An In Situ Carbonaceous Mesoporous Template for the Synthesis of Hierarchical ZSM-5 Zeolites by One-Pot Steam-Assisted Crystallization

Yudian Song, Zile Hua, Yan Zhu, Xiaoxia Zhou, Wei Wu, Linlin Zhang, and Jianlin Shi^{*[a]}

Zeolites, which possess uniform micropores, large specific surface area, and intrinsic acidity, have been widely used in many industrial processes related to adsorption, separation, ion exchange, and catalysis.^[1] However, due to the inherent small pore sizes of conventional zeolites (<1.5 nm), the mass transfer in them is restricted, and consequently their performances need to be further improved, especially in processes involving bulky molecules. A reduction in particle size, for example in nanosized zeolite crystallites, could partially resolve the diffusion problem in microporous zeolites due to their larger external surfaces and the decreased diffusion path length in the micropore channels. However, the collection difficulty in the preparation or during applications limited their ever wider applications.^[2] Alternatively, hierarchical zeolites, which combine the strong acidity and high stability of crystalline microporous zeolites with the enhanced molecular diffusion resulting from additional mesoporosity, have become a research focus in recent years and have been developed through multistep post-synthesis demetallation or desilication treatments and templating synthesis with careful design of the synthesis procedure or the mesoscale templates.^[3]

In the soft templating route, organosilanes,^[4] bifunctional multiple-quaternary ammonium-type surfactants,^[5] and cationic polymers^[6] were explored to avoid the occurrence of phase separation during the preparation of hierarchical zeolites. Interestingly, by using ordinary surfactant templates (e.g., F127 and P123), recently, hierarchical zeolites were successfully synthesized by the steam-assisted crystallization (SAC) process in our group.^[7] However, excessive consumption of the surfactant templates (about 44 wt % in the compositions) increases the material costs and brings about environmental problems. Alternatively, hard templates like nanosized carbon particles,^[8] carbon nanotubes,^[9] and ordered mesoporous carbon materials (CMKs) ^[10] are also attractive. Unfortunately, these synthesis procedures usually

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.201200744.

suffered from process complexity due to the hydrophobicity of the carbon templates, and the intracrystal mesopores are not always open to the external surface of the zeolite crystals.^[6] To overcome this drawbacks, Tang and co-workers introduced mesopores in ZSM-5 by in situ hydrothermal treatment of a solution containing alkali-dissolved SBA-15 containing carbonized surfactant P123 in the mesopores.^[11] As an extension of the carbon template route, Christensen and co-workers synthesized hierarchical zeolites using sucrose as the mesoporous template precursor. However, high-temperature carbonization pretreatment under inert gas protection was required.^[12] Recently, White et al. found that carbonaceous materials could be prepared from renewable inexpensive carbohydrate feedstocks, such as D-fructose, and hydrothermal carbonization could be performed at relatively low temperatures to yield materials with functionally useful surface chemistry.^[13] Based on the similarity of processing conditions for both the hydrothermal carbonization of carbohydrate feedstocks and the zeolite crystallization transformation in the SAC process, we report herein a novel and facile one-pot route to synthesize hierarchical zeolites with an in situ carbonaceous template, in which the zeolite crystallization transformation and carbonaceous template formation were accomplished simultaneously.

Scheme 1 illustrates the representative synthetic route for the preparation of hierarchical zeolites by the one-pot process. In the first step, a homogeneous solution of the primary zeolitic units, microporogen (TPAOH), aluminosilicate species and sucrose was simply prepared, and then the solution gradually converted into the dry gel during the subse-



Scheme 1. Representation of the procedure for preparation of hierarchical zeolites with an insitu carbonaceous template. TEOS=tetraethylorthosilicate, TPAOH=tetrapropylammonium hydroxide.

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quent aging and drying, in which the consumption of sucrose templates was considerably lower (about 14 wt% in the compositions) and high-temperature pre-carbonization processing was unnecessary compared with references [7,11,12]. After that, the resultant dry gel was hydrothermally treated in a water-steaming environment and changed into brown powders (Figure S1 in the Supporting Information), in which the crystallization of zeolite and the in situ hydrothermal carbonization of sucrose subtly took place synchronously. Finally, the microporous and mesoporous templates were removed through calcination in air, and then hierarchical zeolites were successfully prepared (Figure S2 in the Supporting Information).

