Mesoporous Ethane−Silicas Functionalized with *trans*-(1*R*,2*R*)-Diaminocyclohexane as Heterogeneous Chiral Catalysts

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Mesoporous ethane−silicas functionalized with *trans*-(1*R*,2*R*)-diaminocyclohexane were synthesized by one-step co-condensation of 1,2-bis(trimethoxysilyl)ethane and *N*-[(triethoxysilyl)propyl]-(−)-(1*R*,2*R*)-diaminocyclohexane using octadecyltrimethylammonium chloride as the template under basic conditions. For comparison, the mesoporous silica containing *trans*-(1*R*,2*R*)-diaminocyclohexane was also synthesized. The structural characterizations (X-ray powder diffraction, transmission electron microscopy, and N_2 sorption isotherms) show that the two materials have ordered two-dimensional-hexagonal mesostructure and wormhole-like structure, respectively. The integrity of the organic groups in the mesoporous materials is confirmed by Fourier transform infrared and solid-state ^{13}C and ^{29}Si cross-polarization magic-angle-spinning NMR spectroscopies. Mesoporous materials are used as catalysts for the asymmetric transfer hydrogenation of acetophenone after complexing $[Rh(cod)Cl]_2$ to the chiral ligands, *trans*-(1*R*,2*R*)-diaminocyclohexane, in the mesopores. The catalyst with the ethane-bridged framework exhibits 82−96% conversion with 19−23% enantiomeric excess (ee), while the catalyst with pure-silica framework shows 48% conversion with 14% ee under identical reaction conditions. The enhanced catalytic activity of the mesoporous organosilicas is mainly caused by the specific adsorption and physical properties of the mesoporous network bridged with ethane groups, particularly the hydrophobic properties. The enantioselectivity, albeit not yet high enough, demonstrates the possibility for synthesizing a new kind of chiral solid catalysts for potential applications in asymmetric reactions.

1. Introduction

Having high surface areas and tunable pore diameters (2−50 nm), mesoporous silica materials are promising supports to host chiral ligands or chiral catalysts in their mesopores for heterogeneous asymmetric synthesis and chiral separation.[1−3] In general, introducing chiral ligands into mesoporous materials can be achieved either by a post-synthesis grafting method[4] or by a direct synthesis method.[5] The post-synthesis grafting method, which has been popularly used for introducing organic groups into the mesoporous materials, would likely graft organic groups mainly on the external surface of the mesoporous particles or near the pore mouth because of the mass transfer.[6,7] Compared with the post-synthesis grafting method, direct synthesis, based on the co-condensation of $RSi(OR')_3$ and $Si(OR')_4$ in the presence of a template, would likely result in mesoporous materials with organic groups uniformly distributed in the mesopores. However, this method requires that the R group is sufficiently hydrophobic to enter the core of the micelle and not too bulky to avoid its perturbation.[8]

Periodic mesoporous organosilicas (PMOs) with organic groups bridged in the framework have been reported.[9−11] In addition to the high surface areas and narrow pore size distributions, these novel materials have completely different adsorption properties from those of mesoporous silicas. The successful application of mesoporous ethane−silicas (MESs) as packing materials for HPLC demonstrates the special adsorption properties of PMOs.[12] The unique catalytic performance may be expected from the special adsorption properties of PMOs. In this article, we report on the synthesis of chiral mesoporous organosilicas with ethane bridging in the wall and *trans*-(1*R*,2*R*)-diaminocyclohexane protruding into the channel by the surfactant assistant co-condensation

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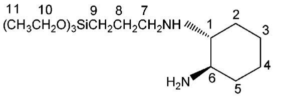
Scheme 1. ^{1}H NMR Assignment for M



1: 2.0 ppm
2: 0.9 ppm, 2.0 ppm
3: 1.3 ppm
4: 1.7 ppm
5: 1.2 ppm, 1.9 ppm
6: 2.3 ppm
7: 2.5 ppm, 2.7 ppm
8: 1.6 ppm
9: 0.6 ppm
10: 3.8 ppm
11: 1.2 ppm

method under basic conditions. These chiral mesoporous materials (complexed with [Rh(cod)Cl]$_2$) exhibit promising activity and enantioselectivity in the transfer hydrogenation of acetophenone. Compared with pure mesoporous silica counterparts, these chiral ethane−silicas are twice more active. The improved catalytic performance is mainly contributed to the presence of the ethane group in the mesoporous framework.

2. Experimental Section

2.1. Chemicals. 1,2-Bis(trimethoxysilyl)ethane (BTME) and octadecyltrimethylammonium chloride (C$_{18}$TMACl) were purchased from Sigma-Aldrich Co., Ltd. Tetraethoxysilane (TEOS) and other reagents were obtained from Shanghai Chemical Reagent Incorporation of Chinese Medicine Group. *trans*-(1*R*,2*R*)-Diaminocyclohexane was separated by chiral resolution of the commercially available mixture of *cis*- and *trans*-diaminocyclohexane (30/70) according to the literature.[13] All solvents are of analytical quality and were dried by standard methods. The preparation of the catalyst and the catalytic reaction were performed under an Ar atomosphere.

