**Supplementary information for:**

# Controllable fabrication of uniform core-shell structured zeolite@SBA-15 composites

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## Experimental section

### Chemicals

Poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) triblock copolymer Pluronic P123 (Mw = 5 800, $PEO_{20}PPO_{70}PEO_{20}$) was purchased from Acros Corp. Tetraethyl orthosilicate (TEOS, ≥ 98 %), tetrapropylammonium (TPAOH, 50 %), tetrapropylammonium bromide (TPABr, 98 %), HCl (36.5 %), $NH_4NO_3$ (≥ 99.5 %), anhydrous magnesium sulfate ($MgSO_4$, ≥ 98.0 %) sodium aluminate ($NaAlO_2$, $Al_2O_3$ ≥ 41 %), ethanol (≥ 99.7 %), benzene (≥ 99.0 %) were purchased from Shanghai Chemical Corp. All chemicals were used as received without any further purification. Millipore water was used in all experiments.

### Preparation of HZSM-5 and Silicalite-1

HZSM-5 particles with Si/Al molar ratio = 93 were obtained according to the method described in the literature.[1] The molar composition of the synthesis mixture was $1SiO_2$: $0.005Al_2O_3$: 0.2TPABr: $35.5H_2O$. Silicalite-1 particles in our present work were prepared from a gel with the molar ratio of 1TEOS: 8TPAOH: $330H_2O$ by a traditional hydrothermal synthesis route. In a typical procedure, 5.0 g of TEOS was added dropwise in a 6.6 wt % TPAOH water solution and stirred for 12 h at 25 °C. Then the clear gel was transferred to a stainless steel autoclave with a Teflon container and hydrothermally treated at 160 °C for 24 h. The products were collected by centrifugation and washed with copious amount of water. It could be mentioned here, from an energy conservation view, in the case of Silicalite-1 or ZSM-5 prepared with an aluminum source without $Na^+$ ions such as aluminum isopropoxide, an as-made zeolite water solution with a fixed solid/solution ratio was suggested to be prepared prior to use, because only one-step calcination at 550 °C for 5 h was needed to remove the templates (*i.e.* $TPA^+$ and triblock copolymer P123) (*vide infra*).

### Preparation of the micro/mesoporous core-shell composites

Uniform micro/mesoporous core-shell composites with zeolite (Silicalite-1 and HZSM-5) single-crystal particles as cores and mesoporous silica SBA-15 as shells were synthesized by an ultra-dilute liquid-phase coating strategy of silica oligomers from acid-catalyzed hydrolysis of TEOS, triblock copolymer P123 as a mesostructural template with or without inorganic salt $MgSO_4$ as an additive. The concentrations of P123 and TEOS were ultra-dilute and about 0.19 and 0.5 wt %, respectively. In a typical synthesis, 0.058 g (0.01 mmol) of Pluronic P123 was dissolved in 30 mL of 2 M HCl at 25 °C, followed by adding 0.174 g (1.4 mmol) of $MgSO_4$. The as-made Silicalite-1 aqueous solution containing 0.15 g of zeolite particles was dispersed in the above solution under ultrasonic treatment for 30 min to obtain a homogeneous mixture. Finally, 0.15 g (0.7 mmol) of TEOS was added dropwise to the mixture under moderate stirring (600 rpm) for 24 h before being transferred to an autoclave and heated at 100 °C for 24 h. The typical core-shell composites with TEOS/zeolite mass ratios of 0.5, 1.0 and 2.0 were synthesized and named as S@S15-30-40, S@S15-45-100 and S@S15-45-120, respectively, which represent that the core-shell composites were consisted of Silicalite-1 (S) cores and mesoporous silica SBA-15 (S15) shells with crystal face-dependent shell-thicknesses of 30/40, 45/100 and 45/120 nm. The shell-thicknesses were determined by measuring more than 100 core-shell particles on transmission electron microscopy (TEM) measurements. The standard deviation for the crystal face-dependent shell-thicknesses is around 10 nm. The as-made samples were collected by centrifugation and washed by a large amount of water till neutrality. One-step calcination was carried out at 550 °C for 5 h in air to get micro/mesoporous core-shell composites. The control sample pure SBA-15 powder was synthesized at the same condition, but in absence of zeolite particles. To control the thicknesses of mesoporous silica shells, the mass ratios of TEOS/zeolite were tuned in the range of 0.5 – 2, wherein the zeolite content kept a constant (0.15 g) and the amounts of silica source TEOS in the recipe of SBA-15 coating with a fixed molar ratio of 0.014P123: 1.0TEOS: 2.0$MgSO_4$: 85.7HCl: 2381$H_2O$ were adjusted in the range of 0.075 – 0.30 g.