The crystallization and porous structural features of synthesized hierarchical ZSM-5 zeolites (designated as HZ-w, where w is the mass of added water in SAC treatment) were characterized by using XRD and N₂ physisorption techniques. The corresponding textural properties are summarized in Table 1. As shown in Figure 1 a, the XRD patterns of

Table 1. Textural properties of synthesized hierarchical zeolites.^[a]

Sample	$S_{\rm BET} [{ m m}^2 { m g}^{-1}]$	$S_{\rm ext} [{ m m}^2 { m g}^{-1}]$	$V_{ m pore} [m cm^3 g^{-1}]$	$D_{\rm pore}$ [nm
HZ-0.08	421	238	0.79	15.5
HZ-0.12	458	247	0.63	13.0
HZ-0.15	419	182	0.47	17.9
HZ-0.20	363	88	0.25	15.4
HZ-HT ^[b]	436	275	0.56	11.2
ZSM-5	287	50	0.14	-

[a] The surface area was calculated using the Brunauer–Emmett–Teller (BET) method. $S_{\text{ext}} = S_{\text{BET}} - S_{\text{micro}}$, where the micropore area was calculated from *t* plot analyses. V_{tot} is the single-point adsorption total pore volume at $P/P_0 = 0.97$. [b] HZ-HT is the hydrothermal treated sample of HZ-0.12 at 100 °C for three days.

the synthesized hierarchical zeolites exhibit the well-resolved characteristic peaks for the MFI zeolite. Generally, the intensity of the X-ray diffractions become stronger with an increasing amount of added water, which means that the increased steam concentration could accelerate the crystallization of zeolite and is consistent with the reported results.^[14] Especially for HZ-0.08, slight crystallization of zeolite can be found, as the amount of water added is far lower than needed for the complete crystallization transformation of dried gel precursors.

The N₂ adsorption/desorption isotherms shown in Figure 1 b of the hierarchical ZSM-5 zeolites demonstrate typical type-IV curves with steep H1 hysteresis loops and exhibit a significant uptake at the relative pressure (P/P_0) of 0.7–0.9, which indicates the existence of the textural mesoporosity. As shown in Table 1, the BET surface area, external surface area, and the total pore volume of hierarchical ZSM-5 zeolites are distinctly larger than those of conventional ZSM-5 (287 m²g⁻¹, 50 m²g⁻¹, and 0.14 cm³g⁻¹). Further, their total pore volumes gradually decreased from 0.79 to 0.63, 0.47, and 0.25 cm³g⁻¹ with an increasing amount of added water amount during SAC treatment, which resulted from the rapid crystallization transformation of amorphous



Figure 1. a) XRD patterns and b) N_2 adsorption/desorption isotherms of hierarchical zeolites synthesized by using different amounts of water in the one-pot SAC process.

precursors under higher steam concentrations.^[15] However, the BET surface area and external surface area of HZ-0.12 (458 m²g⁻¹, 247 m²g⁻¹) are higher than those of HZ-0.08 (421 m²g⁻¹, 238 m²g⁻¹), which may be due to the generation of microporous structures of zeolite crystals, thus compensating the loss of mesoporosity. With an increased amount of water used, nevertheless, the BET surface area and external surface area decreased to 419/182 m²g⁻¹ for HZ-0.15 and 363/88 m²g⁻¹ for HZ-0.2 respectively, along with the improved zeolite crystallinity.

In this one-pot in situ carbonaceous template process for preparation of hierarchically structured zeolites, although the detailed formation mechanism is unclear at present, it is considered that there are at least two intercrossed courses. One is the hydrothermal carbonization of carbohydrate feedstock, where it is believed that just sufficiently "hard" carbonaceous substances could act as mesopore scaffolds, although a complex mixture consisting of polysaccharides, aromatic compounds, and carbon spheres with hydrophilic surface could be formed in this course.^[16] Another is the crystallization transformation of amorphous gels, which, in an ideal circumstance, should be restricted by or be cooperative with the preformed carbonaceous templates for the production of hierarchical micro- and mesoporous zeolites. Since the steam concentration during the SAC treatment showed inverse effect on these two courses, the crystallization transformation of amorphous aluminosilicate precursors and the hydrothermal carbonization of sucrose should be kinetically balanced, which could be realized by tuning the amount of

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added water. For sample HZ-0.08, a small amount of water addition during SAC treatment led to the slight crystallization of dried gel precursor because of the low driving force of crystallization,^[15] while it was in favor of the carbonization of sucrose for the development of mesostructured carbonaceous templates. Meanwhile, when an excessive amount of water was added, such as for sample HZ-0.2, the products were highly crystalline, but with lower mesoporosity, resulting from the relatively higher steam concentration and consequently lower carbonization rate of sucrose.^[15] Thus, only under the use of an appropriate amount of water, such as for samples HZ-0.12 and HZ-0.15, was a compromised state achieved between crystallization transformation of amorphous gels and hydrothermal carbonization of sucrose. Under these conditions, hierarchical ZSM-5 zeolite could be obtained, which also implies that hierarchical zeolites with adjustable micro- and mesoporosity could be synthesized simply by changing the amount of water added during SAC treatment. Moreover, the effect of the amount of sucrose as the mesopore generator precursors on the mesoporosity of hierarchical zeolites was also investigated. As shown in Table S1 and Figure S3 in the Supporting Information, it is clear that the external surface area, pore diameter, and pore volume will increase, but the framework becomes less crystalline when larger amounts of sucrose are introduced.

