Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

for

Asymmetric Reactions on Chiral Catalysts Entrapped within Mesoporous Cage

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Experimental

1 General Process for preparation of heterogeneous chiral catalysts

The method for introducing (S,S)-TsDPEN-RuCl-(cymene) [TsDPEN is 4-(methylphenylsulfonyl)-1,2-diphenyl-ethylenediamine] into SBA-16 is similar to Co(Salen) except that 0.04 g of (S,S)-TsDPEN-RuCl-(cymene) was used in stead of Co(Salen) and the refluxing time was 12 h. SBA-16 with cymene was added to the mixture containing triethylamine (1.2 mL) and dry toluene (1.7 mL) followed by addition of 0.20 mL of diphenyldichlorosilane under Ar atmosphere. After stirring for 12 h at 328 K, the solid was separated by centrifugation, washed thoroughly with CH_2Cl_2. The resulting solid was denoted as RuTsDPEN/SBA-16-2Ph (Ru: 0.133 wt% from elemental analysis). The Ru content of RuTsDPEN/SBA-16-2Ph after the sixth run was 0.107%

2 General Process for tailoring the pore entrance of SBA-16

Mesoporous cage-like material SBA-16 was synthesized according to the modified method.[6a] The mixture of Pluronic F127 and Pluronic P123 ($EO_{80}PO_{70}EO_{80}$) was used as the template. TEOS and aluminium isopropoxide (the molar ratio is 30) were used as inorganic precursor. The gel was hydrothermally treated at 373K for 12 h. The as-synthesized material was calcined at 823 K for 10 h to remove the template. Previously, it was reported that mesoporous silica containing aluminium in the framework is favorable for the adsorption of Mn(Salen)(Journal of Molecular Catalysis A: Chemical, 1997, 179-187). However, elemental analysis by ICP-AES and pyridine adsorption experiment by FT-IR show that no aluminium is incorporated in the mesoporous framework under our strong acidic synthesis conditions (Figure S7).

0.75-1.25 mL of dry toluene (the mixture liquid enough to cover the solid), 1.25 mL of anhydrous pyridine or *n*-butyamine, 5 mmol of organosilane were added to 1.0 g of SBA-16 (evacuated at 398 K for 6 h). After refluxing for 24 h under Ar atmosphere, the resulting solid was isolated by rapid filtration and thoroughly washed with toluene and a mixture of CH_2Cl_2 and diethyl ether. The resultant materials using $CH_3Si(OCH_3)_3$(C1), $CH_3CH_2CH_2Si(OCH_3)_3$(C2), $C_6H_5Si(OCH_3)_3$ (Bz), $CH_3(CH_2)_7Si(OCH_3)_3$(C8) and $CH_3(CH_2)_{11}Si(OCH_3)_3$(C12) as blocking agents were denoted as SBA-16-C1, SBA-16-C3, SBA-16-Bz, SBA-16-C8 and SBA-16-C12, respectively.

3 Characterization and analysis

Small-angle X-ray powder diffraction was performed on Rigaku (Cu Ka, 40 kv, 30 mA), N_2 physical adsorption was carried out on micrometritics ASAP2020 volumetric adsoption analyzer (before the adsorption measurements, samples were out gassed at 393 K for 6h). UV-vis spectra were recorded on the JASCOV-550 with pure CH_2Cl_2 as a reference. FT-IR spectra were collected on Thermo-Nicolet-Nexus 470 infrared spectrometer (evacuated at 528 K for 6 h). Metal Co and Ru content were analysed on Plasma-spec-II (Leeman, U.S.A.). TEM micrographs were taken using a JEM-2000EX transmission electron microscope at 120 KV. The quantitive analysis and configuration analysis of the reaction products were conducted on Agilent6890 GC with HP-Chiral19091G-B213 capillary column.