**MTP catalytic reaction.**

The methanol to propylene conversion (MTP) was carried out at 460 °C in an automatic fixed-bed microreactor under atmospheric pressure. The catalyst load was 1.0 g and the weight hourly space velocity (WHSV) for methanol was 1.2 $h^{-1}$ with a methanol/$H_2O$ molar ratio of 1: 3. The total products were analyzed by an on-line gas chromatograph equipped with a Flame Ionization Detector (FID) and a 50 m CP-ParaPLOT Q capillary column. Both methanol and dimethyl ether (DME) were regarded as reactants for calculation. The mass balance was above 95 %.

**Characterizations and Measurements**

The small-angle X-ray scattering (SAXS) measurements were taken on a Nanostar U small-angle X-ray scattering system (Bruker, Germany) using Cu Kα radiation (40 kV, 35 mA). The unit cell parameters were calculated from the formula $a = 2d_{100}/\sqrt{3}$ for two-dimensional (2-D) hexagonal mesostructure, where $d_{100}$ represents the $d$-spacing values of the 100 diffraction calculated by $d_{100} = 2\pi/q$. Powder XRD patterns were recorded on a Bruker D4 diffractometer with Ni-filtered Cu Kα radiation (40 mV, 40 mA). Nitrogen sorption isotherms were measured at 77 K on Quantachrome Autosorb-1-MP (USA). Before measurements, all of samples were degassed in vacuum at 300 °C for at least 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas ($S_{\mathrm{BET}}$) using adsorption data in a relative pressure range from 0.05 to 0.3. The pore size distributions (PSD) were obtained by applying the equilibrium model of nonlocal density functional theory (NLDFT method). The total pore volume $V_{\mathrm{t}}$ was estimated from the adsorbed amount at a relative pressure $P/P_0$ of 0.995. The micropore volume ($V_{\mathrm{m}}$) and micropore surface area ($S_{\mathrm{micro}}$) were calculated from the $V$-$t$ plot method. TEM images were recorded on a JEOL JEM-2100 F microscope (Japan) operated at 200 kV. The samples for TEM measurements were dispersed directly in ethanol and then collected using copper grids covered with carbon films. Gravimetric adsorption equilibrium analyses were carried out using a fully automated digital microbalance equipped with a vapor generator and connected to a high-vacuum system (Hiden Isochema Instrument, model IGA-002). The diffusion process in the zeolite and core-shell composite was assumed to follow the Fick's law. The mathematical solution for the short-time diffusion equation for a spherical particle assumes the well-known form given by Crank.[2] Field-emission scanning electron microscope (FESEM) measurements were performed on a Hitachi S-4800 microscope (Japan). The samples for observing the growth of SBA-15 were quickly collected and quenched with liquid nitrogen at different times followed by cryodesiccation. SEM images were taken with a Philip XL30 microscope (Holland) operating at 20 kV. Zeta potential was determined through electrophoretic mobility measurements, using a Malver Zetasizer 2000 (UK) instrument. The Si/Al ratio and zeolite content in core-shell composite were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an Varian Vista-MPX ICP instrument. Fourier transform infrared (FTIR) spectra were collected on Nicolet Fourier spectrophotometer (USA), using KBr pellets of the solid samples. Acidic properties of samples were tested by the $NH_3$-temperature-programmed-desorption ($NH_3$-TPD) on AutoChem2920 (USA) apparatus. 0.10 g of samples was loaded in the U-shaped quartz tube and heated at 550 °C for 1 h in helium flow and then cooled to 100 °C for the saturation of the catalyst. $NH_3$-TPD was measured in the temperature range of 100 – 600 °C with a constant heating rate of 10 °C/min. The FT-IR spectra of pyridine adsorption were collected on Nicolet Fourier spectrophotometer (FTIR 360, USA). The samples were pressed into self-supporting wafers with diameters of 2 cm. The wafers (20 − 40 mg) were mounted in an infrared vacuum cell and degassed at 480 °C for 4 h under vacuum (10 − 4 mmHg), then cooled to 120 °C and exposed to pyridine vapor for 1 h. The desorption was performed at 120 °C under vacuum.

References:

1 Z. H. Shen, J. Liu, H. L. Xu, Y. H. Yue, W. M. Hua and W. Shen, *Appl. Catal. A Gen.*, 2009, **356**, 148–153.
2 J. Crank, *The mathematics of diffusion*, Oxford Press: London, 1975.

