



Supporting Information

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# **“Enhanced Cooperative Activation Effect in the Hydrolytic Kinetic Resolution of Epoxides on Co(Salen) Catalysts Confined in Nanocages”**

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## **1. Experiment**

### **1.1 Preparation of the solid catalysts**

SBA-16 was synthesized according to the published method (Reference 3a), 0.5 g of SBA-16 (evacuated at 398 K for 6 h) was dispersed in 3 mL of dichloromethane (DCM) containing desired amounts of Co(Salen)(II) (0.004, 0.0125, 0.05 and 0.08 g). After stirring at 283 K for 24 h under Ar atmosphere, DCM was removed by evaporation. The resultant solid was introduced to a solution containing 0.62 g of dried toluene, 0.70 g of anhydrous pyridine and 0.70 g of propyltrimethoxysilane. After refluxing for 24 h under Ar atmosphere, the resultant solid was isolated by filtration and washed thoroughly with THF. The Co contents in the resultant solid catalysts were 0.055, 0.087, 0.157 and 0.225 w.t.%, respectively, based on the ICP analysis. The solid catalysts were denoted as Co(Salen)/SBA-16.

SBA-16 silylated with propyltrimethoxysilane in the absence of Co(Salen) was denoted as SBA-16-C3.

### **1.2 Estimation of the average number of Co(Salen) 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 Co(Salen) molecules. The number of Co(Salen) per cage ( $n$ ) was calculated by the following equation:

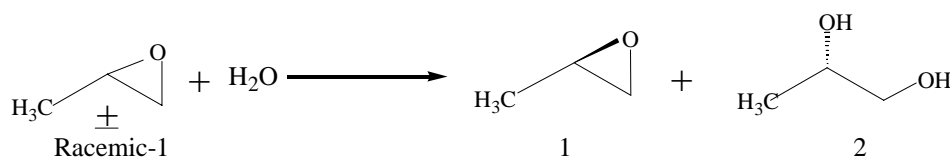
$$n = \frac{N_{Co(1g)} \times 6.02 \times 10^{23}}{\frac{V_{meso}}{\frac{4}{3}\pi(\frac{D}{2})^3}}$$

$N_{Co(1g)}$  is the mole of Co(Salen) per gram of the solid catalyst;  $V_{meso.}=V_{total.}-V_{microp.}$ ;  $D$  is cage size of SBA-16, determined by  $N_2$  adsorption branch and calculated according to the BJH model (Considering the possibility that a little amount of Co(Salen) molecules are confined in the pore entrance).

### 1.3 Characterization

Small-angle X-ray powder diffraction was performed on a Rigaku RINT D/Max-2500 powder diffraction system using Cu  $K\alpha$  radiation of 0.15406 nm wavelength (40 kV, 30 mA).  $N_2$  physical adsorption was carried out on Micromeritics ASAP2020 volumetric adsorption analyzer. Before the sorption measurements, samples were out gassed at 393 K for 6 h. UV-vis spectra were recorded on the JASCOV-550. The liquid sample and solid sample were analyzed with pure dichloromethane and  $BaSO_4$  as a reference, respectively. FT-IR spectra were collected on Thermo-Nicolet-Nexus 470 infrared spectrometer. The weight of pellet is ~20-30 mg. The samples were made into self-supporting wafers and were evacuated in an IR cell at 513 K for 4 h before the measurement. IR background spectra were recorded after the samples were cooled to room temperature. Transmission electron microscopy (TEM) was performed using a JEM-2010 instrument at an acceleration voltage of 100 kV. Co contents were analysed on Plasma-spec-II (Leeman, U.S.A.).

