Supporting Information For

Zeolitic microcapsule with encapsulated platinum nanoparticles for one-pot tandem reaction of alcohol to hydrazone

1. Catalyst characterization

![XRD spectrum](image)

Fig. S1 XRD spectrum of (a) Pt@S1 and (b) Pt/SiO₂. The three peaks at 2 theta equaling to 40, 46 and 68 ° are indexed to (111), (200) and (220) of platinum and the peaks identified with ‘*’ are attributed to silicalite-1.

![IR spectrum](image)

Fig. S2 IR spectrum of Pt@S1. The bands at 1101 and 804 cm⁻¹ were assigned to antisymmetrical and symmetrical stretching vibration of Si-O-Si respectively. The bending vibration of Si-O could be observed at 456 cm⁻¹. Besides, the band appeared at 553 cm⁻¹ confirms the formation of typical MFI structure of silicalite-1.
Fig. S3 Representative N$_2$ adsorption–desorption isotherms of (a) Pt@S1 and (b) commercial Pt/SiO$_2$

<table>
<thead>
<tr>
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<th>$S_{BET}$/m$^2$/g$^{-1}$</th>
<th>$S_{Langmuir}$/m$^2$/g$^{-1}$</th>
<th>$S_{micro}$/m$^2$/g$^{-1}$</th>
<th>$V_{micro}$/cm$^3$/g$^{-1}$</th>
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</thead>
<tbody>
<tr>
<td>Pt@S1</td>
<td>341</td>
<td>461</td>
<td>221</td>
<td>0.12</td>
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<tr>
<td>Pt/SiO$_2$</td>
<td>262</td>
<td>366</td>
<td>8</td>
<td>0</td>
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Fig. S4 TG curve of Pt@S1

Fig. S5 SEM image of Pt@S1 after 10 runs of reaction
2. Experimental

2.1. Materials

Benzothiazole (98%), tert-butyl carbazate (Boc-hydrazide, 98+%), cesium carbonate (Cs₂CO₃), copper iodide (CuI) and 1,10-phenanthroline (anhydrous, 99%) were obtained from Alfa Aesar. Polydiallyldimethylammonium chloride (PDDA, Mw = 200,000, 10 w. t. % in water), poly (sodium 4-styrene sulfonate) (PSS, Mw = 70,000), 3-amino-propyltriethoxysilane (APS) and anhydrous N,N-dimethylformamide (DMF) were purchased from Aldrich. H₂PtCl₆·6H₂O was supplied by Sinopharm Chemical Reagent Company. KBH₄ (94 w. t. %), tetrapropylammonium hydroxide (TPAOH, 25 w. t. % in water), tetrapropylammonium bromide (TPABr), tetraethoxy-orthosilane (TEOS), idobenzene (>97%), and cyclohexanol were obtained from Shanghai Chemical Reagent Company. The commercial noble metal catalyst Pt/SiO₂ (1.0 w. t. %, in granules, Engelhard code C3766) was obtained from Aldrich and crushed before use. All chemicals were used without further purification.

2.2. Catalyst preparation

The mesoporous silica spheres (MSSs) used as the templates were prepared according to Grun et al. ¹,² After modification with APS at room temperature and impregnated in the aqueous solution of 0.4 M H₂PtCl₆, the platinum loaded MSSs (Pt-MSSs) were reduced with 0.01 M KBH₄ aqueous solution and calcinated in air at 600 °C for 3 h. Afterwards, a layer-by-layer procedure was performed with silicalite-1 nanocrystals of 70 nm according to literature. ¹,² Then the seeded particles were treated with hydrothermal transformation in the sol with the composition of TPABr: H₂O: NaOH = 18: 2000: 0.2 for 8 h for the formation of zeolitic microcapsules. ³ The zeolitic microcapsule with Pt encapsulated was separated by centrifugation and washed with distilled water for three times. Finally, the samples were calcinated in air at 550 °C for 6 h to remove the organic ingredients. Some of the as-synthesized Pt@S1 was heavily grinded (B-Pt@S1) and used as reference.

2.3. Catalyst characterization
The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of the catalysts were obtained on Philips XL30 and JEOL JEM-2010 instruments with accelerate voltages of 20 and 200 kV, respectively. The X-ray diffraction (XRD) patterns were obtained on a Rigaku D/MAX-IIA diffractometer with CuKα radiation. The elemental analyses were performed by inductively coupled plasma–atomic emission spectroscopy (ICP-AES). The surface areas of the samples were determined from the nitrogen sorption isotherms at -196 °C using a Micromeritics ASAP 2010 system. Thermogravimetric analysis (TGA) was performed on a Perkin–Elmer TGAT thermal analysis system in air (50 mL min⁻¹) with a heating rate of 10 Kmin⁻¹. Fourier transform infrared (FT-IR) spectra were recorded on a Magna 550 spectrophotometer using KBr pellets. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker (400 MHz) NMR instrument using CDCl₃ as the solvent.

2.4 Synthesis of 1-tert-butoxycarbonyl-1-phenylhydrazine (N-Boc)

Since the commonly used phenylhydrazine is unstable in the oxygen atmosphere for the oxidation reaction, the 1-tert-butoxycarbonyl-1-phenylhydrazine (N-Boc) with the protected tert-butoxycarbonyl (Boc) functional group, compatible with multisteps reaction condition, was first synthesized according to the literature ⁴ with the following equation (Fig. S6). CuI (2 mg, 0.01 mmol, 1 mol %), 1, 10-phenanthroline (18 mg, 0.1 mmol, 10 mol %), and Cs₂CO₃ (456 mg, 1.4 mmol) were first added in an oven-dried Schlenk tube. After evacuating and backfilling with N₂ for several times, 159 mg of Boc-hydrazide, 110 μL of iodobenzene and 1.0 mL of DMF were added to the same system with Schlenk tube carefully sealed. Finally, the reaction mixture was stirred at 80 °C for 21 h and cooled to room temperature. By filtered through a 0.5×1 cm pad of silica gel eluting with ethyl acetate, the product was concentrated and purified by flash chromatography on silica gel. The pale yellow organic precursor of N-Boc was characterized by ¹H NMR method of 400 MHz, with the results as follows: δ 7.50-7.40 (m, 2H), 7.35-7.25 (m, 2H), 7.15-7.05(m, 1H), 4.44 (s, 2H), 1.51 (s, 9H). This data was in accordance with that of pure 1-tert-butoxycarbonyl-1-phenylhydrazine (N-Boc) ⁴.
The tandem reaction of cyclohexanol in liquid phase was conducted as follows: Pt@S1, B-Pt@S1 or commercial Pt/SiO2 catalysts with the same Pt amount of 0.006 mmol (corresponding to 40 mg of Pt@S1 or B-Pt@S1, 120 mg of Pt/SiO2) were added into a mixture containing 0.18 g of cyclohexanol, 4 mL of EtOH and 0.08 g of N-Boc. The solution was then heated to 80 °C under stirring with an air flow of 40 mL min⁻¹.

Another reaction with only oxidation step was performed similarly but without N-Boc added. Meanwhile, 4 mL of an ethanolic solution of benzothiazole with a concentration of $3.0 \times 10^{-5}$ M was injected as the poison molecule at the beginning of the oxidation reaction. All of the final products were analyzed by high-performance liquid chromatography (HPLC).

References: