# Supporting Information For

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

### 1. Catalyst characterization

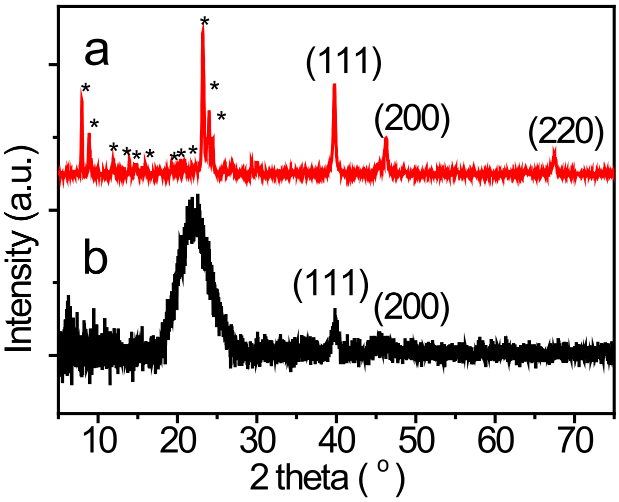

Fig. S1 XRD spectrum of (a) Pt@S1 and (b) Pt/SiO$_2$. The three peaks at 2 theta equaling to 40, 46 and 68 ° are indexed to (111), (200) and (220) of platinum and the peaks identified with '*' are attributed to silicalite-1.

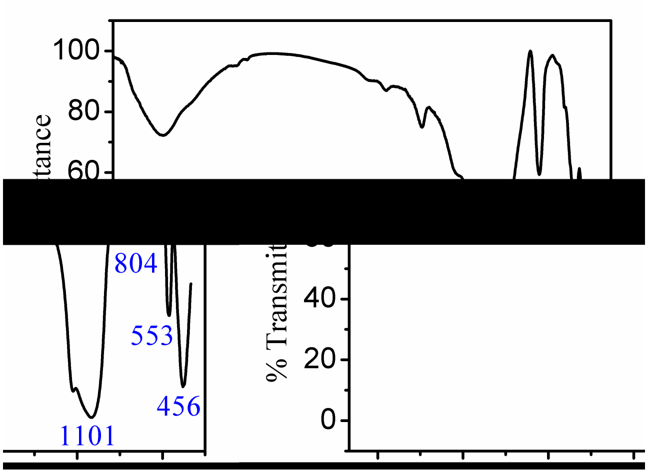
[redacted]

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.

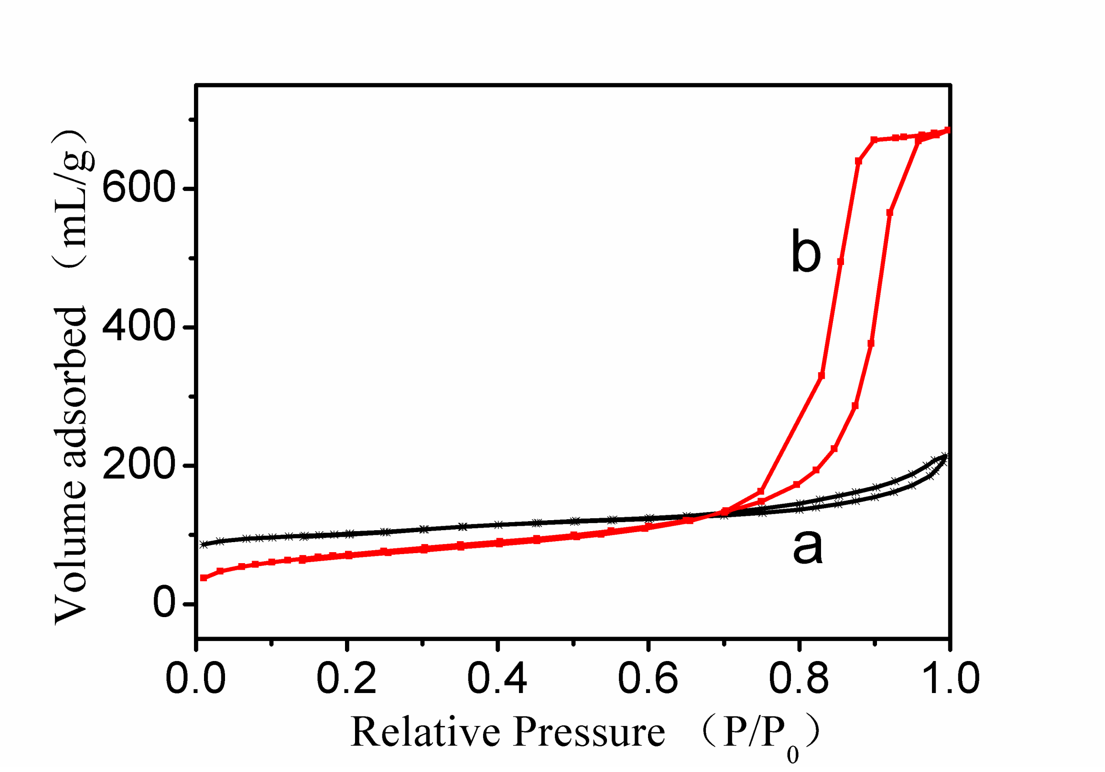

Fig. S3 Representative $N_2$ adsorption–desorption isotherms of (a) Pt@S1 and (b) commercial Pt/$SiO_2$

