Supporting Informations

Enhancement of Catalytic Performance in Asymmetric Transfer Hydrogenation by Microenvironment Engineering of the Nanocage

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Reagents and materials

Pluronic P123 copolymer ($EO_{20}PO_{70}EO_{20}$), pluronic copolymer F127 ($EO_{106}PO_{70}EO_{106}$) and dichloro(*p*-cymene)ruthenium(Ⅱ)dimmer([$RuCl_2$(*p*-cymene)]$_2$) were purchased from Sigma Company. Acetophenone (99 %) and other ketones were purchased from Acros Company and used as received. N-trimethoxysilylpropyl-N, N, N-tri-n-butylammonium bromide (50% in methanol) was purchased from Gelest. Tetraethoxysilane (99 %, TEOS), and other reagents were obtained from Shanghai Chemical Reagent Inc. of Chinese Medicine Group.

(1R,2R)-1,2-Diphenyl-N-(*p*-tolylsulfonyl)ethylenediamine (TsDPEN)[1] and SBA-16 were synthesized according to the literature.[2]

Characterization

N_2 sorption was carried out on a Micromeritics ASAP 2020 volumetric adsorption analyzer after the samples were outgassed at 393 K for 6 h. UV-vis spectra were recorded on SHIMADZU UV-vis 2550 spectrophotometer using dichloromethane as the reference. Diffuse-reflectance UV-vis spectra were recorded on SHIMADZU UV-Vis 2550 spectrophotometer using $BaSO_4$ as the reference. The adsorption of water and benzene vapors were measured at 293 K on Hiden Isochema Intelligent Gravimetric Analyser after the samples degassed for 6 h at 353 K. X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT D/Max-2500 powder diffraction system using Cu Kα radiation of 0.15406 nm wavelength. The element analysis of C, H, and N was performed on varioEL III Elemental analyzer.

Encapsulation of Ru-TsDPEN in the nanocage with different microenvironment

For the preparation of the nanocage with different microenvironment, Ru-TsDPEN was first adsorbed in the nanocages of SBA-16 by refluxing the mixture containing SBA-16 (0.5 g), (R, R')-Ru-TsDPEN (20 mg) and CH_2Cl_2 (3 ml) for 12 h. After CH_2Cl_2 was removed by evaporation, the resultant solid, Ru-TsDPEN@SBA-16, was dispersed in 0.7 mL of toluene together with desired amount of silylation reagent and triethylamine. After heating the mixture at 55 ^oC for 10 h, the solid product was filtered off and washed thoroughly with toluene and CH_2Cl_2. Compared with Soxhlet method, washing with CH_2Cl_2 is more efficient to remove Ru-TsDPEN adsorbed on the outer surface of the host materials. The catalyst was denoted as Ru-TsDPEN@SBA-n, where n refers to the initial molar percentage of R'x100/(R+R') employed for the silylation (R'= N-trimethoxysilylpropyl-N, N, N-tri-n-butylammonium bromide and R= propyltrimethoxysilane).

Characterization of catalysts

The textural properties of SBA-16 used as the host were detected by the N_2 sorption experiment (Fig. S1). The SBA-16 shows type IV adsorption isotherm and H2 type hysteresis loop, which is typical of mesoporous material with cage-like pore structure. All Ru-TsDPEN@SBA-n samples show type IV isotherm but with less defined hysteresis loop and the adsorption and desorption isotherms do not close at low P/P_0. This is probably due to the existence of large amount of organic group on the materials.

Figure S2 shows the XRD patterns of SBA-16 and Ru-TsDPEN@SBA-n. All

Table S1. Physicochemical properties of SBA-16 and the catalysts measured by N_2 sorption

Samples	BET Surface Area m^2/g	Pore Volume cm^3/g^a	Pore Size nm^b
SBA-16	916	0.64	5.5
Ru-TsDPEN@SBA-0	411	0.3	4.7
Ru-TsDPEN@SBA-9	27	0.03	-
Ru-TsDPEN@SBA-38	6.4	0.006	-
Ru-TsDPEN@SBA-100	13	0.02	-

[a] Estimated from the amounts adsorbed at a relative pressure (P/P_0) of 0.99. [b] the pore size distribution calculated from the N_2 adsorption branch using the BJH method.