Furthermore, FESEM for HZ-0.12 was used to reveal the detailed morphology of the hierarchical zeolites (Figure 2 a, b). The low-magnification image shows that the particles are typically ellipsoidal with rough surfaces, while the high-magnification image illustrates that there are plenty of open mesopores on the hierarchical zeolite surfaces. The representative HR-TEM characterization of sample HZ-0.12 (Figure 2 c, d) clearly shows the continuous lattice fring-



Figure 2. Representative electron microscopic images of HZ-0.12. a,b) FESEM images at low and high magnification, respectively. c,d) TEM images at low and high magnification, respectively.

es co-existing with the mesoporous structures, which further confirmed that the resultant hierarchical zeolites are singlecrystalline phases.^[7] Additionally, the hydrothermal stability of the representative sample HZ-0.12 was also investigated. After hydrothermal treatment at 100 °C for three days, the as-synthesized hierarchical zeolites still retained the MFI structure (see Figure S4a in the Supporting Information), and the BET surface area decreased by only 6% (see Figure S4b in the Supporting Information and Table 1), which demonstrated that the hierarchical zeolites possess better hydrothermal stability than reported ordinary amorphous mesoporous materials.^[17]

Friedel–Crafts acylation of aromatic compounds is one of the most important reactions for the synthesis of aromatic ketones, which are valuable intermediates in pharmaceutical industry.^[18] In general, these reactions are catalyzed by homogeneous catalysts such as AlCl₃, FeCl₃, and ZnCl₂, which unfortunately suffer from serious problems such as high moisture sensitivity, difficult separation, and undesirable environmental impact.^[19] Towards the development of environmentally benign process for the production of aromatic ketones, the synthesized hierarchical ZSM-5 zeolites were applied and proved to be efficient heterogeneous catalysts for the Friedel–Crafts acylation of anisole.

Catalytic test conditions employed in our investigation were similar to literature reports,^[18] where the only difference is that nitrobenzene was used as an internal standard instead of solvent. The reaction is shown in Scheme S1 in the Supporting Information. A high selectivity of larger than 97% to the valuable product *p*-methoxyacetophenone (*p*-MAP) was achieved for both the hierarchical ZSM-5 (HZ-0.12) and the commercial microporous ZSM-5 catalysts. However, the catalytic activity of the catalysts differed considerably. Figure 3 shows the anisole conversion as a function of reaction time using hierarchical zeolite HZ-0.12 and ZSM-5 as catalysts. Because of the relatively small size of the anisole molecule, it is able to diffuse throughout the zeolitic micropores without significant hindrances. Thus, in the case of conventional ZSM-5, the conversion of anisole



Figure 3. Time dependence of the anisole conversion in Friedel–Crafts acylation of anisole with acetyl chloride using hierarchical ZSM-5 (HZ-0.12) and conventional ZSM-5 as catalysts. Reaction conditions: catalyst 0.11 g, anisole 12.5 mmol, acetyl chloride 12.5 mmol, nitrobenzene 1.0 g, T = 120 °C.

Chem. Asian J. **2012**, *00*, 0–0

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reached about 20.1% in 3 h of reaction. Comparatively, thanks to the enhanced molecular diffusion in the additional mesoporosity in hierarchical zeolites, HZ-0.12 samples showed noticeably higher initial anisole reaction rate, and the anisole conversion was 37.8% in the same time period of 3 h. This result is consistent with previous reports,^[18] in which Serrano et al. considered a stronger inhibition effect of the adsorbed *p*-MAP product than of the reactant anisole, which were both involved in this acylation reaction. Moreover, the larger mesopore size of hierarchical zeolites was believed to provide less steric restriction and the coke formation than the micropores of pure zeolites and was in favor of improving catalytic performance. Additionally, the combination of a good accessibility and strong acidity in hierarchical zeolite should also be responsible for the improved catalytic properties as compared with amorphous Al-MCM-41.^[3,17,19] Finally, the reusability of hierarchical zeolites was studied, and limited activity loss in the anisole conversion was found after the second cycle (Table S2 in the Supporting Information).

In conclusion, hierarchical ZSM-5 zeolites have been synthesized by a novel and facile one-pot SAC process, in which the mesoporous structures were created by the in situ hydrothermal carbonization of a renewable and low-cost carbohydrate feedstock (i.e. sucrose), accompanied by zeolite crystallization. A balanced zeolite crystallization and mesoporous structure formation can be achieved simply by tuning the amount of water added during SAC synthesis. The synthesized hierarchical zeolites possessed superior hydrothermal stabilities, and as low as 6% loss of specific surface area was observed after three days of hydrothermal treatment. In Friedel-Crafts acylation of anisole, compared with the purely microporous counterparts, the synthesized hierarchical ZSM-5 zeolites showed significantly higher catalytic performances than conventional ZSM-5, with about 38% conversion of anisole and larger than 97% selectivity to *p*-MAP in 3 h of reaction.