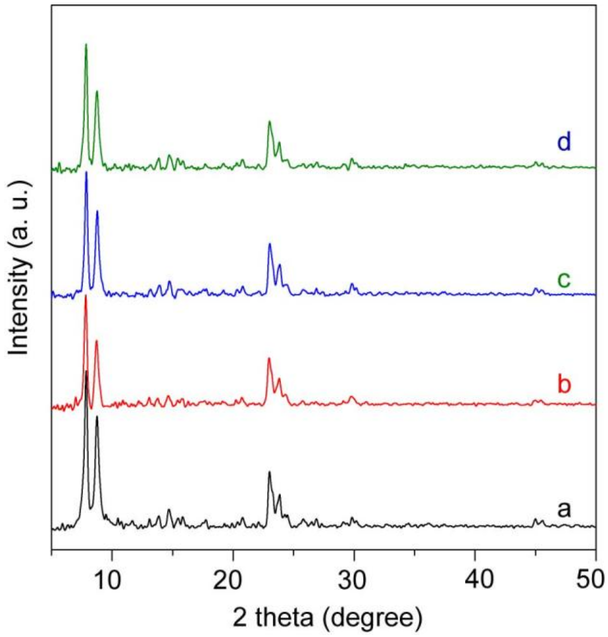

**Fig. S1** Wide-angle XRD patterns of the calcined Silicalite-1 and core-shell composites with different shell-thicknesses: Silicalite-1 (a); S@S15-45-100 (b); S@S15-30-40 (c) and S@S15-45-120 (d).

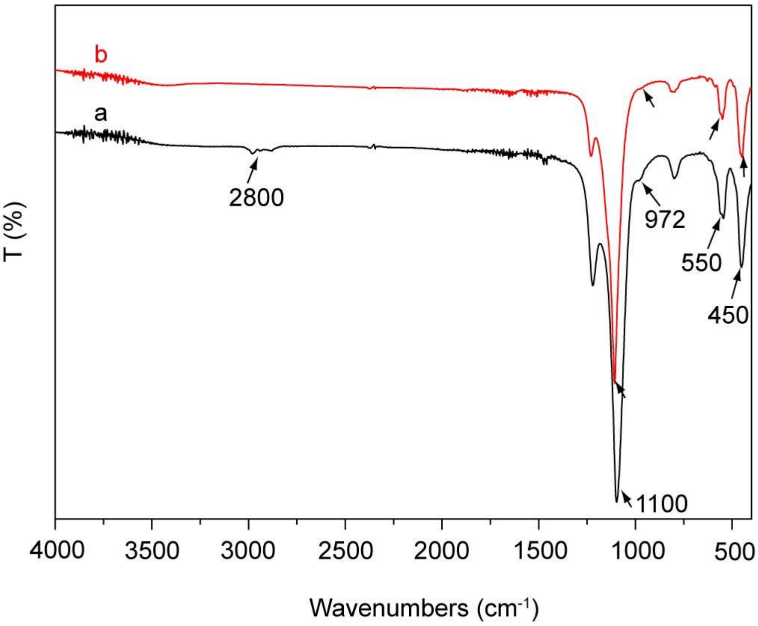

**Fig. S2** FT-IR spectra of the core-shell composite S@S15-45-100 synthesized by an ultra-dilute liquid-phase coating method in acidic medium: (a), as-made and (b), calcined at 550 °C for 5 h in air.