2.2. Synthetic Procedures. *2.2.1. Synthesis of N-[(Triethoxysilyl)propyl]-(−)-(1R,2R)-diaminocyclohexane (**M**).* **M** was synthesized from *trans*-(1*R*,2*R*)-diaminocyclohexane and (3-chloropropyl)-triethoxysilane according to the literature.[14] $[\alpha]_D^{16.1} = -55.2$ (c 1.4, tetrahydrofuran, THF). NMR assignment is given in Scheme 1.

2.2.2. Synthesis of MESs Containing trans-(1R,2R)-Diaminocyclohexane by the Co-Condensation Method (EM-n-N). For a typical synthesis, C$_{18}$TACl (0.21 g) and NaOH (0.24 g) were dissolved in deionized water (24.90 g). A mixture (6.0 mmol) of BTME and **M** was added to the above solution. The mixture was stirred at 20 °C for 12 h and then heated under stirring at 60 °C for 2 days. After filtration, the powder product was washed thoroughly with deionized water and dried under vacuum at 60 °C. The surfactant was extracted by stirring 1 g of as-synthesized material in 200 mL of ethanol containing 12 M HCl (1.5 g) at 60 °C for 7 h. The surfactant-free product containing protonated *trans*-(1*R*,2*R*)-diaminocyclohexane was stirred in 0.01 M NaOH for 30 min at room temperature to obtain the free base. After filtration the powder product was washed with copious amounts of water and ethanol and dried under vacuum at 60 °C. The mesoporous organosilicas containing *trans*-(1*R*,2*R*)-diaminocyclohexane were denoted as EM-*n*-N, where *n* ($n = 9$, 4, 2.3) is the mole ratio of BTME/**M**.

2.2.3. Synthesis of Mesoporous Silica Containing trans-(1R,2R)-Diaminocyclohexane by the Co-Condensation Method (TM-9-N). For comparison, mesoporous silica containing *trans*-(1*R*,2*R*)-diaminocyclohexane (TM-9-N) was also synthesized. C$_{18}$TMACl (0.82 g) and NaOH (0.17 g) were dissolved in H$_2$O (23.35 g) under vigorous stirring. A mixture of TEOS (14.4 mmol) and **M** (1.6 mmol) was added to the above solution. The reaction mixture was stirred at 40 °C for 1 h and then heated under stirring at 60 °C for 4 days. The white precipitate obtained by filtration was washed thoroughly with deionized water and dried under vacuum at 60 °C. The surfactant was extracted using the same method as described above. The material with free R−NH$_2$ was obtained using the same procedure as EM-*n*-N. The sample was designated as TM-9-N, where 9 is the mole ratio of TEOS/**M**.

2.2.4. MES Containing trans-(1R,2R)-Diaminocyclohexane Prepared by the Grafting Method (G-MES). MES containing *trans*-(1*R*,2*R*)-diaminocyclohexane was prepared by the grafting method. The grafting was performed under an Ar atmosphere. A total of 1 g of MES (prepared according to ref 15) was dried under vacuum at 120 °C for 24 h and then was added to freshly distilled anhydrous toluene (20 mL) containing **M** (1 g). The mixture was refluxed under stirring for 24 h. After filtration, the powder product was washed with toluene and dried under vacuum at 60 °C. The product was designated as G-MES.

2.2.5. Complexing Mesoporous Materials Containing trans-(1R,-2R)-Diaminocyclohexane with [Rh(cod)Cl]$_2$. In a Schlenk tube, [Rh(cod)Cl]$_2$ in 15 mL of dry ethanol was added to the mesoporous material containing *trans*-(1*R*,2*R*)-diaminocyclohexane with the mole ratio of *trans*-(1*R*,2*R*)-diaminocyclohexane/[Rh(cod)Cl]$_2$ = 1:0.75. After stirring for 15 h under an argon atmosphere at room temperature, the yellow powder product was filtered and washed with freshly distilled THF to eliminate the free rhodium complex and then dried under vacuum.

2.3. Characterization. X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/Max 3400 powder diffraction system using Cu Kα radiation (40 kV and 30 mA). Transmission electron microscopy (TEM) was recorded on a JEM-2010 at an acceleration voltage of 120 kV. Nitrogen sorption isotherms were measured at 77 K on an ASAP 2000 system in the static measurement mode. The sample was outgassed at 373 K prior to the measurement. The pore diameter was calculated from the desorption branch of the isotherm using the Barrett−Joyner−Halenda method. Solid-state ^{13}C (100.5 MHz) and ^{29}Si (79.4 MHz) cross-polarization magic-angle-spinning (CP-MAS) NMR were obtained on a Bruker DRX-400 spectrometer with the following experimental parameters: for ^{13}C CP-MAS NMR experiments, 8-kHz spin rate, 3-s pulse delay, 4-min contact time, 1000 scans and for ^{29}Si CP-MAS NMR experinments, 8-kHz spin rate, 3-s pulse delay, 10-min contact time, 1000 scans. Tetramethylsilane was used as a reference. N and Rh elemental analyses were respectively performed on an Elementar Vario EL III (Germany) and a Plasma-spec-II (Leeman. Labs. U.S.A). Infrared spectra were recorded on a Thermo Nicolet Nexus 470 Fourier transform infrared (FT-IR) spectrometer. The self-supporting wafer was loaded into an IR cell with CaF$_2$ windows. Before measurement, the wafer was degassed at 120 °C for 2 h under vacuum (10^{-1} Pa). Diffuse-reflectance UV−vis spectra were collected on a JASCO V-550 UV−vis spectrophotometer using BaSO$_4$ as a reference.

2.4. Catalytic Reaction. Asymmetric transfer hydrogenation of acetophenone was carried out under an Ar atmosphere. The rhodium-containing material (7.36 μmol Rh) was vacuumed in a 50-mL flask for 1 h at room temperature. Then a solution containing freshly distilled 2-propanol (12 mL) and PrOK (0.10 mmol) was added. The suspension was stirred for 1 h at room temperature, and acetophenone (0.24 g) was added with a syringe. The reaction mixture was stirred at 83 ± 2 °C for 22 h under an argon atmosphere. The catalytic activity and enantiomeric excess (ee) were measured on an Agilent 6890 gas chromatograph equipped with a flame ionization detector and an HP-Chiral 19091G-B213 capillary column (30 m × 0.32 mm × 0.25 μm).

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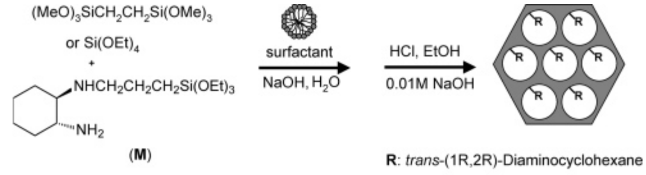
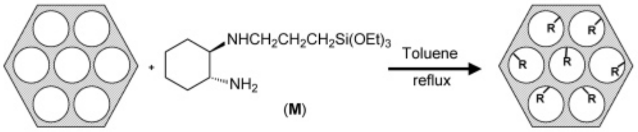
Scheme 2. Illustrated Preparation Procedure for Mesoporous Silicas Containing *trans*-(1*R*,2*R*)-Diaminocyclohexane



(a) Synthesis of EM-n-N and TM-9-N by co-condensation method



(b) Preparation of G-MES by post-grafting method

3. Results and Discussion

3.1. Synthesis of Mesoporous Materials Functionalized with *trans*-(1*R*,2*R*)-Diaminocyclohexane. The detailed synthesis procedure for EM-*n*-N, TM-9-N, and G-MES is illustrated in Scheme 2. The match of hydrolysis and condensation rates between different kinds of silane precursors plays an important role on the formation of well-ordered, highly porous materials by the co-condensation method.[16] The hydrolysis and condensation of *N*-[(triethoxysilyl)-propyl]-(−)-(1*R*,2*R*)-diaminocyclohexane (**M**) and TEOS in the presence of surfactant will be poorly organized because **M** has fewer amounts of interaction sites (hydroxy groups) than TEOS with identical silicon content. The ordered mesostructure is difficult to be formed by the assembly of hydrolyzed species of TEOS and **M**.[17] BTME has the same amounts of interaction sites as those of **M** with identical silicon content. Also, both BEME and **M** have a silicon atom bonded with an organic group; therefore, the differences between BTME and M in the viscosity, miscibility, and diffusivity will be reduced. The hydrolysis and condensation rates of BTME and **M** may be more compatible. As a result, the initial organosilicate-template assembly will be well-organized during the co-condensation of BTME and **M** in the presence of surfactant. The BTME synthetic system may provide more possibilities for the formation of mesoporous materials with ordered mesostructure than the TEOS synthetic system. For comparison, *trans*-(1*R*,2*R*)-diaminocyclohexane was also introduced onto MESs by the grafting method (Scheme 2).