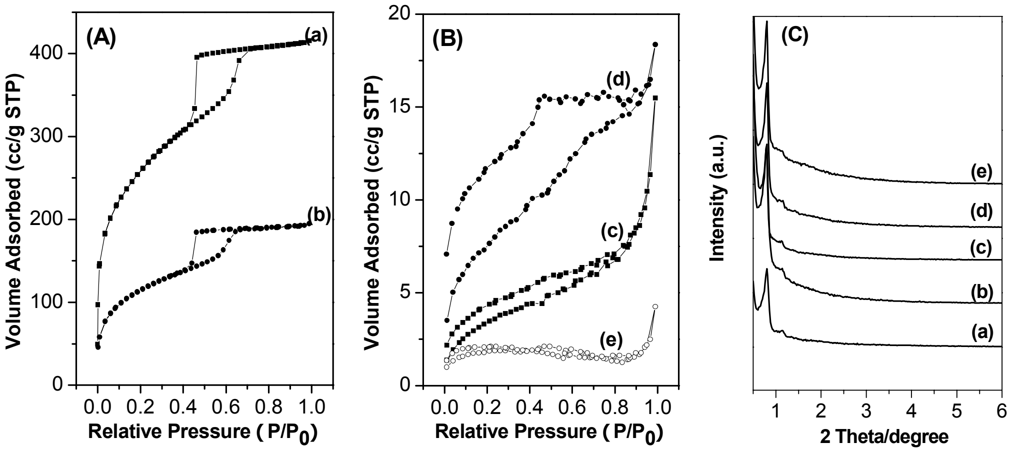


Fig. S1 Nitrogen adsorption-desorption isotherm and XRD patterns of the samples, (a) SBA-16, (b) Ru-TsDPEN@SBA-0, (c) Ru-TsDPEN@SBA-9, (d) Ru-TsDPEN@SBA-38 and (e) Ru-TsDPEN@SBA-100.

materials exhibit two diffractions (110) and (200) peaks, characteristic of mesoporous materials with the cubic $Im\bar{3}m$ structure. This indicated that the structure of the SBA-16 was maintained in the process of the encapsulation of metal complex.

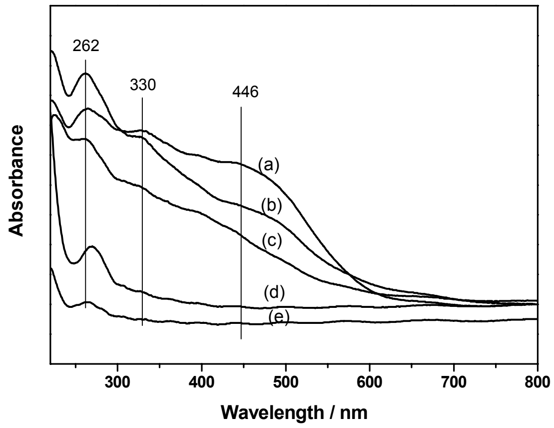


Fig. S2 Diffusion reflectance UV–vis spectra of (a) Ru-TsDPEN, (b) Ru-TsDPEN@SBA-100, (c) Ru-TsDPEN@SBA-0, (d) SBA-0 and (e) SBA-100.

Diffuse reflectance UV-vis spectra of Ru-TsDPEN@SBA-n samples show three bands at 262, 330 and 446 nm similar to that of Ru-TsDPEN (Fig. S2). These bands are not observed in the UV-vis spectra of samples prepared by silylation of SBA-16 without Ru-TsDPEN encapsulation. This result confirms that Ru-TsDPEN is successfully encapsulated in the nanocages of SBA-16 and still keeps the similar structure to the free metal complex.