### 1.4 Hydrolytic kinetic resolution of propylene oxide

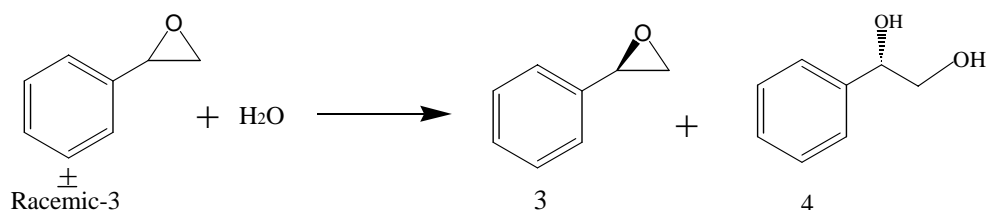


The catalyst was oxidized in toluene/acetic acid in air for 3.5 h before the reaction. After centrifugation, the catalyst was evacuated to remove toluene and acetic acid. 4 mmol of propylene oxide and 3 mmol of H<sub>2</sub>O were added to the reaction vessel containing catalyst. The reaction was performed at 283 K. After the reaction, THF and nonane (as external standard) were added into the reaction system and the solid catalyst was isolated by centrifugation. 1,2-propanediol was derived with 2,2'-dimethoxypropane in the presence of *p*-toluenesulfonic acid. The derivatives were purified with short gel column and then analyzed on Agilent 6890 GC with HP-Chiral19091G-B213 capillary column. The enantioselectivity propylene oxide epoxide is analyzed on Chiral dex A-TA capillary column (DIKMA).

GC analysis conditions of propylene oxide **1**: Chiral dex A-TA, 30 m; inj. temperature, 220 °C; oven temperature, 25 °C; pressure (7.5 kPa); N<sub>2</sub>, total flow (141 mL/min); t<sub>R</sub>=6.0 (major), t<sub>R</sub>= 6.6 min (minor).

GC analysis conditions of 1,2-propanediol **2**: cyclodex B; inj. temperature, 240 °C; oven temperature, 55 °C; pressure (80 kPa); N<sub>2</sub>, total flow (141 mL/min); t<sub>R</sub>= 3.1 min (derivative of (*S*)-1,2-propanediol **2**, minor), t<sub>R</sub>= 3.3 min (derivative of (*R*)-1,2-propanediol **2**, major).

### 1.5 Hydrolytic kinetic resolution of styrene oxide



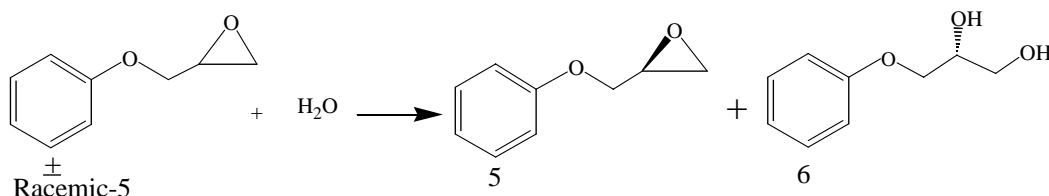
The catalyst was oxidized in toluene/acetic acid in air for 3.5 h before the reaction. The solid catalyst was obtained by centrifugation and evacuated to remove toluene and acetic acid. 2 mmol of propylene oxide and 1.5 mmol of water were added into the reaction vessel containing the solid catalyst to activate the catalyst because it was found that the heterogeneous catalysts undergo an induction period. After 12 hours, the liquid was removed by centrifugation. The activated catalysts were washed with THF for three times and dried under vacuum. The racemic styrene oxide and water

with the molar ratio of 1:0.75 were added. The reaction was performed at 303 K for 48 hours. The 2-phenyl-1,2-ethanediol was derived with dimethoxypropane in the presence of *p*-toluenesulfonic acid. The derivatives were purified with short gel column and then analyzed on Agilent 6890 GC with HP-Chiral19091G-B213 capillary column.

GC analysis conditions of styrene oxide **3**: inj. temperature, 240 °C; oven temperature, 80 °C; pressure (80 kPa); N<sub>2</sub>, total flow (141 mL/min); *t<sub>R</sub>* = 16.2 min ((*R*)-styrene oxide **3**, major), *t<sub>R</sub>* = 17.1 min ((*S*)-styrene oxide **3**, minor).

GC analysis conditions of 2-phenyl-1,2-ethanediol **4**: pressure (80 kPa), N<sub>2</sub>, total flow (141 mL/min); oven: 80 °C (30min), 10 °C/min ramp to 120 °C, 120 °C (30min); *t<sub>R</sub>* = 37.2 min (derivative of (*R*)-2-phenyl-1,2-ethanediol **4**, minor), *t<sub>R</sub>* = 38.3 min (derivative of (*S*)-2-phenyl-1,2-ethanediol **4**, major).