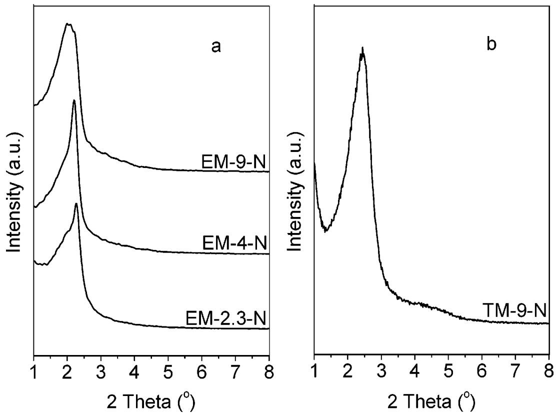


Figure 1. XRD patterns: (a) MESs containing *trans*-(1*R*,2*R*)-diaminocyclohexane (EM-*n*-N), where *n* ($n = 9$, 4, 2.3) is the mole ratio of BTME/**M** and (b) mesoporous silica containing *trans*-(1*R*,2*R*)-diaminocyclohexane (TM-9-N), where 9 is the mole ratio of TEOS/**M**.

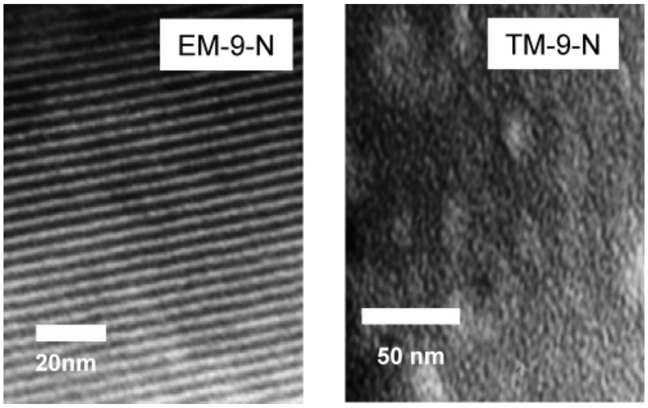


Figure 2. TEM images of MES containing *trans*-(1*R*,2*R*)-diaminocyclohexane (EM-9-N) and mesoporous silica containing *trans*-(1*R*,2*R*)-diaminocyclohexane (TM-9-N).

3.2. Structural Characterization of the Mesoporous Materials Functionalized with *trans*-(1*R*,2*R*)-Diaminocyclohexane. The XRD patterns of the MESs containing *trans*-(1*R*,2*R*)-diaminocyclohexane EM-*n*-N ($n = 9$, 4, 2.3) exhibit one sharp diffraction peak in the low-angle region, indicating that the materials have ordered mesoporous structure (Figure 1a). The TEM image of EM-9-N clearly shows the two-dimensional-hexagonal arrangement of the mesopore throughout the sample (Figure 2), further confirming that EM-*n*-N has well-ordered mesostructure. The d_{100} spacing decreases as the amount of **M** in the initial gel mixture increases, indicating the lattice contraction of the mesoporous materials with higher amounts incorporation of *trans*-(1*R*,2*R*)-diaminocyclohexane.

N_2 sorption isotherms of EM-*n*-N ($n = 9$, 4, 2.3) are given in Figure 3. All the materials exhibit type IV isotherms (definition by IUPAC) with a sharp capillary condensation step at P/P_0 in the range of 0.20−0.35, which is characteristic of mesoporous materials with narrow pore size distributions. An additional hysteresis loop at P/P_0 above 0.4 is also observed for all the samples, demonstrating the existence of the texture pore.[18,19] The pore diameter and the pore volume decrease with increasing concentration of *trans*-(1*R*,2*R*)-diaminocyclohexane in the initial gel mixture (Table 1). This is probably a proof for the incorporation of the *trans*-(1*R*,2*R*)-diaminocyclohexane ligand within the mesopore by the co-condensation method.

TM-9-N was synthesized by co-condensation of TEOS with **M** under basic conditions. A broad peak with a shoulder is observed in the XRD pattern of TM-9-N, which is characteristic of MSU-type mesoporous structure (Figure 1b).

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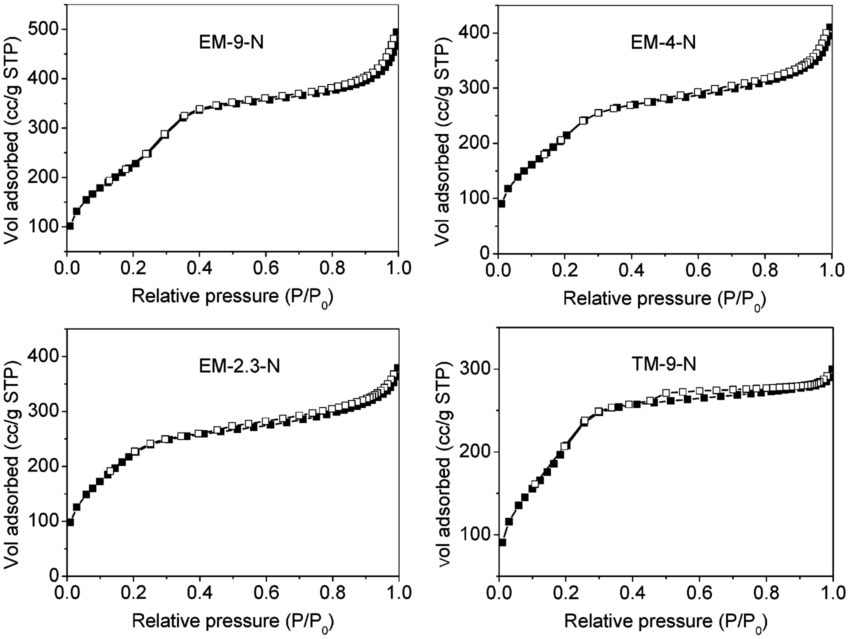