Estimation of the average number of Ru-TsDPEN per cage

The calculation is based on the assumptions that the mesopore volume of SBA-16 is completely contributed by cages and each cage accommodates the same number of Ru-TsDPEN molecules. The number of Ru-TsDPEN per cage (n) was calculated by the following equation:

$$\mathbf{n} = \frac{\mathbf{N}_{\mathbf{Ru(1g)}} \times \mathbf{6.02} \times \mathbf{10}^{23}}{\dfrac{\mathbf{V}_{\mathbf{meso}}}{\frac{4}{3}\pi(\frac{D}{2})^{3}}}$$

$N_{Ru(1g)}$ is the mole of Ru-TsDPEN per gram of the solid catalyst; $V_{meso.}=V_{total.}-V_{microp.}$;

D is cage size of SBA-16.

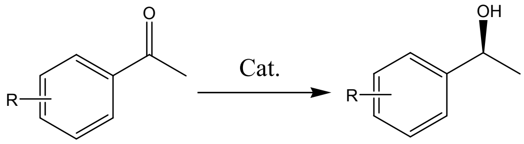
Adsorption experiment

In a typical adsorption experiment, alizarin reds were dissolved in alcohol to make a stock solution (0.04 mg/ml). Kinetic experiments to determine the amount of alizarin red adsorbed as a function of contact time were conducted by contacting 30 mL of 0.04 mg/ml alizarin red solution with 150 mg of Ru-TsDPEN@SBA-100 or Ru-TsDPEN@SBA-0 with stirring at room temperature in a closed vessel. Samples were withdrawn periodically for immediate analysis after centrifugation. Adsorbed amount were measured by the difference of the concentration of the solute before and after adsorption by UV adsorption at 420 nm. A_{ads} calculated by the formula of $A_{ads}=C_0-C/C_0$, where C_0 is the initial concentration, C is the concentration after adsorption.

Asymmetric transfer hydrogenation of aromatic ketones

The heterogeneous catalyst and $HCOONa\cdot 2H_2O$ (0.5 mmol) were added in 0.24 mL of water and degassed three times. Then 0.1 mmol of ketone (S/C=100) were added and the mixture was stirred at 40 ^{o}C for a desired reaction time. After the reaction, the mixture was extracted three times with ether and the conversion and ee value were determined by an Agilent 6890N GC equipped with HP-Chiral 19091G-B213 capillary column.

Table S2 Asymmetric transfer hydrogenation of substituted aromatic ketone using Ru-TsDPEN@SBA-100[a]



R	Time h	Conv. %	Ee %
4'-Br	2.5	>99	89
4'-Cl	2.5	98	87
4'-F	2.5	97	74
4'-Me	2.5	98	87
2'-Br	2.5	98	88

[a] Reactions were carried out at 40 °C, using 0.1 mmol of acp, 0.5 mmol HCOONa·2H_2O and a S/C ratio of 100 in 0.24 mL water.

Recycle of Ru-TsDPEN@SBA-100

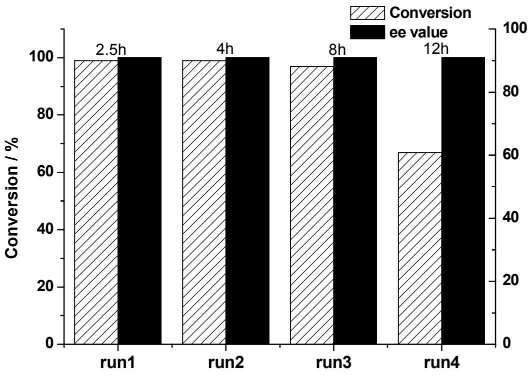


Fig. S3 Recycle of Ru-TsDPEN@SBA-100.

The recycle ability of Ru-TsDPEN@SBA16-100 was studied using acetophenone as substrate (Fig. S3). In the case of recycle, following each reduction the aqueous phase was extracted with ether (2×0.3 mL) and removed by a syringe, and the new reduction was started by introducing another portion of acetophenone (12 mg) along with 1 equiv of HCOOH. The ee value is almost kept for the recycled catalyst. During the catalyst recycle process, a longer reaction time was needed to complete the reaction compared with the fresh catalyst. This is partly due to the loss of solid catalysts during the course of recovery and partly due to the deactivation of the Ru-TsDPEN (a colour change of the catalysts from yellow to red could be observed during the recycle process).[4]

References

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