### 1.6 Hydrolytic kinetic resolution of phenyl glycidyl ether



The catalyst was oxidized in toluene/acetic acid by air for 3.5 h before the reaction. The solid catalyst was obtained by centrifugation and evacuated under vacuum to remove toluene and acetic acid. 2 mmol of propylene oxide and 1.5 mmol of water were added into the reaction vessel containing the solid catalyst to activate the catalyst. The activated catalysts were washed with THF for three times and dried under vacuum. Phenyl glycidyl ether and H<sub>2</sub>O with the molar ratio of 1:0.75 were added. The reaction was performed at 298 K for 48 hours. THF was added into the reaction system to dissolve the opaque white product. The reaction products were analyzed on Agilent 1100 HPLC with chiral OD-H column.

HPLC analysis conditions of phenyl glycidyl ether **5**: Chiral OD-H; hexanes: *i*-PrOH=9:1; 1 mL/min; 214 nm; *t<sub>R</sub>* = 8.38 min (minor), *t<sub>R</sub>* = 11.40 min (major).

HPLC analysis conditions of 3-phenoxy-1,2-propanediol **6**: Chiral OD-H, hexanes: EtOH=9:1, 1mL/min; 260 nm;  $t_R$  = 11.5 min (major),  $t_R$  = 20.2 min (minor).

### 1.7 Homogeneous catalytic reactions

Co(Salen)(II) was dissolved in dichloromethane. Acetic acid was added into the solution. The solvent was stirred under air to oxidize the Co(Salen)(OAc). After three hours, the solvent and acetic acid were removed under vacuum. The epoxides and H<sub>2</sub>O (with the molar ratio of 1:0.75) were added into the reaction vessel containing the catalyst to start the reaction. The analysis procedures of the remnant epoxides and diol were identical to that for the heterogeneous catalytic process.

### 1.8 Recycling experiment

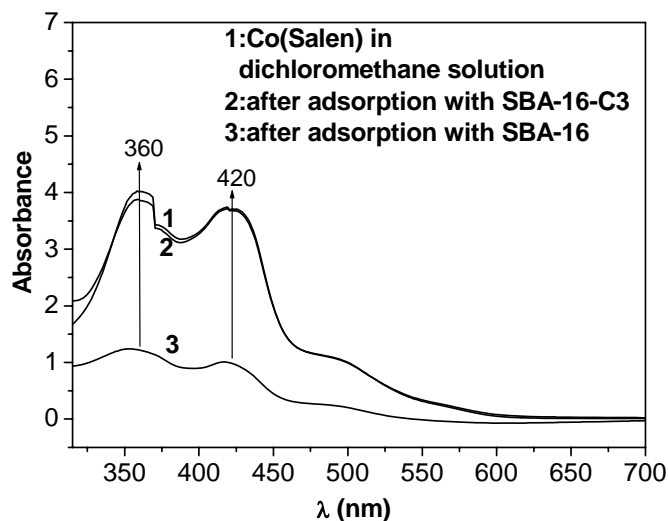
The used catalyst was isolated from reaction mixture by centrifugation. After being washed with THF for four times, oxidized in toluene/acetic acid in air for 3.5 h, isolated by centrifugation and dried in vacuum, the recovered catalyst was used in the next cycle of reaction.

## 2. Results and discussion

### 2.1 Estimation of the pore entrance size of SBA-16 and SBA-16-C3

The pore entrance sizes of SBA-16 and SBA-16-C3 were estimated using Co(Salen)(II) as a probe molecule (Figure S1). When Co(Salen)(II) in DCM is adsorbed into the cage of SBA-16 or SBA-16-C3, the concentration of Co(Salen)(II) in the filtrate should be decreased. The concentration of Co(Salen)(II) in the filtrate was analyzed by UV-vis spectroscopy because the probe molecule exhibits characteristic bands at 360 nm and 420 nm. The absorbance intensity of Co(Salen)(II) in DCM after treatment with SBA-16 is dramatically decreased, suggesting that the pore entrance size of SBA-16 is large enough to allow the diffusion of Co(Salen)(II) into the nanocage of SBA-16. After treatment of the Co(Salen)(II) solution with SBA-16-C3, the absorbance intensity of Co(Salen)(II) in DCM remains unchanged, indicating that Co(Salen)(II) cannot diffuse into the nanocage of SBA-16-C3.

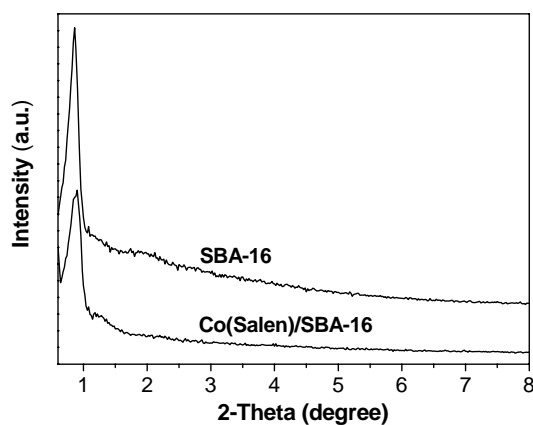
Therefore, SBA-16-C3 can be used as suitable host materials to entrap the Co(Salen)(II) within the nanocages of SBA-16.



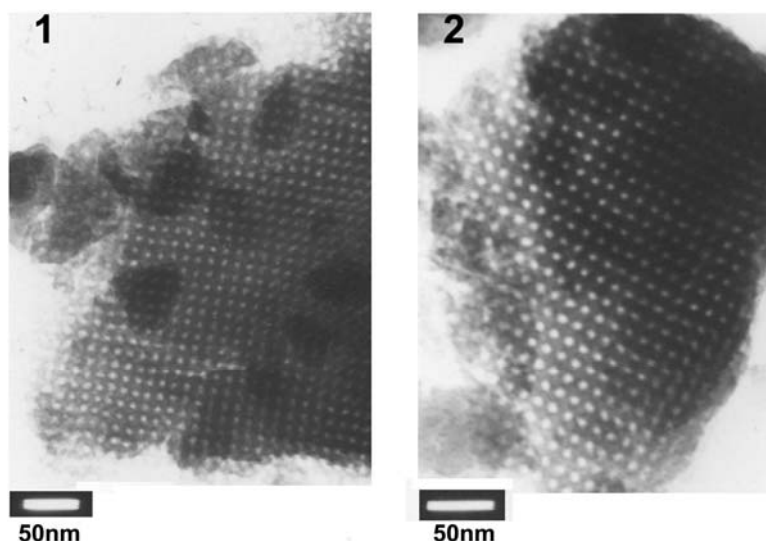
**Figure S1.** UV-vis spectra of Co(Salen) (II) in dichloromethane before and after treatment with SBA-16 and SBA-16-C3 (0.08 g of solid was dispersed in 3.8 mL of dichloromethane (DCM) containing  $1.33 \times 10^{-6}$  mol of (R,R)-Co(Salen) (II). The mixture was stirred in a sealed tube for 5 h. After centrifugation, the solution was measured with UV-vis spectroscopy).

