Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Silica Nanotubes with Mesoporous Walls and Various Internal Morphologies Using Hard/Soft Dual Templates

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Experimental Section

Sample preparation: In a typical procedure, 24 mg of carbon materials was added to a solution of 30 mL H_2O, 20 mL EtOH and 0.124 g CTAB at room temperature. After sonication for several hours, 60 μL of 1 M NaOH aqueous solution was add to the above solution under stirring. Then 0.24 mL TEOS was added drop-wise and stirring for 12 h. The black solid product was then collected, purified and dried. By calcined at 550 °C for 5 h in air flow the white sample was obtained.

MCM-41 was prepared by using TEOS as the silica source and CTAB as templates according the procedure described by Cai et al.[24] Functionalized mesoporous silica nanotubes was prepared by grafting aminopropyl (RNH_2) groups on the pores of the mesoporous silica nanotubes according to the procedure described by Lam et al.[27]

The mesoporous silica nanotubes and MCM-41 supported platinum catalyst (10 wt % Pt loading) was prepared by impregnating. The catalyst was prepared by impregnating 1.05 ml 0.05 M H_2PtCl_6 aqueous solution into 0.1 g mesoporous silica nanotubes or MCM-41 followed by drying at 80 °C and calcinations at 350 °C for 3 h in H_2 flow with a flow rate of 10ml/min.

A flow reactor system was built for the catalytic testing. In cyclohexene and benzene hydrogenation/dehydrogenation reaction, 5 or 50 mg Pt/mesoporous silica nanotubes or Pt/MCM-41 and 450 mg sea sand were mixed as catalyst, and hydrogen gas was used as a carrier gas and reactant at a flow rate of 60 mL/min in all runs. Cyclohexene was introduced into the reactor via hydrogen bubbling at room temperature. The reactant and product analyses were conducted on line using a Agilent 6890 GC equipped with a FID detector.

Procedure for the adsorption test: The equilibrium adsorption of Cd^{2+} and Ni^{2+} on NH_2-mesoporous silica nanotubes was measured for single components systems. The adsorptions were carried out using 0.02 g of NH_2-mesoporous silica nanotubes adsorbent for 25 mL of aqueous solutions containing the metal ions at room temperature under stirring. The adsorption was monitored by taking samples of the adsorption solution after 1 h. The concentrations of the metals in the solution were analyzed by inductively coupled plasma, atomic emission spectrometer (ICP-AES). 1×10^{-4} mol/L aqueous Rhodamine B solution was prepared for adsorption tests. The adsorption of dye was performed by adding 0.01 g of mesoporous silica nanotubes in a 25 mL of dye solution at room temperature under stirring. The dye concentration was monitored by a Uv-Vis Spectrophotometer by measuring absorbance at λ_{max} of 550 nm. The data obtained from the adsorption tests were then used to calculate the adsorption capacity, qt (mol/g), of the adsorbent by a mass–balance relationship, which represents the amount of adsorbed dye per unit amount of dry adsorbent,

$$qt = (C_0 - C_t)V/W$$

where C_0 and C_t are the concentrations of dye in solution (mol/dm^3) at time t = 0 and t = t, respectively, V is the volume of the solution (dm^3), and W is the weight of the dry adsorbent used (g).

Characterization: The microscopic features of the samples were characterized by SEM (JEOL-6701F), TEM (JEOL JEM-1011). The powder X-ray diffraction pattern was collected using a Panalytica X'pert PRO diffractometer. The TGA measurement was carried out under air at a heating rate of 2 °C min^{-1} using a Perkin Elmer Diamond TG/DTA instrument. Adsorption and desorption isotherms for nitrogen were obtained at -196 °C using a Quantachrome Autosorb-1. Elemental analysis was conducted using an inductively coupled plasma (ICP), atomic emission spectrometer Perkin Elmer Optima 5300DV ICP-AES. The dye concentration was analyzed on a Shimadzu UV-1601 UV-Vis Spectrophotometer.

