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ARTICLE

Synthesis of HZSM-5@silicalite-1 core-shell composite and its catalytic application in the generation of *p*-xylene by methylation of toluene with methyl bromide

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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A core-shell HZSM-5@silicalite-1 composite was synthesized by overgrowing silicalite-1 on the external surface of HZSM-5, and was characterized by XRD, SEM, TEM, NH₃-TPD, 1,3,5-triisopropylbenzene (TIPB) cracking and N₂ adsorption-desorption techniques. When used as catalyst for the formation of *p*-xylene through toluene methylation with methyl bromide, the HZSM-5@silicalite-1 composite exhibits *para*-selectivity of up to 76% with no sight of deactivation in an on stream period of 3 h. The excellent catalytic performance is attributed to the inactive silicalite-1 shell that extends the diffusion path length of xylenes while having the acid sites on the external surface of HZSM-5 fully covered.

Introduction

p-Xylene is required in the synthesis of terephthalic acid and terephthalates that are essential for the generation of polyesters.¹ Traditionally, *p*-xylene is produced by steam reforming of crude oils through high-cost and energy-consuming catalytic processes.² The selective formation of *p*-xylene by means of toluene methylation is a competing alternative. With channels of 10-membered rings favor for the diffusion of *p*-xylene rather than that of *o*-xylene and *m*-xylene, HZSM-5 zeolite is used to enable shape selectivity.^{3,4} Nevertheless, there is rapid isomerization of *p*-xylene to *o*-, and *m*-xylene at the acid sites on the external surface of unmodified ZSM-5 zeolite, giving xylene isomers with composition close to that of thermodynamic equilibrium (*p*-xylene 24%, *m*-xylene 51%, *o*-xylene 25%).⁵ For the enhancement of *para*-selectivity, HZSM-5 was modified using methods such as oxide impregnation (using oxides such as MgO,⁶ B₂O₃,⁷ or P₂O₅⁸), surface silanization^{9,10} and pre-coking with a carbonaceous material.¹¹ Despite the significant rise of *para*-selectivity, the catalytic activity and stability of the modified HZSM-5 are poor and the rapid loss of catalytic activity is a major concern. It hence remains a challenge to develop a stable catalyst that is highly active and selective for the production of *p*-xylene.

To minimize the isomerization of *p*-xylene to *o*-, and *m*-xylene, ZSM-5 zeolite is coated with an aluminum-free shell of similar structure. The composites allow better adsorption and/or diffusion of molecules within the zeolite crystallites in comparison with the counterparts that are modified by oxide impregnation. For example, Nishiyama et al.¹² developed an amorphous silica-alumina composite coated with silicalite-1 for the disproportionation of toluene. They reported *para*-selectivity of 90% but low reaction rate due to the diffusion

limitation through the thick silicalite-1 layer. Vu et al.^{13,14} synthesized a composite of HZSM-5 coated with a layer of polycrystalline silicalite-1 via repeated hydrothermal synthesis and achieved 99.9% *para*-selectivity in the alkylation of toluene with methanol. Nonetheless, the silicalite-1 polycrystals deposited after the second round of hydrothermal synthesis were randomly oriented and were not densely packed, resulting in silicalite-1 layer of low mechanical strength. These polycrystalline layers seem to have a low mechanical strength and could be problematic under severe condition (e.g., in a fluidized bed reactor). Core-shell structured composite zeolites can also be synthesized through the pretreatment of core zeolites. Li et al.¹⁵ successfully synthesized HZSM-5@silicalite-1 core-shell composite zeolites by pretreating the ZSM-5 seeds with diluted hydrochloric acid. They deduced that the silicalite-1 grew epitaxially on the HZSM-5, and the HZSM-5 seeds without the pretreatment can result in polycrystalline aggregates and the formation of stand-alone silicalite-1 crystals. Gora et al.¹⁶ reported a self-assembled method for the fabrication of composite zeolites with HZSM-5@silicalite-1 core-shell structure that involved pretreatment procedures of HZSM-5 crystals. It involved the use of Ti-butoxide to obtain MFI crystals of *b*-orientation prior to the hydrothermal synthesis of silicalite-1. The methods described above for the synthesis of core-shell composites are multi-step and complicated. Furthermore, reproducibility is still a major drawback.^{17,18}

In recent years, we conducted researches on aromatics preparation and natural gas conversion.¹⁹⁻²¹ A route has been developed for the catalytic conversion of methane using HBr as mediator in the presence of oxygen and H₂O.²²⁻²³ The method



involves the conversion of methane into CH_3Br over a suitable catalyst, followed by the catalytic transformation of CH_3Br to higher hydrocarbons and/or other compounds. The steps are conducted at atmospheric pressure, and the HBr is recycled and reused. Since CH_4 is relatively cheap, it is highly desirable to develop a new catalytic process for the use of CH_3Br as an alkylation agent to transfer toluene into *p*-xylene.