## 2.2 Characterization of Co(Salen)/SBA-16

### 2.2.1 Structural characterization



**Figure S2.** XRD patterns of SBA-16 and the solid catalyst Co(Salen)/SBA-16 with Co content of 0.157 w.t.%.



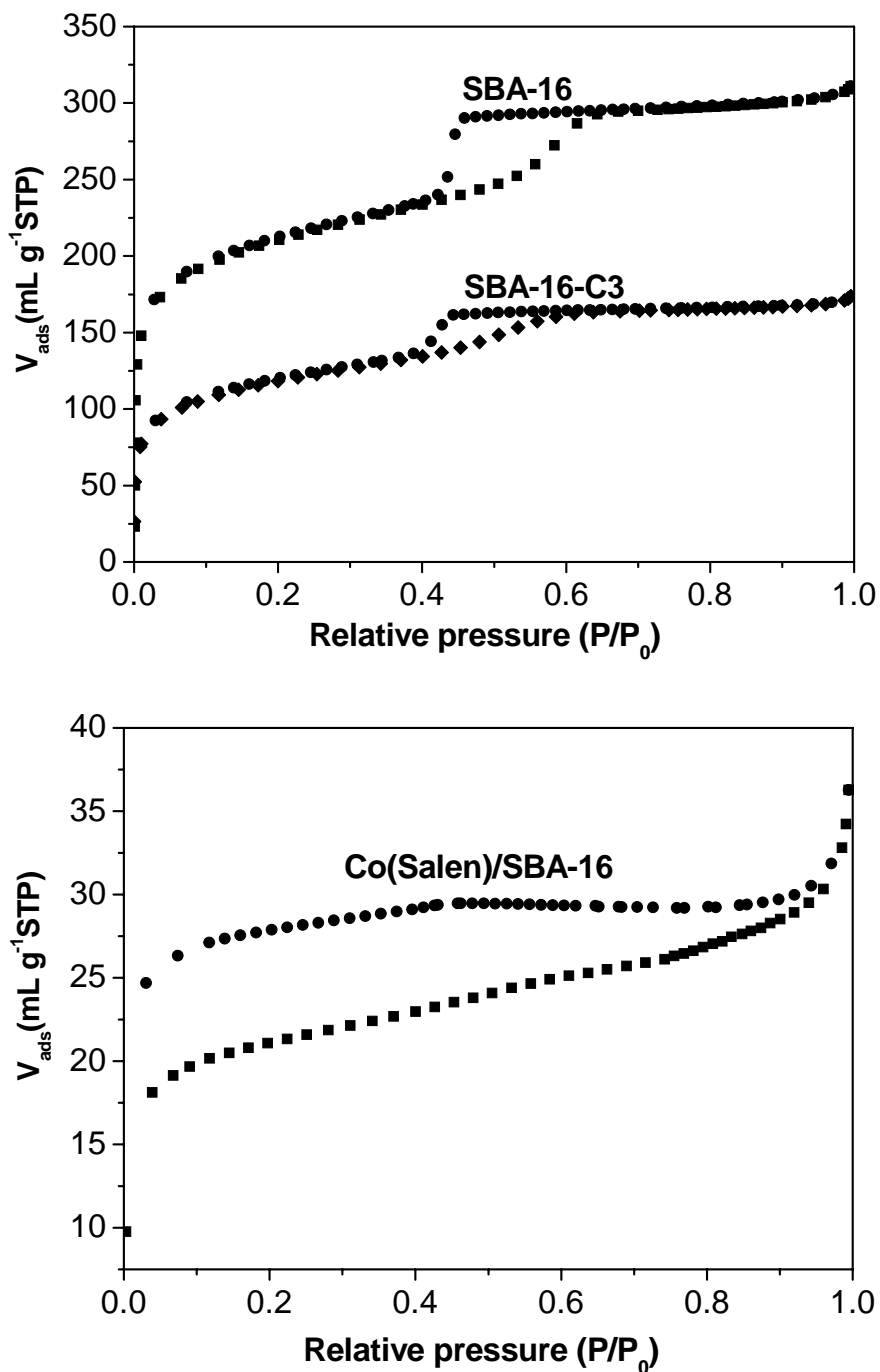
**Figure S3.** TEM images of SBA-16 (1) and Co(Salen)/SBA-16 with Co content of 0.157 w.t.% (2).

Co(Salen)/SBA-16 exhibits almost the similar XRD pattern to SBA-16, suggesting that Co(Salen)/SBA-16 also has the ordered pore arrangement (Figure S2). The TEM technique was also employed to further characterize the mesostructure of Co(Salen)/SBA-16. The (100) projection corresponding to cubic  $Im3m$  structure for SBA-16 and Co(Salen)/SBA-16 were clearly observed in the TEM images of SBA-16 and Co(Salen)/SBA-16 (Figure S3). The comparison of two images indicates the  $Im3m$  mesostructure of SBA-16 was retained during the preparation of the solid catalysts, which is consistent with the XRD result.

The  $N_2$  sorption isotherms of SBA-16, SBA-16-C3 and Co(Salen)/SBA-16 were displayed in Figure S4. The  $N_2$  sorption isotherms of SBA-16 show typical H2 hysteresis loop, which is a typical characteristic for materials with a good-quality cage-like porous structure. The  $N_2$  sorption isotherms of SBA-16-C3 exhibit type IV isotherm patterns with H2 hysteresis loops, confirming that the cage-like structure of SBA-16 was maintained after silylation. After silylation, the surface area, pore volume and pore size of SBA-16 apparently decreased (Table S1). This confirms that



the propyl group was grafted on the surface of SBA-16. Compared with SBA-16-C3, the surface area, pore volume and pore size of Co(Salen)/SBA-16 further decreases, indicating that Co(Salen) was successfully introduced into the cage of SBA-16.



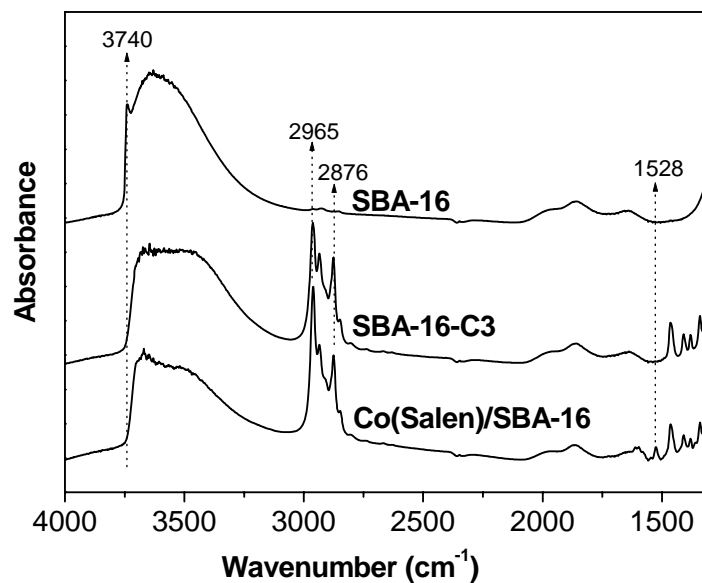
**Figure S4.** N<sub>2</sub> sorption isotherms of SBA-16, SBA-16-C3 and Co(Salen)/SBA-16 with Co content of 0.055, 0.087, 0.157 and 0.225 w.t.%.

**Table S1.** Textural properties of SBA-16, SBA-16-C3 and Co(Salen)/SBA-16

Mesoporous materials	Surface area <sup>[a]</sup> (m <sup>2</sup> /g)	Pore volume <sup>[b]</sup> (cm <sup>3</sup> /g)
SBA-16	723	0.48
SBA-16-C3 <sup>[c]</sup>	411	0.27
Co(Salen)/SBA-16 <sup>[d]</sup>	72	0.06

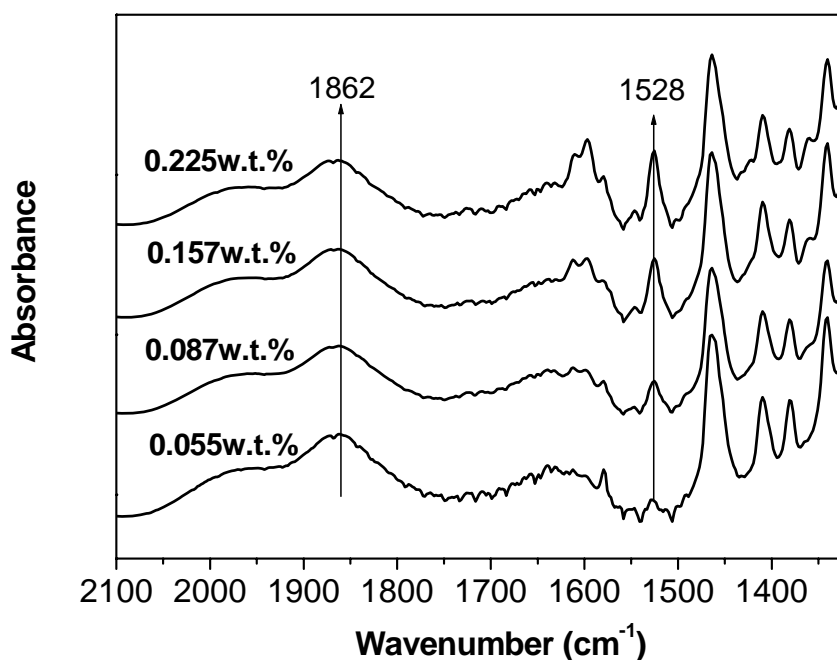
[a] BET surface area; [b] Estimated at the relative pressure of  $P/P_0=0.99$ ; [c] SBA-16 modified with propyltrimethoxysilane; [d] Co weight content in the solid catalyst is 0.157 w.t.%.