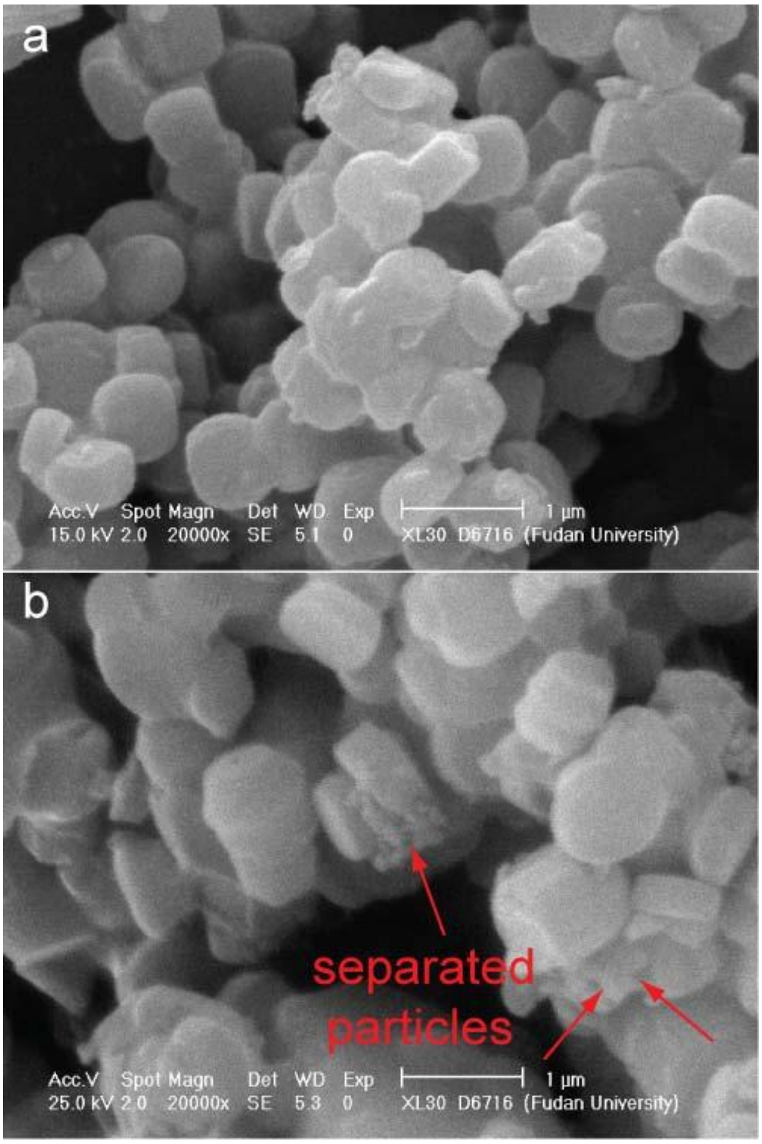

**Fig. S3** SEM images of the core-shell composites after being calcined at 550 °C for 5 h in air: (a), S@S15-30-40 and (b), S@S15-45-120 with TEOS/zeolite mass ratios of 0.5 (a) and 2 (b), respectively, synthesized by an ultra-dilute liquid-phase coating method in acidic medium.

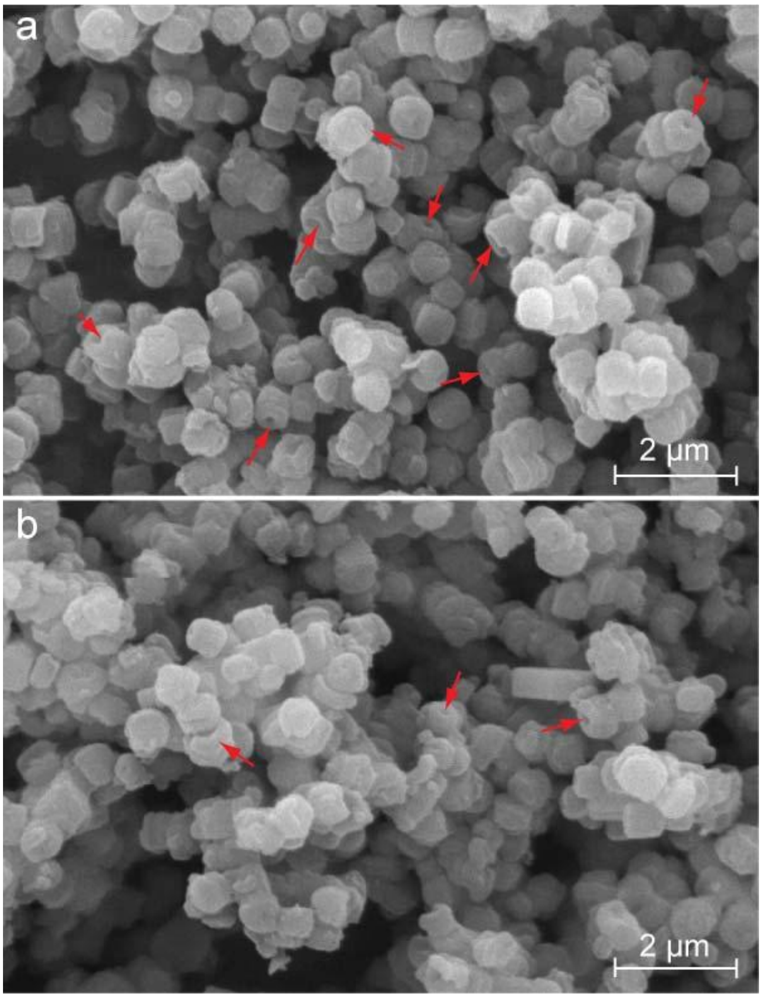

**Fig. S4** SEM images of the calcined core-shell composites synthesized by tuning the amounts of $MgSO_4$ additive in the case of S@S15-45-100 with TEOS/zeolite mass ratio of 1: (a) without addition of $MgSO_4$, and (b) with a relative small amount of $MgSO_4$ (molar ratio of $MgSO_4$/TEOS = 1). Red arrows denote the core-shell particles covered with “doughnut-like hats”.

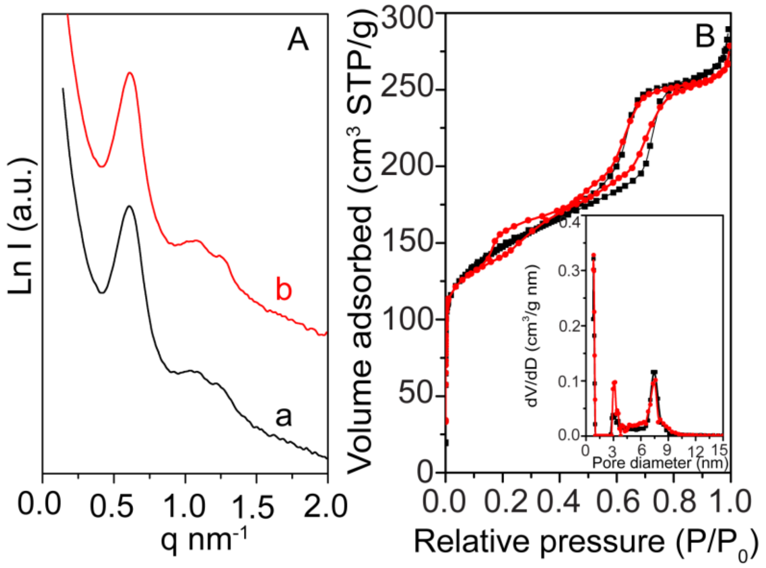

**Fig. S5** SAXS patterns (A), $N_2$ sorption isotherms (B) and pore size distribution curves (inset of B) of the calcined core-shell composites by tuning the amount of $MgSO_4$ additive in the case of S@S15-45-100 with TEOS/zeolite mass ratio of 1. (a), without addition of $MgSO_4$ and (b), with a relative small amount of $MgSO_4$ (molar ratio of $MgSO_4$/TEOS = 1).

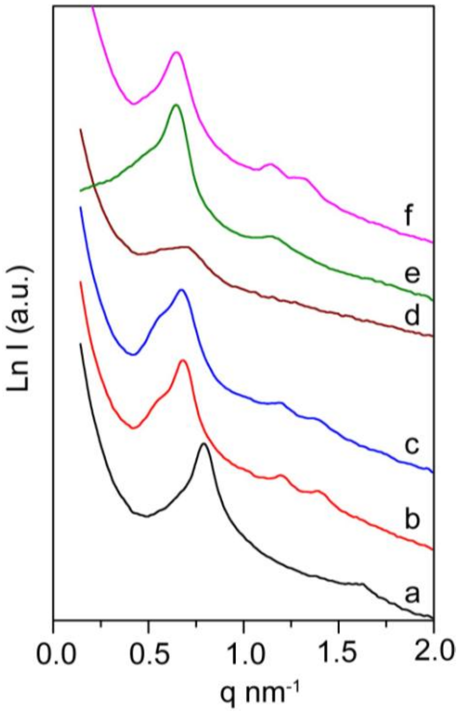

**Fig. S6** SAXS patterns of the calcined products synthesized at various synthesis parameters in the case of S@S15-45-100 with TEOS/zeolite mass ratio of 1, stirring rates of 0 (a), 200 (b) and 1200 rpm (c); HCl concentrations of 0.5 (d) and 1.0 M (e); a relative high reaction temperature of 40 °C (f).

