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Core-Shell Structured Mesoporous Silica as Acid-Base Bifunctional Catalyst with Designated Diffusion Path for Cascade Reaction Sequences

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Catalyst preparation.

(a) MS-A@MS-B. MS-A@MS-B was prepared by a two-step co-condensation route. In a typical synthesis, the inner core MS-A was firstly prepared according to the following method: 2 g of CTAB and 7 mL of 2 M NaOH aqueous solution was added into 480 mL of deionized water. Then TEOS (10 mL) and MPTMS (500 μ L) was added sequentially into above solution under vigorous stirring. After stirring for 10 h at ambient temperature, precipitate was collected by centrifugation, washed with deionized water and dried. To convert the thiol group into the sulfonic acid group, the solid was added into hydrogen peroxide solution (35 wt%) and stirred for 12 h. Finally, the resultant solid was washed and dried for further use.

The MS-A was then coated with MS-B shell by previously reported method with slight modifications.¹ The as-obtained MS-A (0.1 g) with CTAB template remained in the mesopores was first dispersed in a mixed solution containing H₂O (40 mL), ethanol (30 mL), CTAB (0.15 g) and 25 wt% NH₃·H₂O (570 μ L). The mixture was subjected to ultrasonic treatment to form uniform suspension. Then a mixture of silica precursors composed of

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TEOS (144 μ L) and APTMS (11 μ L) was added, and the as-obtained solution was vigorously stirred for another 24 h. The solid was recovered and refluxed in acidic ethanol to remove the surfactant CTAB.

(b) Pure MS was prepared using the same method as MS-A without addition of APTMS.

(c) MS@MS-B was prepared by coating a functionalized mesoporous silica shell on the pure MS core with the same synthesis procedure in (a).

(d) MS-A@MS was synthesized by following the same preparation method of MS-A@MS-B, but without adding APTMS during the shell-coating process.

One-pot deacetalization-Knoevenagel condensation reaction.

Toluene (3 mL), benzaldehyde dimethyl acetal (1.0 mmol), ethyl cyanoacetate (1.2 mmol), para-xylene (0.5 mmol) and catalyst (20 mg) were added into a glass vessel. The resulting reaction mixture was vigorously stirred at 80 °C. After 0.5 h, the reaction was stopped by cooling to room temperature. The solid catalyst was separated by filtration, and the filtrate was analyzed by GC (Agilent 6890N) with capillary column (DB-5, 30.0m × 320 μ m × 0.25 μ m) and FID, and the products were further confirmed by GC-MS (SHIMADZU, GCMS-QP 2010S) with capillary column (DB-5 ms, 30.0m × 320 μ m × 0.25 μ m).

One-pot deacetalization-Henry reaction.

Nitromethane (5 mL), benzaldehyde dimethyl acetal (1.0 mmol), para-xylene (0.5 mmol) and catalyst (20 mg) were added into a glass vessel. The resulting reaction mixture was vigorously stirred at 90 °C for 40 h, the reaction was stopped by cooling to room temperature. The solid catalyst was separated by filtration, and the filtrate was analyzed by GC (Agilent 6890N) with capillary column (DB-5, 30.0m × 320 μ m × 0.25 μ m) and FID, and the products were further confirmed by GC-MS (SHIMADZU, GCMS-QP 2010S) with capillary column (DB-5 ms, 30.0m × 320 μ m × 0.25 μ m).

Characterization.

Transmission electron microscopy (TEM) was carried out on a JEOL 1011F electron microscope running at 100 kV. Nitrogen adsorption–desorption isotherm was obtained on Quantachrome Autosorb AS-1 at 77K. For pore size and pore volume determination, a non-local density functional theory (NLDFT) equilibrium model of N₂ on silica was used. The small-angle XRD measurement was carried out on Rigaku D/max-2400 diffractometer equipped with a secondary graphite monochromator with CuK α radiation (wavelengths $\lambda = 0.154$ nm). Data was collected in a step-scan mode in the range of 1-6 degree with step-width of 0.02 and speed of 1 degree /min. ²⁹Si and ¹³C solid-state NMR spectra were obtained on an AVANCE III 400 spectrometer operating at 79.30 MHz for ²⁹Si and 100.38 MHz for ¹³C equipped with a 4 mm rotor spun at 5 kHz. The surface electronic states were analyzed by XPS (ESCALab220i-XL). Elemental analysis was carried out on the elemental analyzer (Flash EA 1112).

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Figure S1. a) N_2 adsorption-desorption isotherm of MS-A@MS-B. Inset shows the NLDFT pore size distribution curve obtained from the desorption data. b) Small-angle XRD pattern of MS-A@MS-B.