## 2.2.2 Spectroscopic characterization

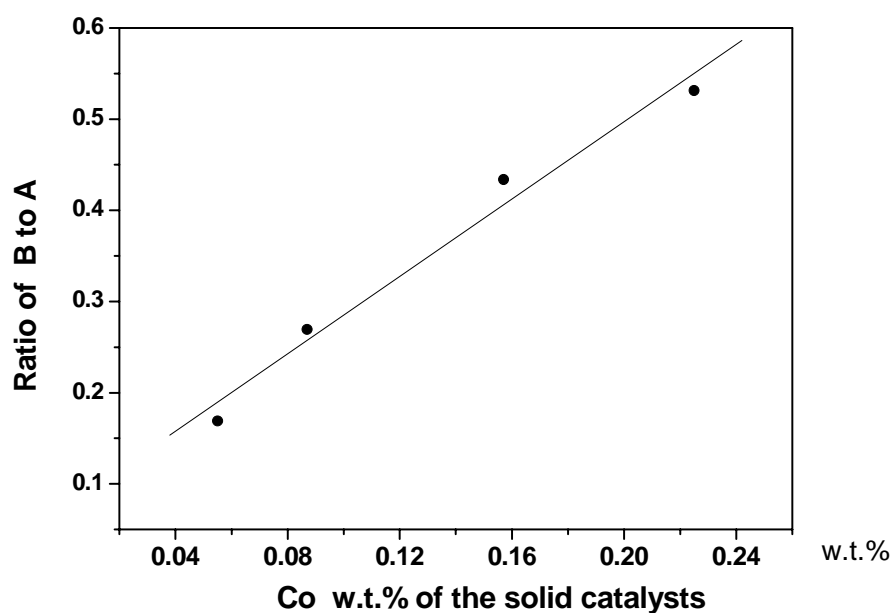


**Figure S5.** FT-IR spectra of SBA-16, SBA-16-C3 and Co(Salen)/SBA-16 with Co content of 0.157 w.t.%.

In the FT-IR spectra (Figure S5), the peak at  $3740\text{ cm}^{-1}$  is assigned to the stretching vibration of silanol group on the surface of SBA-16. For SBA-16-C3 and Co(Salen)/SBA-16 samples, this peak disappears because of the reaction of silanol group with the silylation agent. The peaks at  $2965$  and  $2876\text{ cm}^{-1}$  of SBA-16-C3 can be ascribed to C-H stretching vibration of propyl group, further confirming that silanol groups were silylated with propyltrimethoxysilane. Compared with SBA-16 and SBA-16-C3, a new peak at  $1528\text{ cm}^{-1}$  appears in the FT-IR spectrum of Co(Salen)/SBA-16, which can be ascribed to the characteristic peak of Co(Salen). This indicates that the Co(Salen) was successfully confined in the cage of SBA-16.

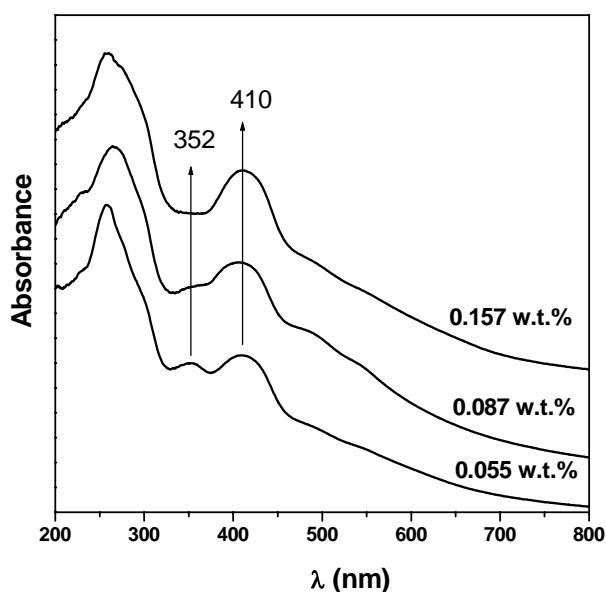


**Figure S6.** FT-IR spectra for the Co(Salen)/SBA-16 with different Co(Salen) loading.



**Figure S7.** The linear correlation of the ratio of B to A with Co w.t.% in the solid catalysts. A: peak area of Si-O-Si at  $1862\text{ cm}^{-1}$ ; B: peak area of Co(Salen) at  $1528\text{ cm}^{-1}$ .

In the FT-IR spectra of the solid catalysts with different Co content (Figure S6), the peak intensity of characteristic peak of Co(Salen) at  $1528\text{ cm}^{-1}$  increase with the increase of the Co content. The peak area ratio of  $1528\text{ cm}^{-1}$  to  $1862\text{ cm}^{-1}$  (the Si-O-Si band) can be used to estimate the relative content of Co(Salen) in the solid catalysts (J. Am. Chem. Soc., 1987, 109, 7141). This ratio has good linear relation with the Co content in the solid catalysts (Figure S7), further confirming the result of ICP analysis.