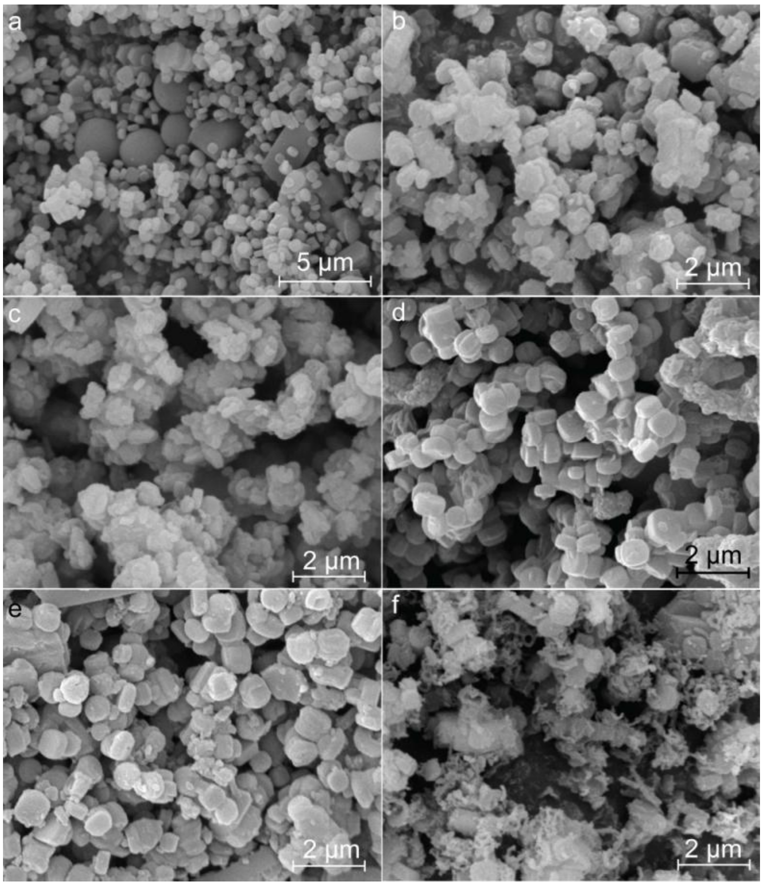

**Fig. S7** SEM images of the calcined core-shell composite products synthesized at various stirring rates of 0 (a), 200 (b) and 1200 rpm (c) and HCl concentrations of 0.5 (d) and 1.0 M (e), respectively, as well as a relative high reaction temperature of 40 °C (f).

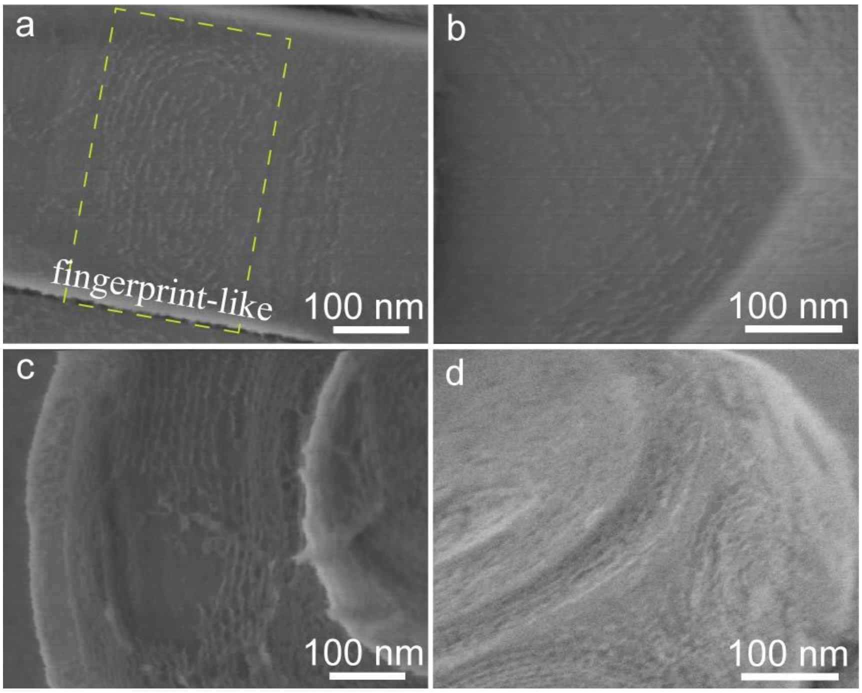

**Fig. S8** FESEM images of the calcined core-shell product prepared by an ultra-dilute liquid-phase coating strategy under a quiescent condition (0 rpm): fingerprint-like mesostructured silica coating with ~ half of a unit-cell thickness (a-c), indicating the regular arrangement of mesopores; a core-shell particle with independent mesoporous silica shells on respective crystal faces (d), indicating the separated coating process on anisotropic crystal faces.