Table S1 Textural property of the Pt@S1 and Pt/$SiO_2$

| | $S_{BET}$/($m^2 \cdot g^{-1}$) | $S_{Langmuir}$/($m^2 \cdot g^{-1}$) | $S_{micro}$/($m^2 \cdot g^{-1}$) | $V_{micro}$/($cm^3 \cdot g^{-1}$) |
|---|---|---|---|---|
| Pt@S1 | 341 | 461 | 221 | 0.12 |
| Pt/$SiO_2$ | 262 | 366 | 8 | 0 |

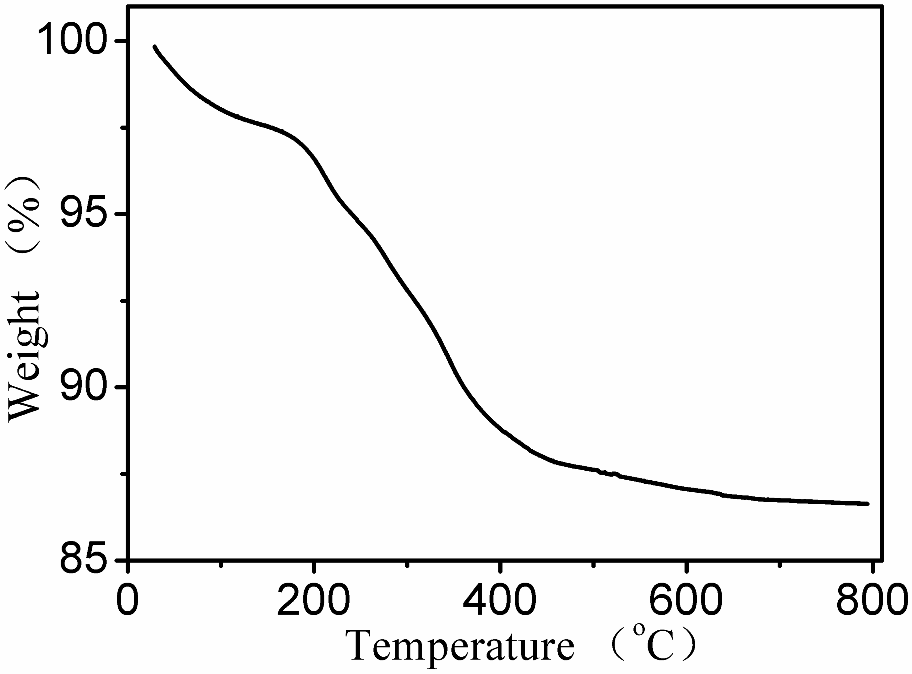

Fig. S4 TG curve of Pt@S1

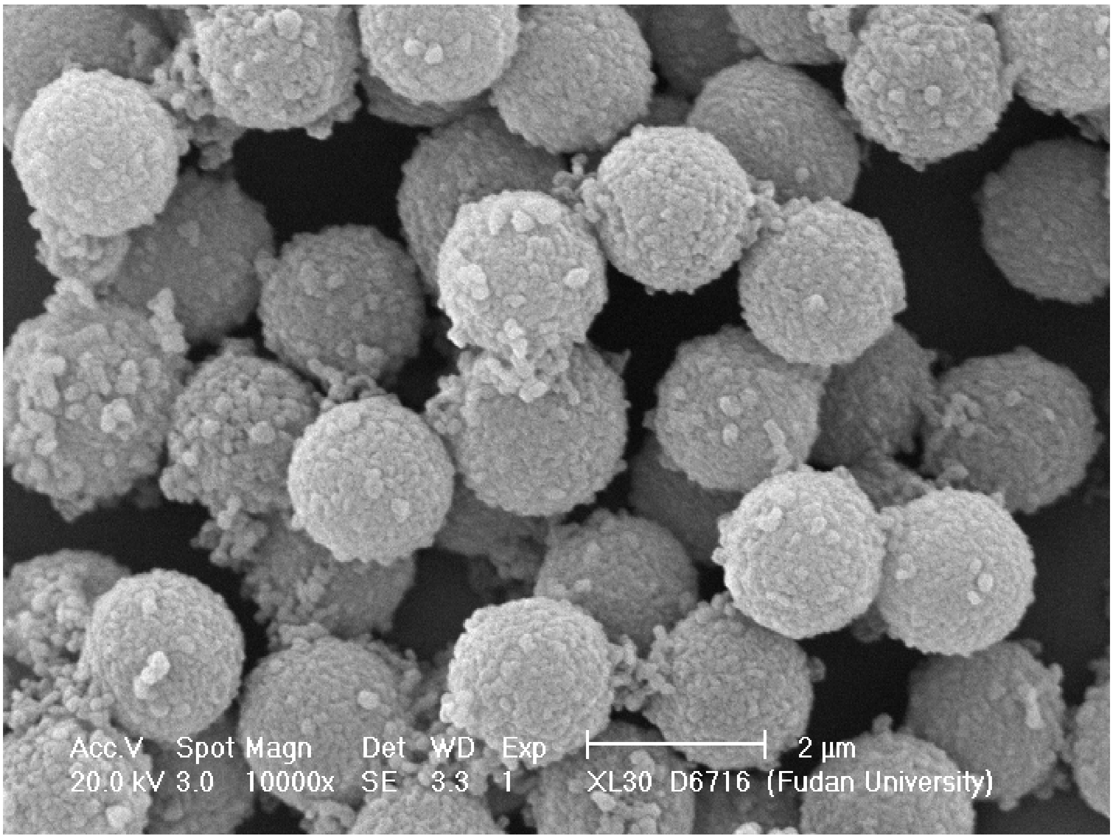

Fig. S5 SEM image of Pt@S1 after 10 runs of reaction

## 2. Experimental

### 2.1. Materials

Benzothiazole (98%), tert-butyl carbazate (Boc-hydrazide, 98+%), cesium carbonate ($Cs_2CO_3$), 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. $H_2PtCl_6 \bullet 6H_2O$ was supplied by Sinopharm Chemical Reagent Company. $KBH_4$ (94 w. t. %), tetrapropylammonium hydroxide (TPAOH, 25 w. t. % in water), tetrapropyl ammonium bromide (TPABr), tetraethoxy-orthosilane (TEOS), idobenzene (>97%), and cyclohexanol were obtained from Shanghai Chemical Reagent Company. The commercial noble metal catalyst $Pt/SiO_2$ (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 $H_2PtCl_6$, the platinum loaded MSSs (Pt-MSSs) were reduced with 0.01 M $KBH_4$ aqueous solution and calcinated in air at 600 $^{o}$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: $H_2O$: 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 $^{o}$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 $^{o}$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 $CDCl_3$ 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 $Cs_2CO_3$ (456 mg, 1.4 mmol) were first added in an oven-dried Schlenk tube. After evacuating and backfilling with $N_2$ 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 $^{o}$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 $^{1}$H 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].

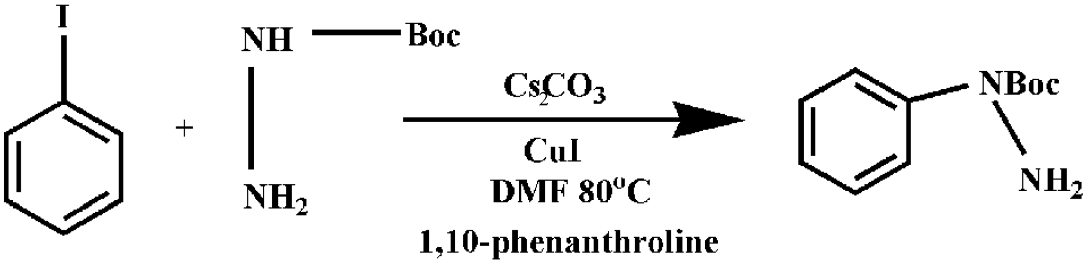

Fig. S6 The equation of the fabrication of N-Boc

## 2.5. Tandem catalytic reaction

The tandem reaction of cyclohexanol in liquid phase was conducted as follows: Pt@S1, B-Pt@S1 or commercial Pt/$SiO_2$ 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/$SiO_2$) 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 $3.0\times10^{-5}$ 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).

## Referrences:

1 N. Ren, Y. H. Yang, J. Shen, Y. H. Zhang, H. L. Xu, Z. Gao and Y. Tang, *J. Catal.*, 2007, **251**, 182.

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3 J. Shi, N. Ren, Y. H. Zhang and Y. Tang, *Microporous and Mesoporous Mater.*, 2010, **132,** 181.

4 M. Wolter, A. Klapars and S. L. Buchwald, *Org. Lett.,* 2001, **3,** 23.