Table S1: Physical parameters for SBA-16 before and after modification

Materials	Surface area (m^2/g)	Pore volume (cm^3/g)	BJH pore diameter (nm)
SBA-16	892	0.61	5.9
SBA-16-C1	497	0.43	5.7
SBA-16-C3	450	0.37	5.5
SBA-16-Bz	432	0.37	5.2
SBA-16-C8	246	0.26	5.1
SBA-16- C12	6	0.02	/

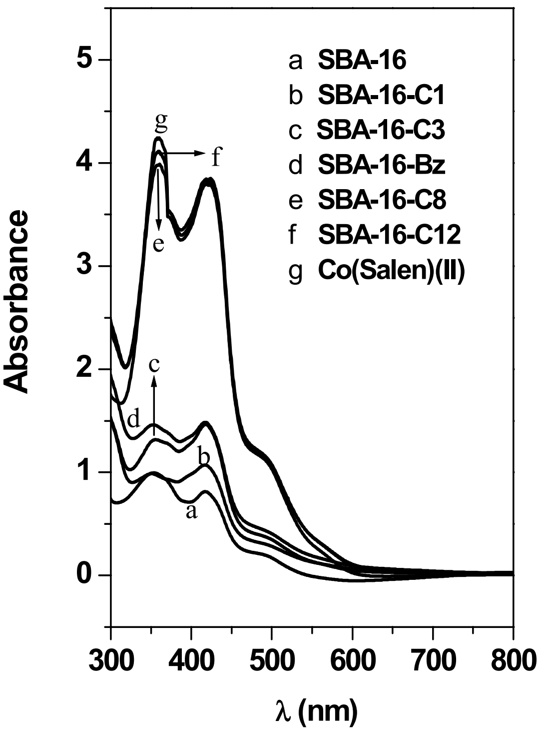

Figure S1. UV-vis spectra of Co(Salen) (II) in dichloromethane before and after absorption with SBA-16-X samples (0.08 g of SBA-16 or SBA-16-X was dispersed in 3.8 mL of CH_2Cl_2 containing 1.33×10-6 mol (R,R)- Co(Salen) (II). The mixture was stirred in a sealed tube for 5 h. After centrifugation, the solution was measured with UV-vis spectroscopy).