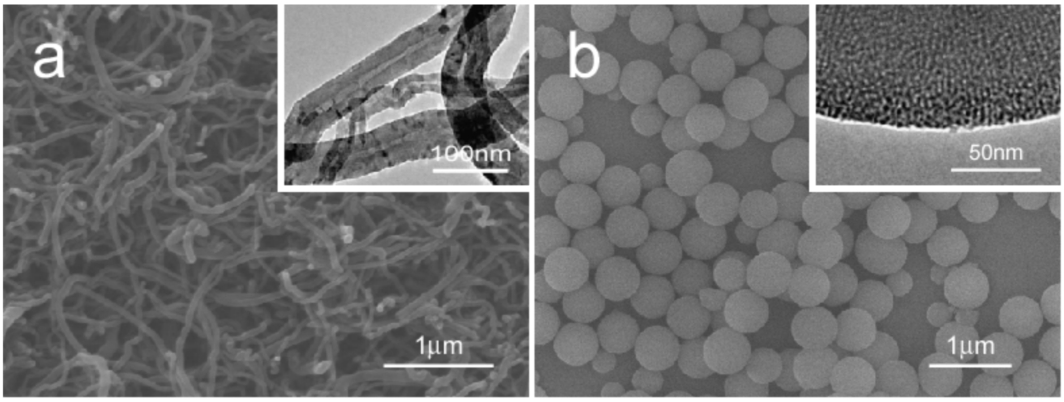

Fig. S1 SEM and TEM image of the sample prepared without addition of CTAB (a and inset) or CNTs (b and inset).

Table 1. Adsorption capacities of the mesoporous silica nanotubes for various species

Adsorbent	Adsroption capacitya (mg/g)		
	Rhodamine B	Cd^{2+}	Ni^{2+}
MSN	55	0.1	8.8
MSN-NH_2		61	29

[a] The initial concentration of rhodamine B, Cd^{2+}, and Ni^{2+} aqueous solution is 1×10^{-4}, 2×10^{-3}, and 2×10^{-3} mol/L, respectively.

For Pt (10 wt %)/mesoporous silica nanotubes, the formation Pt particles is clearly observed in the TEM and high-magnification TEM images (Figure S2a and b). It shows no formation of big Pt particles on the external surface of mesoporous silica nanotubes. These results indicate that the Pt particles are located in the internal mesopores. The Pt particle size distribution in Figure S2c shows the average Pt particles is ca. 2.3 nm.

Figure S3a and b are the SEM and TEM images of MCM-41. These Results show that the size of MCM-41 particles is almost several μm in diameter. And MCM-41 has an ordered mesoporous structure. TEM image (Figure S3c) shows that the formation Pt particles is clearly observed and no formation of big Pt particles on the external surface of MCM-41. These results indicate that the Pt particles are located in the internal mesopores. The Pt particle size distribution in the inset of Figure S3d shows the average Pt particles is ca. 2.2 nm.

