.5418 Å). N<sub>2</sub> adsorption-desorption isotherms were obtained at -196 °C on a Quantachrome Nova TouchWin and Micromeritics 2420 sorptometer. Samples were degassed at 120 °C for a minimum of 12 h prior to analysis. Pore size distribution plot was obtained by the Tarazona nonlocal density functional theory (NLDFT) model assuming cylinder pore geometry with adsorption branch data. The micropore volume was calculated according to de

Bore model, regarding the materials as polar material and choosing the relative pressure points between 0.4-0.6. FT-IR spectra were recorded by using a Bruker IFS-66V/S. FT-IR spectrometer employing the KBr disk method. Raman spectra of zeolites was performed on a Renishaw inVia Raman microscope. The yield of the catalytic product was analyzed by Highperformance liquid chromatography-mass spectrometry (HPLC) with an external standard substance Agilent 1290-micrOTOF Q II (LC Column: Agilent ZORBAX SB-C8, 1.8 µm, 2.1 mm x 50 mm; Flow rate: 0.1 ml/min; Eluent: Linear gradient elution water: acetonitrile (7/2 to 3/8, v/v); Temperature: 30 °C; Run time: 3. mins; Detector: Agilent ICF System, Spec: 190 nm~ 400 nm. Xray photoelectron spectroscopy (XPS) data were collected on a Thermo ESCALAB 250 operated at 15 kW (mono chromatic Al-Ka radiation, 1486.6 eV). Mass spectra were recorded in the positive-ion mode on a Bruker- Esquire HCT instrument interfaced by an electrospray ionization source. 1H NMR spectra was obtained with (CD<sub>3</sub>)<sub>2</sub>SO as the solvent on a Germany Bruker DMX 300 MHz spectrometer.

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#### **Conflict of interest**

The authors declare no conflict of interest.

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A topotactic synthetic methodology allows the synthesis of nanosized hierarchical MFI zeolite spheres and particles by choosing silica speres as precursor and TPAOH as SDA. Dissolved silica species rebond around TPA<sup>+</sup> and zeolite structures generate in the defect surface of mesopore walls from desilication of the initial silica spheres. With further crystal growth, zeolite nanoparticles can be obtained.

Ang Li, Xue Wang, Tao Wang, Huali Liu, Tunan Gao, Meihong Fan, Qisheng Huo and Zhen-An Qiao\*

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