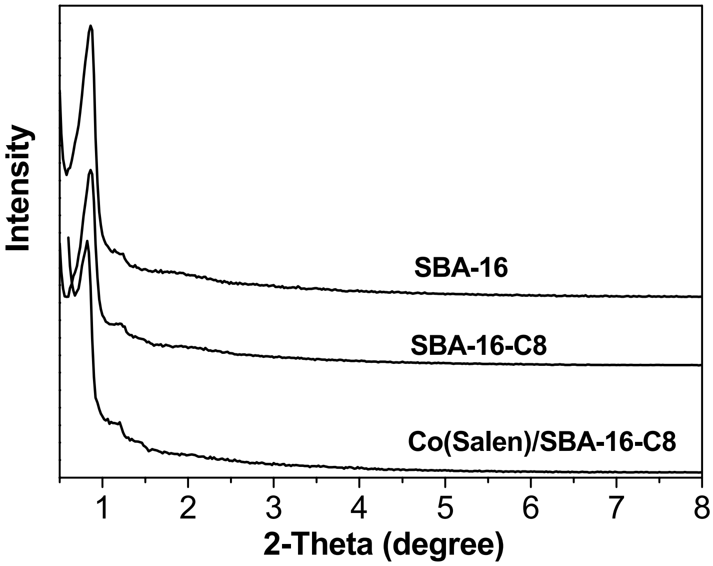

Figure S2. XRD patterns of SBA-16, SBA-16-C8 and Co(Salen)/SBA-16-C8

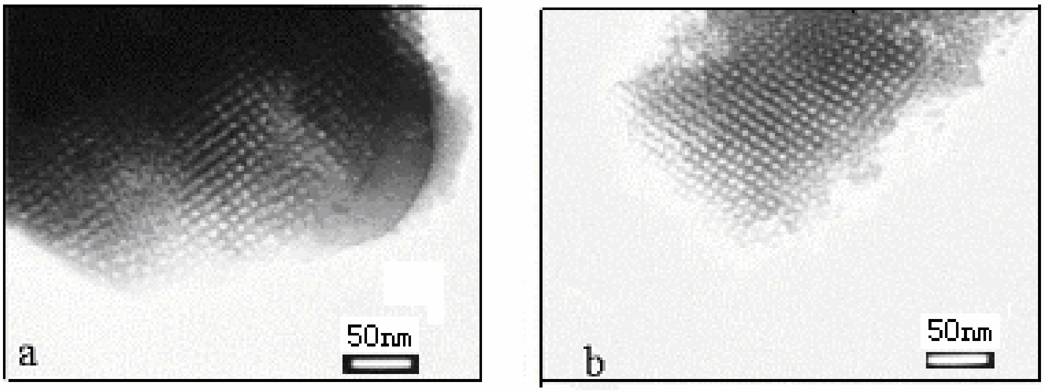

Figure S3. TEM images of [a] SBA-16 and [b] Co(Salen)/SBA-16-C8

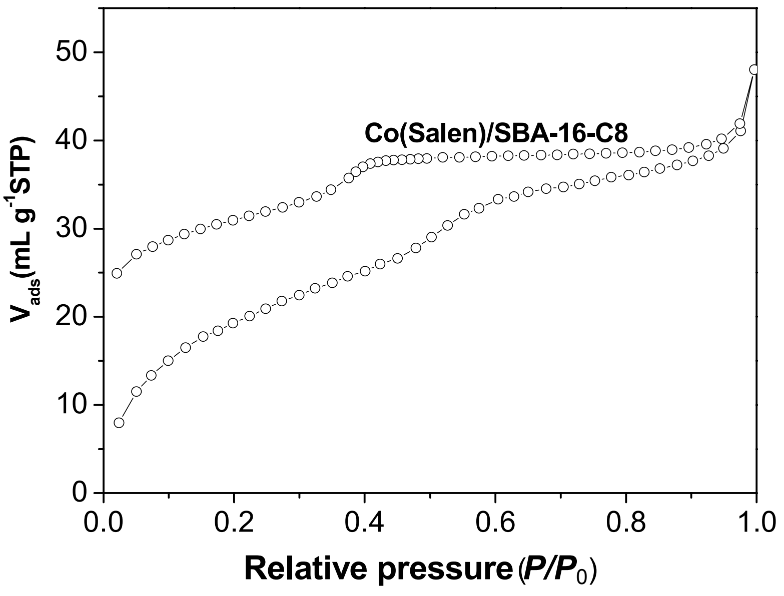

Figure S4. N_2 sorption isotherm of Co(Salen)/SBA-16-C8

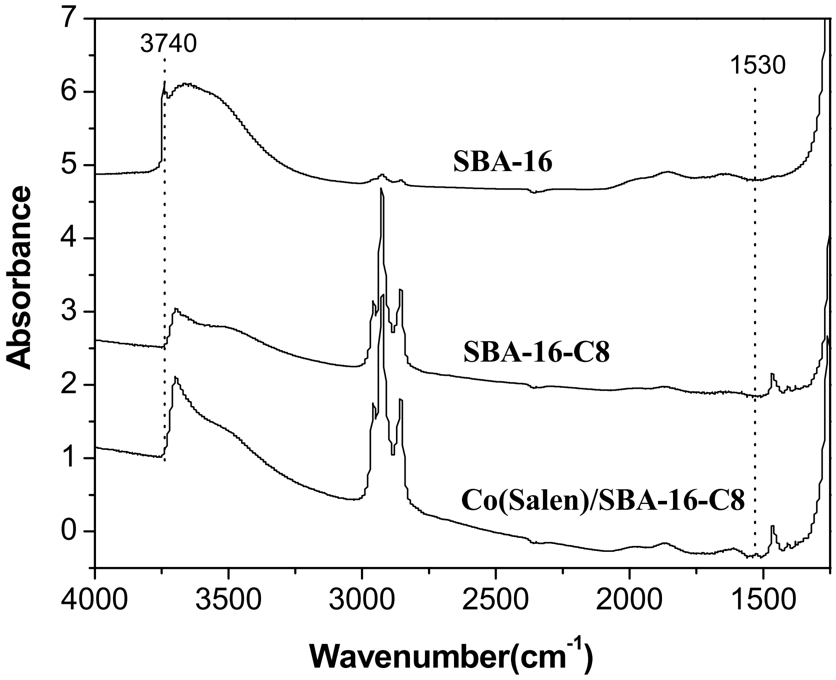

Figure S5. FT-IR spectra of SBA-16, SBA-16-C8 and Co(Salen)/SBA-16-C8