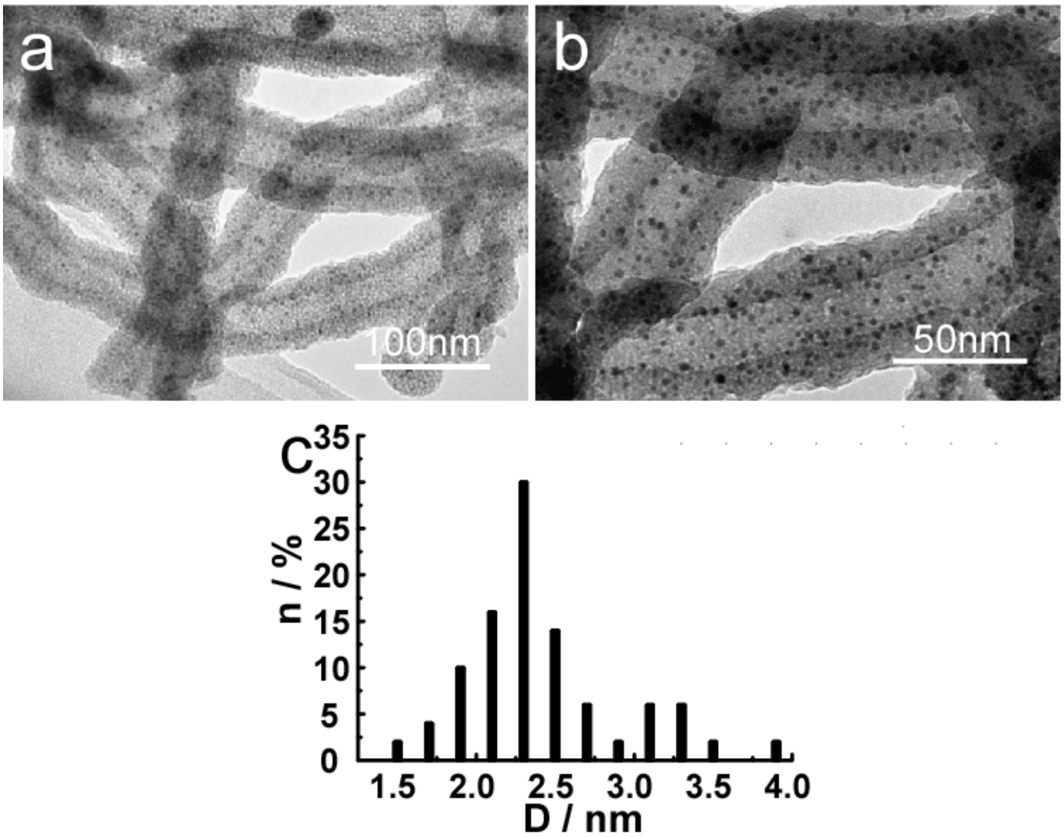

Fig. S2 (a and b) TEM and high-resolution TEM images, (c) Pt particle size distribution of Pt (10 wt %)/mesoporous silica nanotubes.

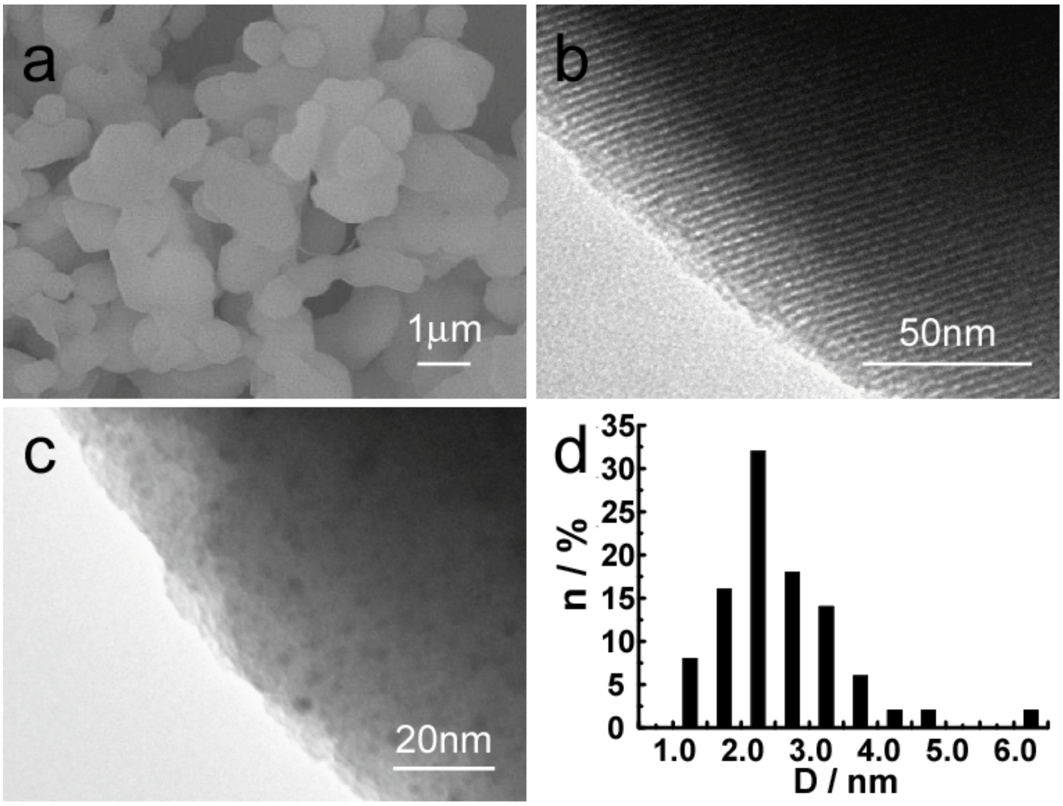

Fig. S3 (a) SEM and (b) TEM images of MCM-41; (c) TEM image and (d) Pt particle size distribution of Pt (10 wt %)/MCM-41.