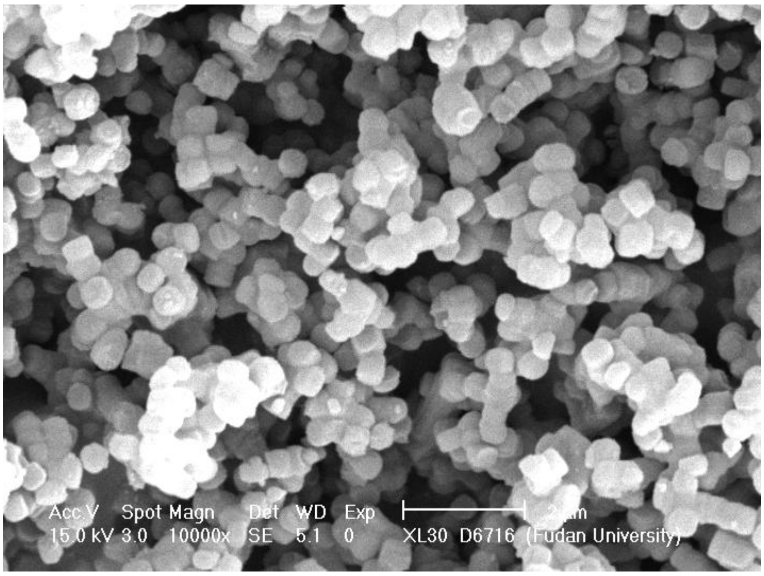

**Fig. S9** SEM image of the calcined core-shell composite HZ@S15 with HZSM-5 (Si/Al = 93) as cores synthesized at the similar condition with the sample S@S15-45-100 by an ultra-dilute liquid-phase coating process in acid medium without $MgSO_4$.

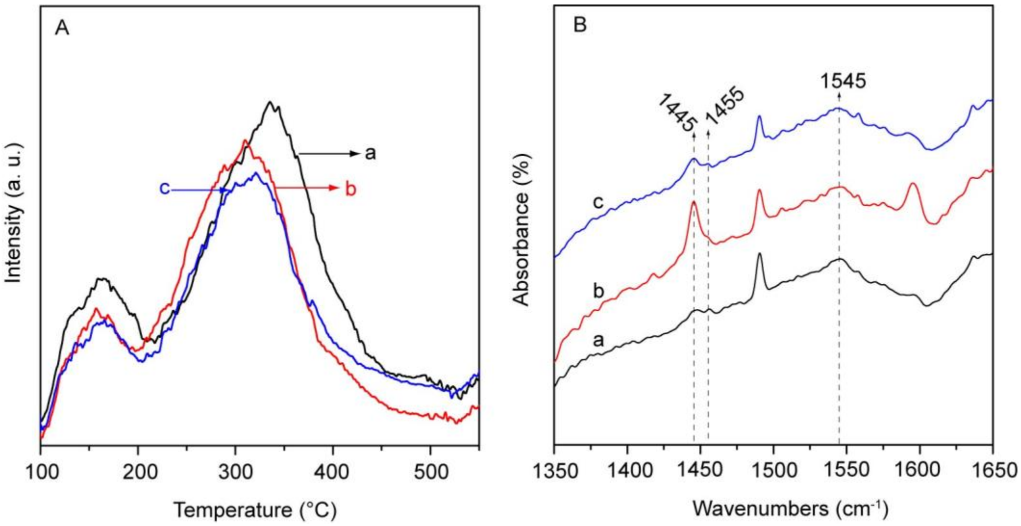

**Fig. S10** $NH_3$-TPD profiles (left) and pyridine adsorption FTIR spectra (right) of pure HZSM-5 (a), mechanical mixture (b) with 70 *wt* % of HZSM-5 and 30 *wt* % of SBA-15 (denoted as HZSM-5&S15) and core-shell composite catalyst HZ@S15 (c).