Figure 3. Nitrogen adsorption−desorption isotherms of MESs containing *trans*-(1*R*,2*R*)-diaminocyclohexane EM-*n*-N ($n = 9$, 4, 2.3) and mesoporous silica containing *trans*-(1*R*,2*R*)-diaminocyclohexane TM-9-N.

Table 1. Physicochemical Data for EM-*n*-N ($n = 9$, 4, 2.3), TM-9-N, and G-MES

sample	*d* spacing (nm)	BET surface area (m^2/g)	pore vol[a] (cm^3/g)	pore diameter (nm)	a_0[b] (nm)	wall thickness[c] (nm)
EM-9-N	4.5	851	0.70	3.3	5.3	2.0
EM-4-N	4.0	817	0.59	2.9	4.6	1.7
EM-2.3-N	3.9	856	0.55	2.6	4.5	1.9
TM-9-N	4.0	890	0.55	2.5	4.6	2.1
G-MES[d]	5.3	880	0.60	2.8	6.1	3.3

[a] Total pore volume obtained from the volume of N_2 adsorbed at $P/P_0 = 0.99$. [b] a_0 is the lattice parameter, $a_0 = 2d_{100}/\sqrt{3}$. [c] Wall thickness = a_0 − pore diameter. [d] Prepared by grafting of **M** onto MES.

The TEM image further confirms that TM-9-N has a disordered three-dimensional network of “wormhole-like” mesoporous channels (Figure 2). The disordered mesostructure of TM-9-N may be caused by the different hydrolysis and condensation rates between TEOS and **M**. A typical type IV isotherm curve is observed for TM-9-N (Figure 3).

The above results show that the match of hydrolysis and condensation rates between different kinds of silane precursor plays important role on the synthesis of bi- and multi-functionalized mesoporous materials with ordered mesostructure.

3.3. Characterization of the Mesoporous Materials by FT-IR and Solid-State NMR. The FT-IR spectrum of TM-9-N is presented in Figure 4. The strong vibrations at 2935 and 2863 cm^{-1} are assigned to the CH stretching of propyl chain of **M**. The band at 1452 cm^{-1} is the characteristic CH vibration of cyclohexane of *trans*-(1*R*,2*R*)-diaminocyclohexane. The broad bands at 3364 and 3330 cm^{-1} are ascribed to the asymmetric and symmetric NH_2 stretching, respectively. The band at 1590 cm^{-1} corresponds to the NH_2 scissoring vibration.[20] The existence of the NH_2 scissoring vibration (at 1590 cm^{-1}) and the disappearance of asymmetric and symmetric NH_3^+ deformation (at 1635 and 1539 cm^{-1}) reveal the successful deprotonation of protonated chiral diamine (formed during the surfactant extraction process).[21] The disappearance of the C−H vibration of $C_{18}TMACl$ at 1480 cm^{-1} indicates the complete removal of the surfactant using the EtOH−HCl extraction method.[22]

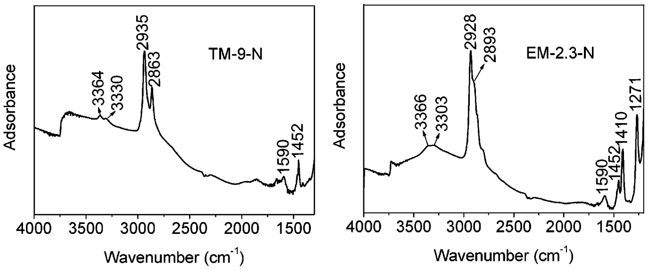

Figure 4. FT-IR spectra of mesoporous silica containing *trans*-(1*R*,2*R*)-diaminocyclohexane (TM-9-N) and MES containing *trans*-(1*R*,2*R*)-diaminocyclohexane (EM-2.3-N).

The FT-IR spectrum of EM-2.3-N is similar to that of TM-9-N. The characteristic peaks corresponding to *trans*-(1*R*,2*R*)-diaminocyclohexane are clearly observed at 1452, 1590, 3366, and 3303 cm^{-1}. The intense bands between 2928 and 2800 cm^{-1} are due to the mixture of CH stretching of the propyl chain of **M** and the ethane moiety in the material. The new peaks at 1410 and 1271 cm^{-1} are attributed to the CH vibrations of the bridged ethane group.