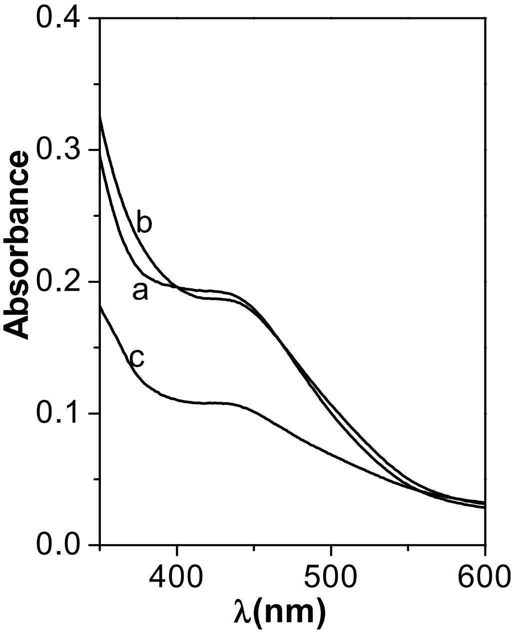

Figure S6. Uv-vis spectra of the RuTsDPEN in dichloromethane before and after absorption with SBA-16-X; [a] RuTsDPEN in dichloromethane; [b] SBA-16-2Ph; [C] SBA-16-Me.

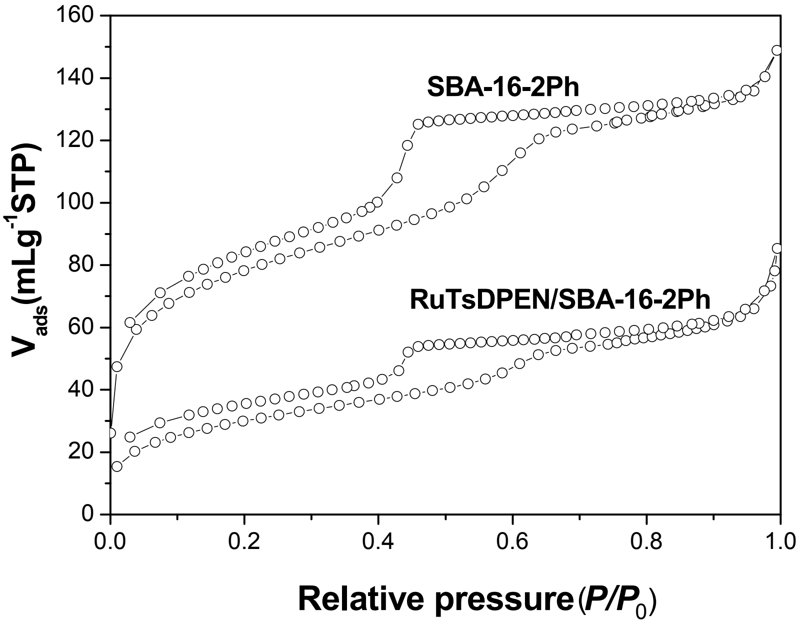

Figure S7. N_2 sorption isotherms of SBA-16-2Ph (modified with diphenyldichlorosilane) and RuTsDPEN/SBA-16-2Ph.

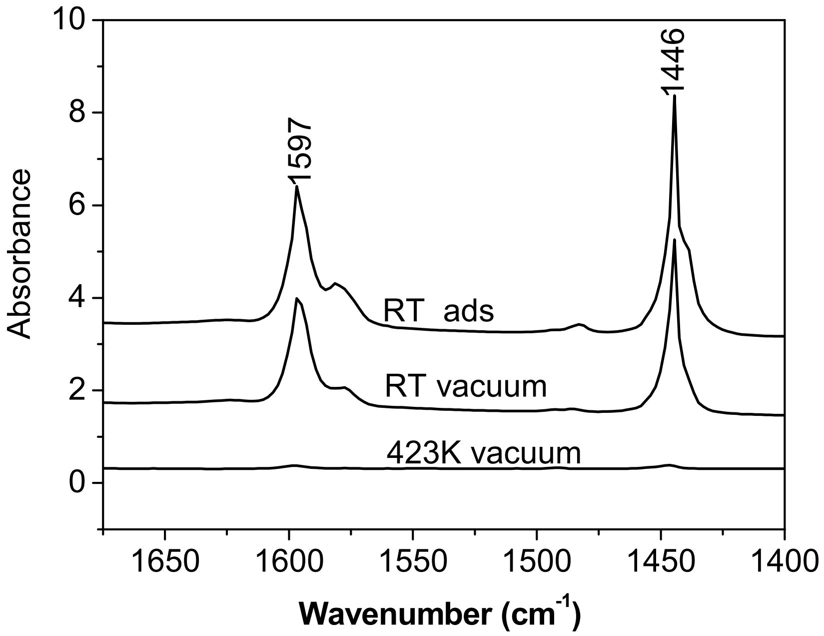

Figure S8. FT-IR spectra of adsorbed pyridine on SBA-16