**Figure S8.** UV-vis spectra of the solid catalysts with different Co content (diffusion reflectance).

UV-vis spectra of the solid catalysts with different Co content were shown in Figure S8. Similar to the UV-vis spectroscopy of Co(Salen) in solution (Figure S1), the spectra of the solid catalysts, Co(Salen)/SBA-16, show two characteristic band at 352 and 410 nm. Compared with Co(Salen) solution (360 and 420 nm), the slight blue shifts of these two peak were observed. This is probably due to the weak host–guest interaction between the nanocages of SBA-16 and Co(Salen). It should be noted that the intensity of the band at 352 nm decreases with the Co(Salen) loading increasing, which is probably related with the local density of Co(Salen) in the nanocages.

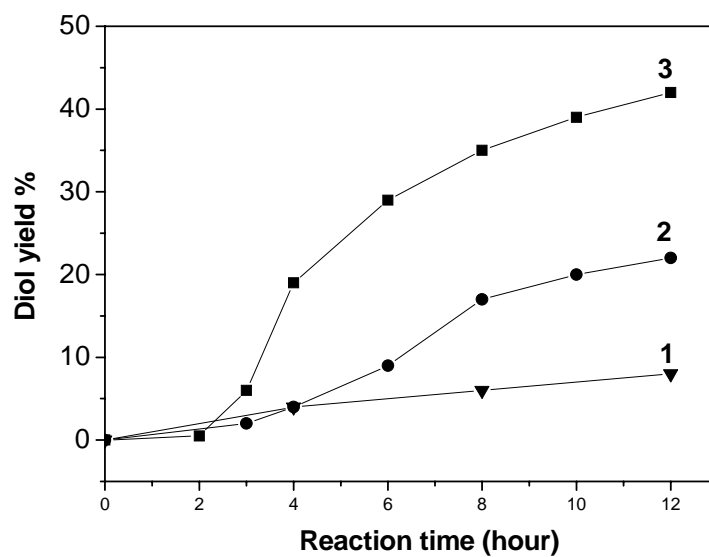
### 2.3 The HKR of propylene oxide on Co(Salen)/SBA-16 and homogeneous Co(Salen) at the same “volume active site density”

**Table S2.** The HKR of propylene oxide on Co(Salen)/SBA-16 and homogeneous Co(Salen) at the same “volume active site density” <sup>[a]</sup>

Catalyst	Co	Co(Salen) molecules	Conv <sup>[b]</sup>	TOF <sup>[c]</sup>	Epoxide	Diol
	w.t %	in a volume of 65 nm <sup>3</sup>	(%)	(h <sup>-1</sup> )	ee %	ee %
Co(Salen)/SBA-16	0.055	1.2	8	27	8	93
	0.087	1.9	30	100	40	94
	0.157	3.4	49	163	96	98
	0.225	4.9	50	167	99	98
Co(Salen)		1.2	49	115	96	98
		1.9	50	149	97	98
		3.4	49	228	96	98

[a] the same “volume active site density” refers to the Co(Salen) density in the homogeneous system is similar to the local density of Co(Salen) in the nanocage of SBA-16; the molar ratio of H<sub>2</sub>O to racemic epoxide was 0.75:1, 283 K; [b] conversion=(ee<sub>ep</sub>/ee<sub>diol</sub>) / (1+ ee<sub>ep</sub>/ee<sub>diol</sub>) × 100%, according to reference [5d]. [c] TOF (average) is calculated according to the following equation: TOF= N<sub>converted propylene oxide</sub>/(N<sub>Co(Salen)</sub> × t), where N denotes molar numbers, and t denotes reaction time (h).

## 2.4 Kinetic plots of the HKR of propylene oxide on solid catalysts



**Figure S9.** Kinetic plots of HKR of propylene oxide catalyzed by the solid catalysts.

(1): Co(Salen)/SBA-16 with Co content of 0.055 w.t.%; (2): Co(Salen)/SBA-16 with Co content of 0.087 w.t.%; (3): Co(Salen)/SBA-16 with Co content of 0.157 w.t.%.

The molar ratio of epoxide to H<sub>2</sub>O was 1:0.75; the molar ratio of epoxide to Co(Salen) was 4000; reaction temperature, 283 K.