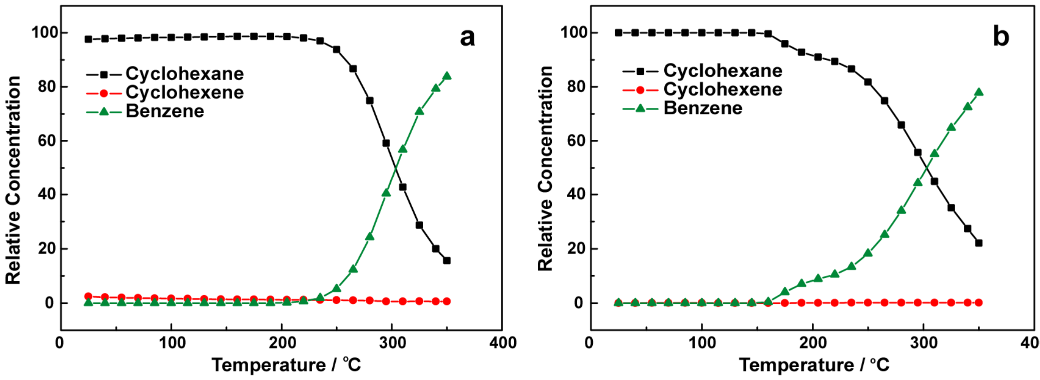

Fig. S4 Cyclohexene conversion over mesoporous silica nanotubes (a) and MCM-41 (b) supported Pt catalyst as a function of temperature.

TGA results in Figure S5 shows the decomposition of CTAB and carbon nanotubes during the calcination. The TGA curve indicates a three-step weight loss pattern, in the temperature range of 30 to 150 °C, 150 to 500 °C, and 500 to 650°C, and DTG analysis displays three largest weight-loss rates occur at 220, 300, and 580 °C, respectively. The first weight loss is ascribed to the removal of physical adsorbed water. The second weight loss is attributed to the degradation of CTAB.[23-25] The third weight loss is attributed to the removal of carbon nanotubes.

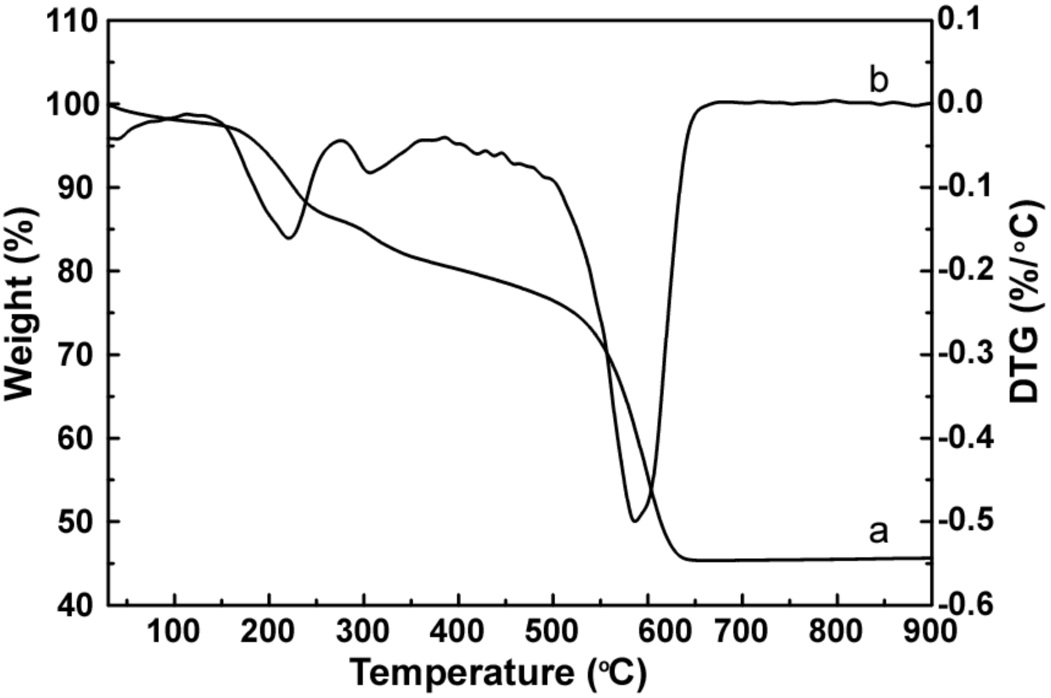

Fig. S5 (a) TGA and (b) DTG analysis of as-prepared carbon CNTs@mesoporous silica.