In this paper, HZSM-5 crystals with different crystal sizes were chosen as representative zeolite cores to be coated with an ordered silicalite-1 shell by a facile base-catalyzed sol-gel coating strategy using TPAOH as template and TEOS as silica source. We successfully generated a series of core-shell structured molecular sieves, viz. the HZSM-5@silicalite-1 composites. The catalysts were tested in the reaction of toluene methylation with CH_3Br . In fact, CH_4 acts as indirect alkylation agent since HBr is recycled in the system. To the best of our knowledge, the synthesis of this kind of composite molecular sieves using base-catalyzed sol-gel coating strategy and its application in toluene methylation with CH_3Br have never been reported before.

Results and discussion

Preparation and characterization of HZSM-5@silicalite-1 composite

HZSM-5 crystals with a Si/Al ratio of 75 prepared by hydrothermal method were chosen as a representative core material to construct silicalite-1 shells by the TPAOH-directed sol-gel coating route. FE-SEM images show that the parent HZSM-5 has hexagonal pseudoprism morphology (Figure 1A) with smooth crystal-faces and sharp edges, which are typical of crystalline zeolite. After coating with silicalite-1 shells using TPAOH as template, the as-prepared HZSM-5@silicalite-1 core-shell structured composites are uniform in size (Figure 1B). Despite the retention of the hexagonal pseudoprism morphology, there are changes such as obtuse edges and coarseness of crystal faces. Transmission electron microscopy (TEM) images (Figure 1C) show that the parent HZSM-5 is hexagonal in shape and has an average crystal dimension of $850 \times 650 \times 450$ nm, in good agreement with the SEM results. In Figure 1D, one can see that each HZSM-5 core was uniformly coated by a silicalite-1 layer 120 nm in thickness. However, based on the SEM and TEM pictures, it is not possible for us to quantitatively compare the crystal size of the core-shell structured composite with that of the parent core. Furthermore, we do not observe any sight of silicalite-1 crystals that are formed through homogeneous nucleation in the coating solution. For the large crystal cores, uniform silicalite-1 shell can also be coated on the mono-dispersed zeolites (Figure S1, Supplementary Information), and the shell thickness can be tailored pending on the amount of TEOS used. Figure 2 and Figure S2 (Supplementary Information) are the XRD patterns of the parent HZSM-5, large-crystal HZSM-5 and their HZSM-5@silicalite-1 composites. For HZSM-5@silicalite-1, the XRD profiles do not show the characteristic peaks of amorphous silica or any sight of impurities other than the MFI structure, indicating that the composites are HZSM-5@silicalite-1 zeolites.

Low-temperature nitrogen physisorption technique was used to evaluate the integrity of the silicalite-1 shell, and the BET surface areas and pore volumes are listed in Table 1. The BET surface area and total pore volume of the calcined HZSM-5@silicalite-1 composite are more or less similar to those of the

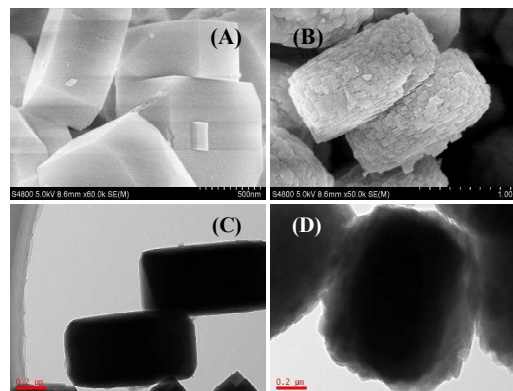


Figure 1. SEM images of (A) parent HZSM-5 and (B) core-shell structured composite molecular sieve HZSM-5@silicalite-1. TEM images of (C) parent HZSM-5 and (D) core-shell structured composite molecular sieve HZSM-5@silicalite-1.

