Experimental

1. Materials

Tetraethyl orthosilicate (TEOS, 99%), n-butanol (99%), cyclohexane (99%), aqueous ammonia (25-28wt%), ethanol (99.5%) cobaltous acetate (Co(CH₃COO)₂·4H₂O, 99%), cobaltous chloride (CoCl₂·6H₂O, 99%), cobaltous nitrate (Co(NO₃)₂·6H₂O, 99%), cobaltous acetate (CoSO₄·7H₂O, 99%), nickelous acetate (Ni(CH₃COO)₂·4H₂O, 99%), cupric acetate (Cu(CH₃COO)₂·H₂O, 99%) and silver nitrate (AgNO₃, 99%) were obtained from Tianjin Kermel Chemical Reagent Development Center, China. Poly (oxyethylene) nonylphenol ether (NP-7, Industrial Grade) was purchased from Dalian Chemical. Tetramethyl orthosilicate (TMOS, 99%) was purchased from Sinopharm Chemical Reagent Co., Ltd., Aladdin reagent Corporation. Deionized water used in all experiments was obtained from a Milli-Q system (Millipore). Raw material of CHHP was a cyclohexane solution provided by Liaoyang Synthetic Fiber Co. Ltd. (China). After purification, it contains CHHP (0.309 mmol mL⁻¹) and adipic acid (0.017 mmol mL⁻¹)

2. Preparation of hollow silica nanospheres

Silica nanospheres are prepared using a well-established water-in-oil reverse microemulsion procedure. In a typical synthesis procedure, solution A was prepared by mixing appropriate amounts of NP-7, n-butanol and cyclohexane. Cobaltous acetate were dissolved in aqueous ammonia to form metal ammonia complex aqueous solution B. W/O microemulsion was obtained by mixing solution A and B, and mechanically stirred for 30 min at room temperature to make the emulsion stable. Then appropriate tetramethyl orthosilicate (TMOS) was dripped slowly to the microemulsion. The molar ratio of the mixture was: 1(NP-7)/4.32(n-Butanol)/15(cyclohexane)/15.56(water)/1(Si)/Y(Co). The concentration of aqueous ammonia was 2, 8 and 12 wt%. Y is the molar ratio of metal to silicon (Y = 0, 0.01, 0.02 and 0.03). The mixture was stirred for 12 h followed by addition of ethanol to break the microemulsion. The materials were washed a couple of times under reflux with ethanol to remove surfactants and dried at 80 °C for 12 h.
3. Characterization

Ultraviolet–visible diffuse reflectance spectroscopy (UV–Vis DRS) were collected on a Shimadzu (Tokyo, Japan) UV-2550 spectrophotometer equipped with a diffuse reflectance attachment. N₂ physical adsorption–desorption measurement was carried out at 77 K on an Autosorb-1 Quantachrome instrument. Samples were pre-degassed at 100 °C for about 10 h to remove water and other physically adsorbed species. Microstructures of the materials were examined by transmission electron microscopy (TEM) on a FEI Tecnai G² Spirit electron microscope at an accelerating voltage of 120 kV and High resolution scanning electron microscopy (HRSEM) on a 5500 scanning electron microscopy.

3. Decomposition of CHHP

The reaction was carried out in a 50 mL stainless steel autoclave under magnetic stirring. In a typical procedure, 0.02 g catalysts and 10 mL cyclohexyl hydroperoxide solution were added in the reactor. The reaction was conducted at a temperature ranging 130 °C for 30 min under N₂ atmosphere. The recycled catalyst was washed with ethanol before used. The products were identified by an Agilent 6890N GC/5973 MS detector and quantitated by an Agilent 7890D GC equipped with an OV-1701 column (30 m × 0.25 mm × 0.3 μm) and titration. After transformation of the hydroperoxide into cyclohexanol by adding triphenylphosphine to the reaction mixture, cyclohexanol and cyclohexanone were determined by internal standard method using nonane as an internal standard. The concentration of CHHP was determined by iodometric titration and the acid and ester by acid-base titration. The selectivity of cyclohexanol and cyclohexanone was calculated by combining the result of GC of cyclohexanol or cyclohexanone and the iodometric titration of CHHP.
Fig. S1 TEM image of hollow silica nanospheres with Co/Si = 0.02.
**Fig. S2** HRSEM image of hollow silica nanospheres with Co/Si = 0.02.
Fig. S3 N₂ adsorption-desorption isotherm of Co-SiO₂.
**Fig. S4** Pore size distribution calculated from non-local density functional theory (NLDFT) models.
Fig. S5 EDS spectrum of hollow silica nanospheres with Co/Si = 0.02.
Fig. S6 Photo of silica nanospheres prepared without (a) and with (b) adding cobalt salts.
Fig. S7 TEM image of SiO$_2$ after immersing in 12 wt% aqueous ammonia for 12 h.
**Fig. S8** TEM image of silica nanospheres using TEOS as silica source.
Fig. S9 The phenomenon of adding aqueous ammonia to the cobaltous acetate aqueous solution. Cobaltous acetate aqueous solution (a); cobalt hydroxide before (b) and after (d) centrifugation and cobalt ammonia complex before (c) and after (e) centrifugation. As ammonia was added to the cobaltous acetate aqueous solution, a green metal hydroxide precipitate formed and then dissolved to form the metal ammonia complex.
Scheme S1. Proposed formation mechanism of the silica nanospheres with multi-nanochambers.

Silicate species  Cobalt hydroxide cluster