Figure S2. a) ²⁹Si solid-state NMR spectrum of MS-A@MS-B. ($T^2 : -58 \text{ ppm}; T^3 : -66 \text{ ppm}; Q^2 : -90 \text{ ppm}; Q^3 : -100 \text{ ppm}; Q^4 : -109 \text{ ppm}$). b) ¹³C solid-state NMR spectrum of MS-A@MS-B. The asterisked peaks denote residual surfactant and methoxy/ethoxy groups.

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Figure S3. S 2p XPS spectra of MS-SH, MS-A, MS-A@MS-B and broken MS-A@MS-B. The peaks at around 163.6 eV and 168.8 eV corresponded to the thiol group and the sulfonic acid group, respectively.

As shown in Figure S3, S 2p regions of the sample MS-SH, MS-A, MS-A@MS-B and broken MS-A@MS-B (prepared by intentionally grinding the MS-A@MS-B sample) indicated that almost all the thiol groups in the MS-SH were successfully converted to the sulfonic acid groups in the MS-A by H₂O₂. After the shell coating, the S 2p peak that could be observed in the MS-A was almost undetectable in the MS-A@MS-B sample, likely due to the shielding of MS-B coating (XPS beam can only penetrate less than 20 nm from the surface). The S 2p peak corresponding to the sulfonic acid group was detected on grinded MS-A@MS-B sample, likely because the MS-A inner core was exposed after grinding.

Table S1. One-pot domino reaction sequence composed of acid-catalyzed hydrolysis and base-catalyzed Henry reaction.^a

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	оме acid site H2O CHO basic site CH3NO2							
	Α	В	D					
Entry	Catalyst	Conv. of A (%)	Yield of B (%)	Yield of D (%)				
1	MS-A@MS-B	100	0	≈ 100				
2	MS-A@MS	16.7	16.7	0				
3	MS @MS-B	trace	trace	trace				
4	MS-A@MS-B/AP	0	0	0				
5	MS-A@MS-B/PTSA	17.0	17.0	0				
6	AP/PTSA	0	0	0				
7 ^b	physical mixture	100	7.0	93.0				
8	MS	0	0	0				

^aReaction conditions: A (1 mmol), nitromethane (5 mL), catalyst (20 mg), reaction temperature = 90 °C, reaction time = 40 h. Conversion and yield were determined using GC data. AP: 1-aminopropane, PTSA: p-toluene sulfonic acid. ^bPhysical mixture composed of 20 mg of MS-A@MS and 20 mg of MS@MS-B.

Table S2. Recycling results of MS-A@MS-B and the physical mixture (MS-A@MS + MS@MS-B) in the onepot deprotection-Knoevenagel cascade reaction sequence.^a Electronic Supplementary Material (ESI) for Chemical Communications This journal is O The Royal Society of Chemistry 2012



Run	MS-A@MS-B			Physical mixture (MS-A@MS + MS@MS-B)		
	Conv. of A (%)	Yield of B (%)	Yield of C (%)	Conv. of A (%)	Yield of B (%)	Yield of C (%)
1	100	0	≈ 100	93.7	15.7	78.0
2	100	0	≈ 100	90.0	17.0	73.0
3	94.2	trace	≈ 94.2	84.4	19.0	65.4
4	90.0	trace	≈ 90.0	75.2	25.1	50.1

^aReaction conditions: A (1 mmol), ethyl cyanoacetate (1.2 mmol), toluene (3 mL), catalyst (20 mg of MS-A@MS-B or physical mixture composed

of 20 mg of MS-A@MS and 20 mg of MS@MS-B), reaction temperature = 80 °C, reaction time = 0.5 h. Conversion and yield were determined using GC data.

Table S3. Recycling results of MS-A@MS-B and the physical mixture (MS-A@MS + MS@MS-B) in the onepot deprotection-Henry cascade reaction sequence.^a



Run	MS-A@MS-B			Physical mixture (MS-A@MS + MS@MS-B)		
	Conv. of A (%)	Yield of B (%)	Yield of D (%)	Conv. of A (%)	Yield of B (%)	Yield of D (%)
1	100	0	≈ 100	100	7.0	93.0
2	100	0	≈ 100	100	12.5	87.5
3	95.1	trace	≈ 95.1	91.5	14.7	76.8
4	91.0	trace	≈ 91.0	78.3	23.0	55.3

^aReaction conditions: A (1 mmol), nitromethane (5 mL), catalyst (20 mg of MS-A@MS-B or physical mixture composed of 20 mg of MS-A@MS and 20 mg of MS@MS-B), reaction temperature = 90 °C, reaction time = 40 h. Conversion and yield were determined using GC

data.

Reference

1 Z. Chen, Z.-M. Cui, F. Niu, L. Jiang and W.-G. Song, *Chem. Commun.*, 2010, 46, 6524.