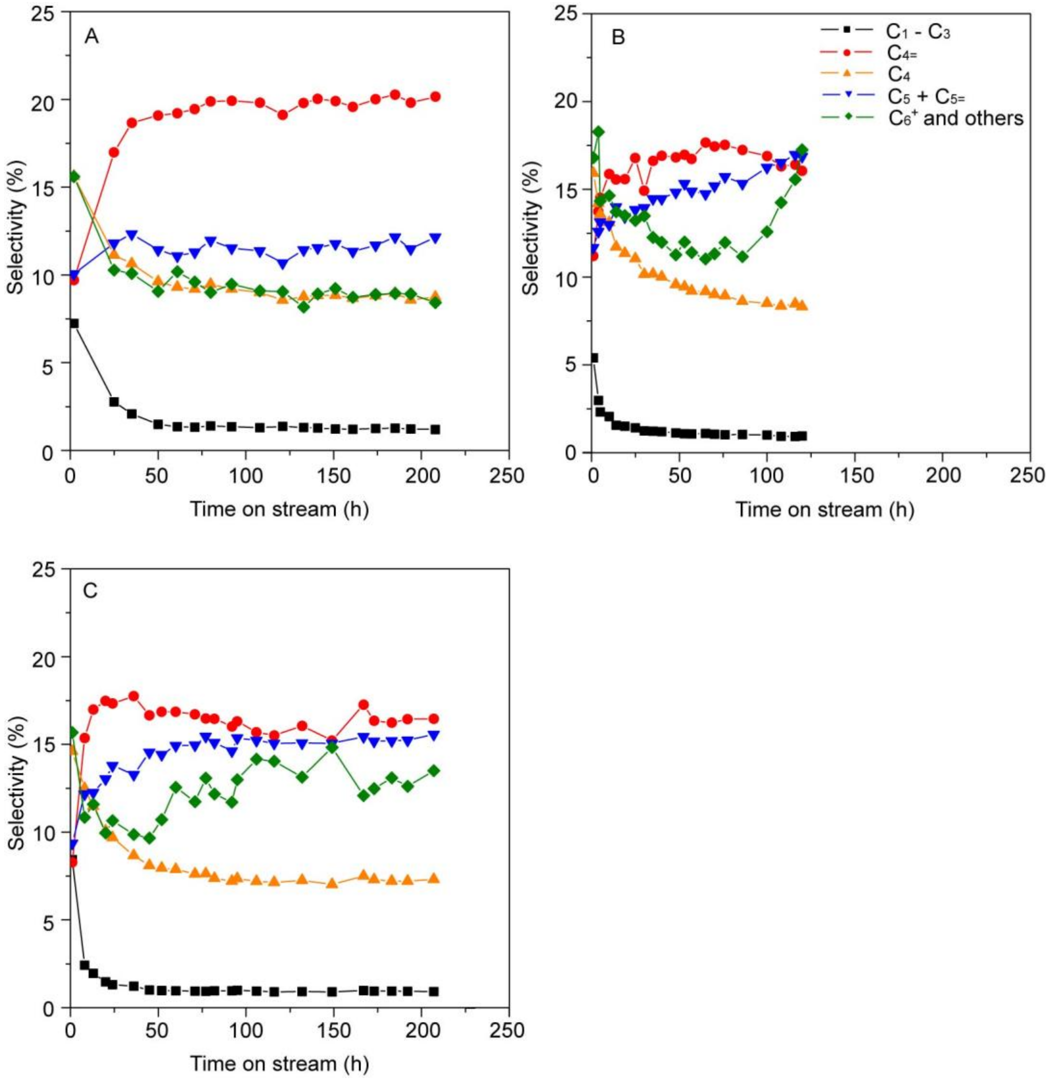

**Fig. S11.** Products selectivity as a function of time in MTP reaction over pure HZSM-5 (A), mechanical mixture HZSM-5&S15 with 70 wt% HZSM-5 and 30 wt% SBA-15 (B) and the core-shell composite catalyst HZ@S15 (C).

**Table S1** The results of MTP conversion over the core-shell composite HZ@S15 and HZSM-5 catalysts with different Si/Al ratios and acidities[f].

| Catalysts | HZSM-5[e] | HZSM-5&S15 | HZ@S15 |
|---|---|---|---|
| Si/Al ratio | 93 | - | 135 |
| Acidity (mmol/g)[a] | 0.043 | 0.038 | 0.029 |
| Average conversion in the overall 200 h (%) | 99.6 | 95.8 | 98.4 |
| Average selectivity in the overall 200 h (%) | | | |
| $C_2H_4$ | 6.8 | 5.8 | 4.3 |
| $C_3H_6$ | 38.8 | 38.1 | 39.4 |
| $C_1 – C_3$[b] | 1.8 | 1.8 | 1.4 |
| $C_4$[b] | 9.6 | 10.4 | 8.4 |
| $C_4H_8$ | 19.0 | 16.1 | 16.1 |
| $C_5 + C_5^{=}$[c] | 11.5 | 14.6 | 14.4 |
| $C_6^{+}$[d] and others | 12.5 | 13.4 | 16.0 |
| P/E ratio[e] | 6.1 | - | 10.7 |

*a*: Acidity was calculated by $NH_3$-TPD measurements.

*b*: $C_1 – C_4$ saturated hydrocarbons.

*c*: $C_5 + C_5^{=}$ saturated hydrocarbons and olefin.

*d*: $C_6$ and higher nonaromatic and aromatic hydrocarbons.

*e*: Average P/E ratio in the overall 200 h.

*f*: Reaction conditions: T = 460 °C, WHSV = 1.2 $h^{-1}$, $P_{total}$ = 1 atm, $H_2O$: $CH_3OH$ = 1: 3 (molar ratio).