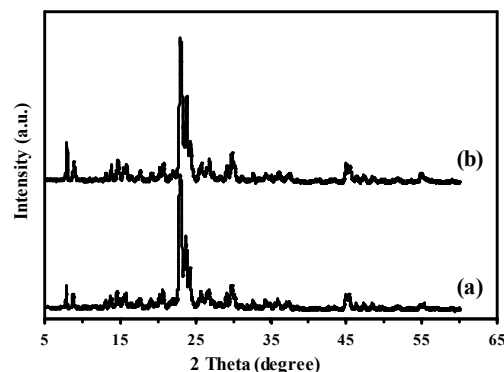


Figure 2. XRD profiles of (a) parent HZSM-5 and (b) HZSM-5@silicalite-1.

original parent HZSM-5 core, indicating the open porous structure of the silicalite-1 shell. However, without the high-temperature calcination step to remove the organic templates inside the micropores of silicalite-1 shell, the composite is much lower in surface area and pore volume. The results strongly suggest the presence of a well-integrated and dense shell.²⁴ We deduce that the crystallite surface of HZSM-5 was deprotonated in the basic medium, leading to a negatively charged surface. A strong interaction then occurred between the deprotonated Si-O⁻ and positively charged cationic surfactant micelles, resulting in a crystallite surface rich in TPA^+ . The silicate oligomers from TEOS hydrolysis then interacted with TPA^+ attached on the crystallite surface to bring about a coating-and-assembly process that occurred around the zeolite. Therefore, through facile TPAOH-directed sol-gel coating, uniform composite molecular sieves with a characteristic core-shell structure can be obtained.

Table 1. BET surface area and pore volume of various samples.

Samples	BET surface area (m ² /g)	Total pore volume (cm ³ /g)
Parent HZSM-5	380	0.136
As-calcined HZSM-5@silicalite-1 composite	384	0.147
As-synthesized HZSM-5@silicalite-1 composite	156	0.054

The results of temperature-programmed desorption of ammonia (NH_3 -TPD) are depicted in Figure 3. The patterns of the parent HZSM-5 shows two clear peaks at around 159 and

354 °C that correspond to the weak and strong acid sites, respectively (Figure 3, a). Two peaks at around 151 and 314 °C (Figure 3, b) are observed in the NH₃-TPD patterns of the core-shell HZSM-5@silicalite-1, which show left-shifts of approximately 8 and 40 °C relative to that of parent HZSM-5, respectively. The amount of total acidic sites on the core-shell HZSM-5@silicalite-1 is approximately 0.33 mmol g⁻¹, approximately 63% of that of the parent HZSM-5 (0.52 mmol g⁻¹, Table 2). In our previous work,²⁵ we confirmed that the high-silica MFI silicalite-1 samples are extremely low in acidity. The weakening of acidity and the reduction of acidic sites over the core-shell composite can plausibly be related to the surface of HZSM-5 core being covered by the high-silica shell, in agreement with the results of Qian et al.²⁶

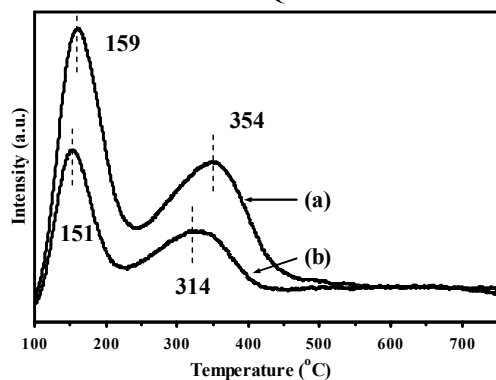


Figure 3. NH₃-TPD patterns of (a) parent HZSM-5 and (b) HZSM-5@silicalite-1.

It has also been reported that with a critical diameter of 9.5 Å, TIPB can rarely diffuse into the MFI zeolite structure where most of the acid sites are located.²⁷ The cracking reaction of TIPB is often used to measure the acidic sites on the external surface of zeolites. Table 2 shows the cracking results of TIPB over HZSM-5 and HZSM-5@silicalite-1 catalysts. It can be seen that the conversion of TIPB over HZSM-5@silicalite-1 is much lower than that over HZSM-5 catalyst, suggesting that most of the acid sites on the external surface of HZSM-5 zeolite are covered by silicalite-1 shell. The result is in consistent with that determined by NH₃-TPD characterization.