The integrity of *trans*-(1*R*,2*R*)-diaminocyclohexane functionalities was further identified by ^{13}C CP-MAS NMR. The ^{13}C CP-MAS NMR spectrum of TM-9-N displays signals corresponding to cyclic CH_2 and the inner carbon atom of *n*-propyl groups in the range of 20.0−29.0 ppm and NCH/NCH$_2$ in the range of 53.0−60.0 ppm (Figure 5). The sharp signal at 9.0 ppm is ascribed to the carbon atom bonded to

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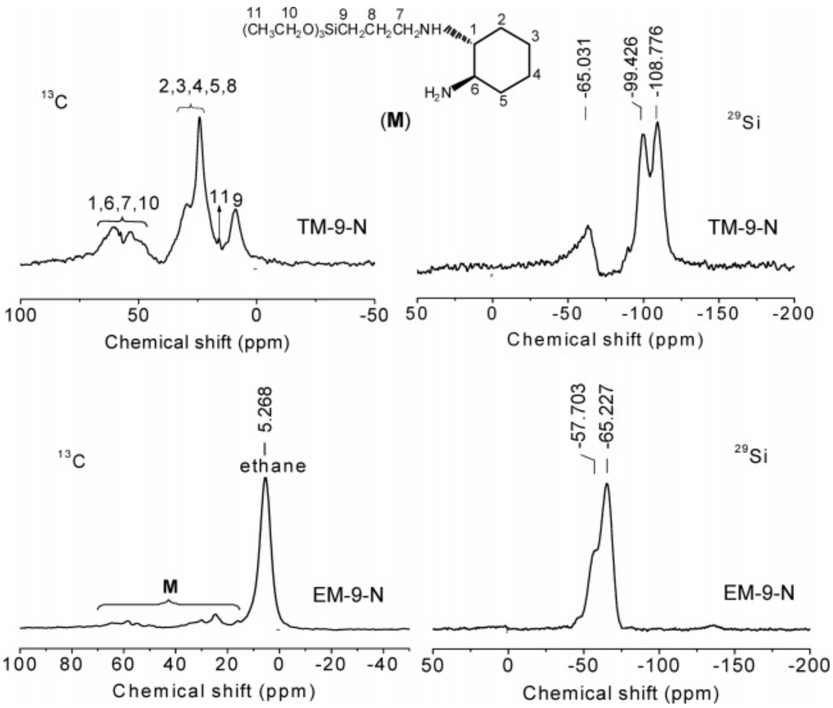

Figure 5. Solid-state ^{13}C CP-MAS NMR and ^{29}Si CP-MAS NMR spectra of mesoporous silica containing *trans*-(1*R*,2*R*)-diaminocyclohexane (TM-9-N) and MES containing *trans*-(1*R*,2*R*)-diaminocyclohexane (EM-9-N).

silicon.[15,17,23] These results confirm the incorporation of *trans*-(1*R*,2*R*)-diaminocyclohexane ligands in TM-9-N.[15,17,23]

In the ^{29}Si CP-MAS NMR spectrum of TM-9-N, three signals at −65.0, −99.4 and −108.8 ppm are observed, corresponding to T^3 [$SiC(OSi)_3$], Q^3 [$ROSi(OSi)_3$, R= H, Et] and Q^4 (SiO_4), respectively (Figure 5). The appearance of the Q^3 signal indicates the presence of some residual noncondensed OH or OEt groups attached to the silicon atom.[24] The ^{13}C CP-MAS NMR spectrum of EM-9-N clearly shows the signals in the range of 16.0−30.0 ppm and 50.0−64.0 ppm attributed to *trans*-(1*R*,2*R*)-diaminocyclohexane (Figure 5). The sharp signal at 5.3 ppm is ascribed to the ethane moiety bridged in the mesoporous framework. ^{29}Si CP-MAS NMR spectrum of the EM-9-N material displays two broad peaks centered at −57.7 and −65.2 ppm (Figure 5). The signal at −57.7 ppm is from the mixture of Si species bonded with the chiral moiety $T^{2'}$ [$SiC(OH)(OSi)_2$] and Si species bridged by the ethane moiety T^2 [$SiC(OH)(OSi)_2$], while the signal at −65.2 ppm is assigned to the mixture of Si species related with the chiral moiety of $T^{3'}$ [$SiC(OSi)_3$] and Si species bridged by the ethane moiety of T^3 [$SiC(OSi)_3$]. The absence of *Q* sites with the signals at −90 to −120 ppm suggests that the Si−C bond is stable enough to survive the processes of synthesis, surfactant extraction, and deprotonation.

The FT-IR and ^{13}C and ^{29}Si CP-MAS NMR spectra demonstrate that the *trans*-(1*R*,2*R*)-diaminocyclohexane moiety is successfully incorporated into the network of mesoporous silica and MES.