Experimental Section

Synthesis of Materials

In a typical run, a mixture of aluminum isopropoxide (0.2 g, 1 mmol) and tetraethylorthosilicate (TEOS, 10.4 g, 50 mmol) was added to distilled water (18 g, 1 mol) under continuous stirring at 40 °C. After 2 h, tetrapropylammonium hydroxide (TPAOH, 25% in water, 4.10g, 5mmol) was added dropwise into the solution. The mixture was stirred vigorously for 4 h. Then sucrose (0.69 g, 2 mmol) was added. The molar ratio of the resultant solution was SiO2:0.01 Al2O3:0.1 TPAOH:0.04 sucrose:20 H2O. Stirring was continued to form a solidified gel. Then the resultant gel was aged for about 7 h and dried at 50 °C for about 12 h. Subsequently, as reported for the steaming-assisted crystallization (SAC) process,^[20] this asprepared gel (1.0 g) was crystallized at 150 °C for 10 h, while a certain amount of water was added in the bottom of a two-layer-structured autoclave. Finally, the powder was calcined at 600 °C for 8 h in air to remove the organic templates. Depending on the water usage (w g) during the SAC treatment, the obtained hierarchical zeolite was labeled as HZ-w. where w = 0.08, 0.12, 0.15, and 0.2. For comparison, conventional ZSM-5 with the Si/Al ratio of 50 was purchased from Nanjing Jinling Petrochemical Co., Ltd. Before catalysis tests, all catalysts were ion-exchanged

three times with $\rm NH_4^+$ using a $10\,wt.\,\%~\rm NH_4NO_3$ solution and then calcined again in air at 550 $^{\circ}\rm C$ for 5 h to convert them into the H^+ form.

Characterization

Powder X-ray diffraction (XRD) patterns were recorded by using a Rigaku D/Max 2200PC diffractometer with Cu K α radiation (40 kV and 40 mA) with a scanning rate of 4 min⁻¹ over the 2 θ range of 5–50°. The nitrogen adsorption isotherms were measured on a Micromeritics Tristar 3000 porosimeter at 77 K for mesoporosity and microporosity. The surface area and micropore and mesopore distributions were calculated according to the BET and BJH theories. SEM micrographs of uncoated powders were obtained using a field emission scanning electron microscope Hitachi S4800. Transmission electron microscopy was performed with a JEOL-2010F instrument.

Catalytic Tests

The Friedel-Crafts acylation of anisole with acetyl chloride as the acylating agent was carried out in a 25 mL three-necked round-bottom flask with magnetic stirrer and a temperature-controlled heating jacket under N2 atmosphere. A chilled water reflux condenser was used to minimize the evaporation of acetyl chloride. To obtain accurate calculation of conversion, nitrobenzene was used as the internal standard for anisole. In a typical reaction, the catalyst (0.11 g), anisole (1.35 g, 12.5 mmol), and nitrobenzene (1 g) were mixed with continuous stirring under room temperature. Subsequently, acetyl chloride (0.98 g) was added dropwise into the reactor and then the heating process was run until the reaction temperature reached 120°C. Liquid samples were withdrawn periodically using a microsyringe after a certain reaction time and then analyzed by GC-MS (Agilent, 6890/5973N). Since acetyl chloride was volatile, conversion was calculated based on anisole. In addition, the spent catalyst was recycled by filtration, washing with acetone, drying, and calcining in air atmosphere at 550 °C for 4 h.

Acknowledgements

The authors gratefully acknowledge the support of this research by National Natural Science Foundation of China (Grant No. 50872140, 21177137), Science Foundation of State Key Laboratory of Heavy Oil Processing (2012-1-04) and Science Foundation for Youth Scholar of State Key Laboratory of High Performance Ceramics and Superfine Microstructures (SKL200901).

Keywords: heterogeneous catalysis • mesoporous materials • steam assisted crystallization • template synthesis • zeolites

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Received: August 13, 2012 Revised: September 3, 2012 Published online:

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Zeolites

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An In Situ Carbonaceous Mesoporous Template for the Synthesis of Hierarchical ZSM-5 Zeolites by One-Pot Steam-Assisted Crystallization



Blackened catalyst: Zeolites with large external surface area and mesopore volume were synthesized by a one-pot templating strategy, in which the crystallization proceeded concurrently with in situ carbonization templating to produce a mesoporous structure. The hierarchical materials exhibited superior catalytic performance over conventional zeolites in Friedel–Crafts acylation of anisole.

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