Table 2. Acidity characterized by techniques of NH₃-TPD and TIPB cracking reaction over the parent HZSM-5 and HZSM-5@silicalite-1

Samples	Weak acidic sites (mmol/g)	Strong acidic sites (mmol/g)	Total acidic sites (mmol/g)	Conversion of TIPB (%)
Parent HZSM-5	0.28	0.24	0.52	16.9
HZSM-5@silicalite-1	0.18	0.15	0.33	1.2

Catalytic performance

Toluene alkylation with methyl bromide as a typical shape-selective reaction was used to evaluate the catalytic performance of the HZSM-5@silicalite-1 catalysts. The catalytic performance of the parent HZSM-5 and HZSM-5@silicalite-1 catalysts with different core particle sizes are compared as depicted in Figure 4. One can see that compared with the parent HZSM-5, both HZSM-5@silicalite-1 catalysts show higher *para*-selectivity but lower toluene conversion. The parent HZSM-5 without silicalite-1 shell shows the highest activity (toluene conversion is 70.1%) and *p*-xylene selectivity

(24.4%) is close to its equilibrium value among the xylene isomers. It may be attributed to the remaining acidic sites on the external surface that promote rapid isomerization of *p*-xylene formed inside the pores. With the coating of HZSM-5 core with silicalite-1 shell, the catalyst exhibits higher *para*-selectivity. It is deduced that the silicalite-1 shell extends the diffusion path length of xylenes, eliminating nonselective alkylation on the external acid sites of the zeolites as a result. As characterized by the cracking experiment of TIPB, the amount of external acid sites decreases effectively after the coating of silicalite-1, in effect having the isomerization of *p*-xylene distinctly suppressed. At the same time, the two core-shell catalysts are lower than the parent HZSM-5 in toluene conversion. Catalytic synthesis of *p*-xylene by toluene alkylation is a typical acid-catalyzed process,²⁸ accordingly, it is reasonable to relate the higher conversion of toluene of the parent HZSM-5 with the higher acid concentration as indicated in NH₃-TPD studies. With the decrease of acid sites per gram of zeolite composite in comparison to that of parent HZSM-5, there is lower toluene conversion over the HZSM-5@silicalite-1 catalysts.

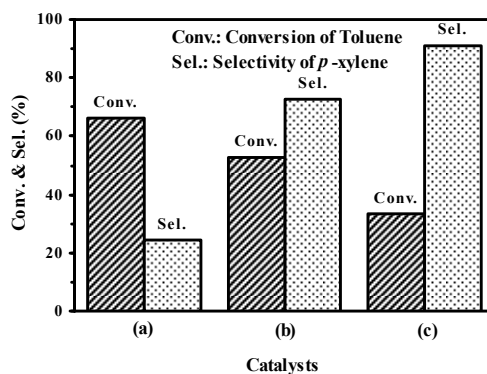


Figure 4. Conversion of toluene and selectivity of *p*-xylene over (a) parent HZSM-5, (b) HZSM-5@silicalite-1 and (c) large-crystals core HZSM-5@silicalite-1 (Reaction conditions: $n_{\text{CH}_3\text{Br}} : n_{\text{toluene}} = 2 : 1$, $\text{WHSV}_{\text{toluene}} = 2 \text{ h}^{-1}$, 400 °C, 60 min, N₂ flow 10 ml/min).