Chirality identification of the solid materials remains a challenging topic.[25] In this work, we tried to dissolve TM-9-N in an aqueous NaOH solution (1 M), and then the optical activity of the solution was measured. The value of specific optical activity measured was −11.6° g^{-1} for the dissolved TM-9-N. No optical activity was observed for the solution dissolved with MCM-41. These results indicate that chirality of *trans*-(1*R*,2*R*)-diaminocyclohexane could be kept when it is incorporated to the mesoporous materials by the co-condensation method in a basic medium.

3.4. Catalytic Properties of the Mesoporous Materials Functionalized with *trans*-(1*R*,2*R*)-Diaminocyclohexane. The content of chiral ligand in the materials was calculated from elemental analyses (Table 2). With the BTME/**M** ratio in the initial gel mixture increasing, more amounts of **M** can be incorporated in the mesoporous organosilicas. Compared with the theoretical value, it can be concluded that ~30 mol % of **M** in the initial gel mixture could be incorporated in the MESs, while the mesoporous silica could incorporate 45 mol % of **M** in the initial gel mixture. The higher amounts of M in the mesoporous silica framework may be due to the lower pH value employed for the synthesis of TM-9-N.

The mesoporous materials containing *trans*-(1*R*,2*R*)-diaminocyclohexane were reacted with $[Rh(cod)Cl]_2$ to generate the catalysts. The formation of the rhodium complex with *trans*-(1*R*,2*R*)-diaminocyclohexane was proved by diffuse-reflectance UV−visible spectroscopy (Figure 6). EM-2.3-N shows a peak in the range of 200−250 nm and a shoulder peak in the range of 250−400 nm in the UV−vis spectrum. After complexing with $[Rh(cod)Cl]_2$, EM-2.3-NRh exhibits a new peak at 380 nm, indicating that the rhodium complex

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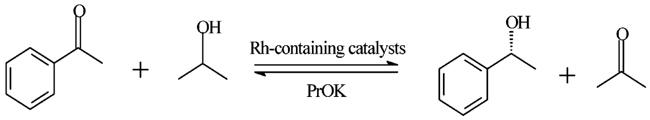
Table 2. Catalytic Properties of Mesoporous Materials Containing *trans*-(1*R*,2*R*)-Diaminocyclohexane in the Asymmetric Transfer Hydrogenation of Acetophenone from Isopropanol[a,b]

sample	chiral ligand[c] (mmol/g)	Rh (mmol/g)	Rh/chiral ligand	Rh (μmol/m^2)	conv.,[d] %	ee, % (S)	TON
M[e]					89	21	243
TM-9-NRh	0.62 (1.34)	0.27	0.44	0.30	48	14	131
EM-9-NRh	0.24 (0.72)	0.12	0.50	0.14	82	19	225
EM-4-NRh	0.38 (1.36)	0.24	0.63	0.29	95	22	257
EM-2.3-NRh	0.57 (1.94)	0.35	0.61	0.41	96	23	260
G-MES-Rh[f]	0.92	0.53	0.58	0.60	92	27	217

[a]



[b] Reaction conditions: catalysts (7.36 μmol Rh), PrOH (12 mL), PrOK (0.1 mmol), acetophenone (2 mmol), reaction temperature (83 ± 2 °C), reaction time (22 h). [c] The quantity of chiral ligand in the solids is calculated by N elemental analysis; data in the parenthesis are theoretical values based on the formula $[O_{1.5}SiCH_2CH_2SiO_{1.5}]_n[RSiO_{1.5}]$. [d] Conversion is based on acetophenone. [e] Complexing $[Rh(cod)Cl]_2$ with **M** (homogeneous process). [f] Prepared by grafting of **M** onto mesoporous ethane−silica followed by complexing with $[Rh(cod)Cl]_2$.

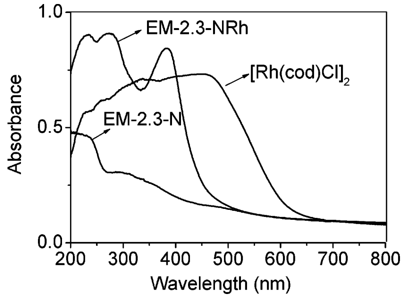


Figure 6. UV−vis spectra of $[Rh(cod)Cl]_2$ (solid powder) and MESs containing *trans*-(1*R*,2*R*)-diaminocyclohexane (EM-2.3-N) before and after complexing with $[Rh(cod)Cl]_2$.