It is known that the particle size of a catalyst is important for *para*-selectivity. The HZSM-5@silicalite-1 catalysts that were different in core size (the SEM images are shown in Figure 1 and Figure S1) were successfully synthesized by changing the kind and amount of template. With increase of HZSM-5 core size from 0.85 to 12 μm, the *para*-selectivity over the HZSM-5@silicalite-1 increases from 72% to 91% while there is obvious decrease of toluene conversion (from 52% to 33%). It is apparent that the *para*-selectivity is related to particle size. With enlargement of particle size, the channels are too long for rapid departure of products from the reaction system, causing a reduction in the conversion of reactants. Mirth et al.²⁹ reported toluene alkylation and isomerization on a H-ZSM-5 catalyst and suggested that the high *para*-selectivity obtained above 573 K could be explained by the fact that the reaction rate was governed by a diffusion limitation at high temperature. Above 573 K, the rate of isomerization is higher than that of methylation, resulting in the accumulation of *m*-xylene and *o*-xylene in the pores. The diffusivity of the xylene isomers are quite different ($p : m : o = 1000 : 1 : 10$), and the *para*-selectivity could be improved by increasing the ratio of diffusion. In our reaction conditions, we observe that *para*-selectivity increases from 72% to 91% by varying the particle size from 0.85 to 12 μm, in accord with the results of Mirth et al. Thus, the reaction rate must be controlled by a diffusion limitation for both the

uncoated and coated catalysts. The effectiveness of the catalyst is low for the uncoated catalyst. Even though *p*-xylene forms selectively over H-ZSM-5 in the diffusion control region, the isomerization on acid sites on the external surface reduces the *para*-selectivity for the uncoated catalyst. But the silicalite layer could remove the acid sites on the external surface of H-ZSM-5 and inhibit isomerization of *p*-xylene.

Long-running investigation was carried out over the parent HZSM-5 and HZSM-5@silicalite-1 catalysts (Figure 5). Over the parent HZSM-5, the toluene conversion at the early stage is more than 70%, but decreases to 32% after 240 min, and the *para*-selectivity is close to the equilibrium value but increases slightly with reaction time. There is difference in performance across the catalysts due to variation of surface acidity. We dissolved the used catalysts with hydrofluoric acid and extracted the organic compounds with carbon tetrachloride. Based on GC-MS analysis result (the deposited carbon species are mainly polyalkylbenzene and naphthalene) and our previous studies,^{8, 21} we deduce that CH₃Br is first activated on the acid sites, yielding intermediates such as CH₃⁺ and CH₂, followed by methylation, oligomerization, and coking reactions. Since polyalkylbenzene and naphthalene are relatively big in size, it is hard for them to escape once they are formed inside the channels. With the covering of the active sites by the formed coke, there is decline in toluene and CH₃Br conversions but enhancement in *para*-selectivity.³⁰ Over the HZSM-5@silicalite-1 catalyst, the toluene conversion and *para*-selectivity are higher than 50% and 76%, respectively, after a reaction time of 240 min. The silicalite-1 shell could extend the diffusion path length of xylenes, resulting in the excellent *para*-selectivity. On the other hand, the result also indicates that the acid sites on the external surface of HZSM-5 are in effect removed due to the covering of the HZSM-5 surface with silicalite-1 as illustrated in the TIPB cracking experiment. The coating of HZSM-5 with the silicalite-1 shell also effectively prohibit coke formation near the surface of the HZSM-5 catalysts as a result of diffusion resistance. In other words, toluene alkylation occurs mainly near the surface of HZSM-5, and the removal of acid sites on the external surface of HZSM-5 affects the reaction rate then inhabits coke formation, thus there is stability improvement of the coated catalyst.¹³

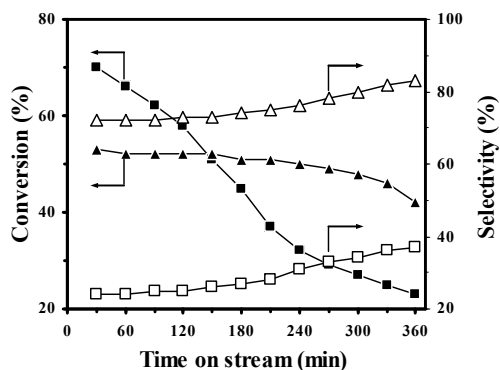


Figure 5. Conversion of toluene and selectivity of *p*-xylene over parent HZSM-5 (squares) and HZSM-5@silicalite-1 (triangles). (Reaction conditions: see Figure 4)

Experimental

Material preparation

ZSM-5 zeolites with a Si/Al ratio of 75 were synthesized by hydrothermally at 180 °C for 48 h. The reactant materials used

for the synthesis were silica sol, aluminum sulfate, tetrapropylammonium hydroxide (TPAOH), and sodium hydroxide. The molar composition was 100 SiO₂: 0.67 Al₂O₃: 30 TPAOH: 16.5 NaOH: 3800 H₂O. For comparison purposes, large ZSM-5 crystals were synthesized as well by using triethanolamine (TEOA) as an additive at a TEOA/SiO₂ ratio of 0.1, while the TPAOH/SiO₂ ratio was adjusted to 0.1. The synthesized Na zeolite was ion-exchanged with NH₄NO₃ to replace the Na⁺ with NH₄⁺. Following this, NH₃ was removed and the H form of the zeolite was obtained. The HZSM-5@silicalite-1 core-shell composite molecular sieves with densely packed silicalite-1 shells were prepared through a surfactant-directed sol-gel coating process. In a typical synthesis of HZSM-5@silicalite-1 composites with a shell thickness of approximately 200 nm, a HZSM-5 zeolite (Si/Al = 75) water suspension containing zeolite particles (3.0 g) was dispersed in a mixture containing TPAOH (1.22 g) and water (30 g) under ultrasonic treatment for 30 min. Next, TEOS (2.14 g) was added dropwise and stirred for 3 h at 80 °C. The mixture was heated in an autoclave at 180 °C under static condition for 48 h. Afterwards the as-generated core-shell composites were collected by centrifugation and washed with water, and dried overnight at 110 °C. Finally, the organic templates were removed by calcination at 550 °C for 5 h.

Catalyst characterizations

Powder X-ray diffraction (XRD) experiment was conducted on a Bruker D8 Advance diffractometer using Cu K α radiation. The data were recorded at a scan rate of 0.02° (2 θ) s⁻¹ in the 5–60° range. The surface area of catalyst was measured by the Brunauer-Emmett-Teller (BET) method on a Tristar 3000 instrument; before each measurement, the sample was heated to 300 °C and kept at this temperature for 5 h. The BET specific surface area (S_{BET}) was calculated based on the adsorption data in the relative pressure range of 0.04 to 0.20.³¹ Temperature-programmed desorption of ammonia (NH₃-TPD) experiments were carried out on a Micromeritics 2920II apparatus equipped with a thermal conductivity detector (TCD) to analyze the acid property of the catalysts. The acidity of the external surface of the catalyst was measured by cracking 1,3,5-triisopropylbenzene (TIPB). The procedure was described elsewhere.⁸ Field emission scanning electron microscopy (FE-SEM) studies were performed on a Hitachi S-4800 emission-scanning microscope with a Schottky Emitter at an accelerating voltage of 5 kV and a beam current of 1 mA. Transmission electron microscopy (TEM) images were taken using a JEM-3010F transmission electron microscope at an accelerating voltage of 200 kV.

Catalytic evaluation

The catalytic methylation reaction was carried out under atmospheric pressure in a continuous fixed-bed quartz tube reactor (8 mm i.d.). The CH₃Br was prepared from methanol and hydrobromic acid over commercial HZSM-5 (SiO₂/Al₂O₃ = 380) at 210 °C. We observed complete conversion of methanol and 100% selectivity to CH₃Br. The synthesized CH₃Br gas was carried by N₂ into the methylation reactor, and toluene was introduced. The product collected at an ice/water trap was analyzed over a gas chromatograph (Agilent 7820A) equipped with an Agilent AB-FFAP capillary column (30 m × 0.25 mm × 0.25 μ m) and FID. Toluene conversion and selectivity to *p*-xylene were calculated in mol% based on aromatics.

Conclusions

Shape-selective methylation of toluene with methyl bromide was studied over HZSM-5@silicalite-1 composite catalyst. HZSM-5 crystals with different crystal sizes were chosen as representative zeolite cores and coated with an ordered silicalite-1 shell according to a facile base-catalyzed sol-gel coating strategy using TEOS as silica source and TPAOH as template. The silicalite-1 shell extends the diffusion path length for xylenes and fully covers the acid sites on the external surface of HZSM-5, improving catalyst stability as well as *para*-selectivity in the methylation of toluene as a result.

Acknowledgements

This project was financially supported by National Natural Science Foundation of China (Grant Nos. 21273067 and U1162109). C.T. Au thanks the Hunan University for an adjunct professorship.

Notes and references

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Electronic Supplementary Information (ESI) available: [SEM images and XRD profiles of the large parent HZSM-5, and the core-shell structured HZSM-5@silicalite-1]. See DOI: 10.1039/b000000x/

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