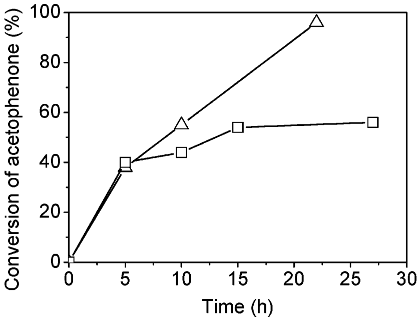


Figure 7. Determination of the heterogeneity of the EM-4-NRh catalyst by a filtration test. (△) Conversion of acetophenone as a function of reaction time (EM-4-NRh); (□) conversion of acetophenone as a function of reaction time (EM-4-NRh was removed after 5 h).

was coordinated with *trans*-(1*R*,2*R*)-diaminocyclohexane in the material.[26]

The prepared catalysts were tested for the asymmetric transfer hydrogenation of acetophenone. All the catalysts are active for this reaction (Table 2). 2-Phenethyl alcohol was the only product detected. TM-9-NRh exhibits 48% conversion of acetophenone with 14% ee, while the homogeneous catalyst (formed by complexing $[Rh(cod)Cl]_2$ with **M** in situ) gives 89% conversion of acetophenone with 21% ee. The catalysts with the ethane-bridged framework (EM-*n*-NRh) show promising activity of 82−96% conversion of acetophenone with 19−23% ee. The activity and enantioselectivity of EM-*n*-NRh are comparable with those of the homogeneous catalyst. This result indicates that most (if not all) ligands retain their chirality on the mesoporous materials. EM-4-NRh and EM-2.3-NRh with relatively higher concentration of chiral ligand and a Rh active site show similar activity and enantioselectivity. The lower catalytic activity and enantioselectivity of EM-9-NRh may be due to the low concentration of chiral ligand existing in EM-9-NRh.

It is interesting to note that all the catalysts with the ethane-bridged framework exhibit higher catalytic activity and enantioselectivity than the catalyst with the pure-silica framework. TM-9-NRh and EM-*n*-NRh ($n = 9, 4, 2.3$) have similar BET surface areas, pore diameters, and pore volumes (Table 1) and comparable Rh densities (Table 2). Further, TM-9-N with three-dimensional MSU-type structure should have a faster diffusion rate of the reactants and the products during the catalysis than EM-*n*-N with two-dimensional hexagonal mesostructure.[19] Therefore, the low activity and enantoselectivity observed for TM-9-NRh is not due to the structural restriction. The surface of EM-*n*-NRh, with the ethane moiety as an integral part of the mesoporous framework, is more hydrophobic than that of TM-9-NRh. So, the increased catalytic activity is mainly contributed to the enhanced surface hydrophobicity of EM-*n*-NRh.

G-MES-Rh was prepared through grafting of **M** onto MES followed by complexing wih $[Rh(cod)Cl]_2$. Although G-MES-Rh has the highest concentration of both chiral ligand and Rh active site, the catalytic activity is slightly lower than that of EM-4-NRh and EM-2.3-NRh. The lower activity of G-MES-Rh may be due to the fact that some catalytic active sites crowded on the outside of mesoporous particles or near the pore mouth cannot be accessed by reactants during the catalysis. The higher enantioselectivity (27% ee) of G-MES-Rh can be attributed to the higher density of chiral ligand.

To confirm that the catalytic reaction is indeed heterogeneous, the EM-4-NRh catalyst was removed from the reaction mixture when the conversion of acetophenone reached 40% (Figure 7). The filtrate was continuously stirred at the same reaction temperature. Additional 15% conversion of acetophenone with the same ee value was observed after another 12 h reaction for the filtrate. Compared with 95% conversion in the presence of EM-4-NRh after 22 h, we can propose that the asymmetric transfer hydrogenation of

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acetophenone is mainly catalyzed by solid catalyst, and the leached catalytic species do not play a significant role in the reaction. Further, the Rh elemental analysis of the filtrate after reaction shows that about 4.6% of Rh in the material is leached after one reaction cycle.

4. Conclusions

The MESs containing *trans*-(1*R*,2*R*)-diaminocyclohexane were successfully synthesized by co-condensation of BTME with *N*-[(triethoxysilyl)propyl]-(−)-(1*R*,2*R*)-diaminocyclohexane under basic conditions. The *trans*-(1*R*,2*R*)-diaminocyclohexane in the pore of the mesoporous materials retains the chirality as evidenced by the optical measurement and the enantioselectivity of the catalysts in the asymmetric transfer hydrogenation of acetophenone. The catalysts with ethane group bridging in the mesoporous framework exhibit higher catalytic activity and enantioselectivity than the catalyst with corresponding mesoporous silicas. The improved catalytic performance is mainly attributed to the presence of the ethane group in the mesoporous framework. The present synthetic strategy is a general method to synthesize mesoporous materials containing other chiral ligands. In addition, modulating the organic groups in the framework can change the surface properties of the mesoporous materials at the molecular level. Thus, the mesoporous materials with different organic groups in the framework and chiral ligands in the mesopore are a new class of promising heterogeneous chiral catalysts.

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