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Core-shell structured mesoporous silica: a new immobilized strategy for rhodium catalyzed asymmetric transfer hydrogenation[†]

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A core-shell structured heterogeneous rhodium catalyst exhibited excellent catalytic activity and enantioselectivity in asymmetric transfer hydrogenation of aromatic ketones in aqueous medium, which could be recovered easily and used repetitively twelve times without affecting obviously its enantioselectivity.

Development of silica-supported mesoporous heterogeneous catalysts for asymmetric catalysis has attracted a great deal of interest due to their relatively large surface area and pore volume, and tunable pore dimension and well-defined pore arrangement. These salient features are beneficial not only to control the dispersibility of active species but also to adjust the chiral microenvironment of active centers, showing potential superiority in stereocontrol performance.¹ Recently, lots of successful examples, such as nanochannel-type MCM-41/ SBA-15² and nanocage-type SBA-16 mesoporous materials.³ have appeared in the literatures that show highly catalytic activity and enantioselectivity in various asymmetric reactions. However their practical applications are still hindered due to the complicated process of preparation and the low recyclability of heterogeneous catalysts. Thus, exploitation of novel silica-based mesoporous materials to overcome these intrinsic disadvantages plays an important role in industrial applications.

Core-shell structured mesoporous silica spheres (CSSMSS) as a type of novel silica-based materials⁴ show potential advantage in asymmetric catalysis, in which the core of silica spheres is convenient to assemble various chiral functionalities while the shell of silica spheres is beneficial to prevent the leaching of chiral organometallics, showing potential superiority in recyclability of heterogeneous catalysts. Furthermore, functionalized CSSMSS materials can be prepared by a facile process, in which the co-condensation of inorganosilanes and functionalized organosilanes followed by continuous growth of inorganosilanes is convenient to afford various CSSMSS materials. More importantly, cetyltrimethylammonium chloride (CTAC)

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as a structure-directed template possesses a potential function of phase transfer. Thus, use of residual CTAC within CSSMSS as a phase transfer catalyst in a biphasic catalysis system can enhance catalytic efficiency significantly.

We were interested in the mesoporous silica-supported catalysts, in particular, in an effort to achieve the high recyclability of heterogeneous catalysts.⁵ In this contribution, we develop a new strategy to assemble a chiral Cp*RhTsDPEN⁶ complex (Cp* = pentamethyl cyclopentadiene, TsDPEN = 4-methylphenylsulfonyl-1,2-diphenylethylenediamine) within the core of CSSMSS for the first time, which shows excellent catalytic efficiency and high recyclability in the asymmetric transfer hydrogenation of aromatic ketones in aqueous medium. More importantly, the residual CTAC within CSSMSS materials as a phase transfer catalyst can enhance greatly the catalytic performance. In particular, as a new immobilized strategy, the incorporation of a chiral 1,2-cyclohexanediamine-based Rh(II) heterogeneous catalyst is also investigated.

The core–shell structured mesoporous silica spheres with the Cp*RhTsDPEN functionality in the internal core of silica spheres, abbreviated as Cp*RhTsDPEN-CSSMSS (3), were prepared as outlined in Scheme 1. The TsDPEN-functionalized internal core (2) was obtained *via* co-condensation of chiral silica resource 1^{5a} and tetraethoxysilane (TOES), in which a mixture of CTAC and TEA led to high nucleation and the slow growth of the generated seeds resulted in the mesoporous silica nano-particles.^{4a} The continuous growth in the presence of additional



Scheme 1 Preparation of the heterogeneous catalysts 3.

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Fig. 1 (a) TG/DTA curves of 3, (b) nitrogen adsorption-desorption isotherms of CSSMSS and 3.

TOES and CTAC then formed the external shell of the spheres. Finally, direct complexation with $[Cp*RhCl_2]_2^{5a,b}$ followed by the trimming of the nanopore *via* thorough Soxhlet extraction afforded the catalyst **3** as light red powders (see ESI† in Fig. S1). The thermal gravimetric (TG/DTA) analysis (Fig. 1a) disclosed that about 3.1% of the Cp*RhTsDPEN functionality was anchored within the core of CSSMSS materials by comparison of TG of pure CSSMSS (see ESI† in Fig. S5), which was nearly consistent with 4.12 mg (0.040 mmol) of Rh loading per gram for catalyst detected by inductively coupled plasma (ICP) optical emission spectrometric analysis. In addition, the 1:1 mole ratio of Rh to S atom was calculated from mass% of S obtained from elemental analyses (0.13% is equal to 0.040 mmol), suggesting generation of the single-site Cp*RhTsDPEN functionality within the core of CSSMSS.

The incorporation of the Cp*RhTsDPEN functionality within the core of CSSMSS was further confirmed by the solid-state NMR spectra. From the ¹³C CP MAS NMR spectrum (ESI[†] in Fig. S2), it is clear that the catalyst 3 presented a similar structural arrangement to that of the Cp*RhTsDPEN,⁷ proving the formation of the same well-defined single-site active center as Cp*RhTsDPEN, in which the typical peaks of TsDPEN moieties (16 ppm for Ar-CH₂, 70-74 ppm for N-CH-Ph, and 127-134 ppm for C_6H_5) and the typical peaks of CpMe₅ moieties (95 ppm for C_5 and 8 ppm CpCH₃) could be observed. Meanwhile, the ²⁹Si CP MAS NMR spectrum (ESI† in Fig. S3) demonstrated that the catalyst 3 possessed the inorganosilicate frameworks with (HO)Si(OSi)₃ and Si(OSi)₄ as the main networks due to the typical strong Q³–Q⁴ peaks. The typical T³ peak suggested that the Cp*RhTsDPEN functionalities were bonded to the inorganosilicate frameworks during the formation of $RSi(OSi)_3$ (R = chiral functionality) as a part of the silica core. 5a,b,8

As shown in Fig. 1b, the nitrogen sorption measurements revealed that the catalyst **3** was mesoporous, in which slightly small values of nanopore size, surface area and pore volume relative to pure CSSMSS were attributed to Cp*RhTsDPEN functionalities within the silica core to make the nanopore narrow.^{5b-d} The SEM image revealed clearly that the catalyst **3** presented the uniform size of silica spheres with an average diameter of around 450 nm (Fig. 2a), while the TEM image confirmed its core–shell mesostructure in which a silica core was coated by a silica shell of ~ 50 nm in thickness (Fig. 2b). In particular, a TEM chemical mapping showed clearly that the rhodium metallic centers were uniformly distributed within the core, suggesting that Cp*RhTsDPEN active centers in the catalyst **3** are highly dispersive within CSSMSS material that will govern its chiral performance.



Fig. 2 (a) SEM images, (b) TEM image, and (c) a chemical mapping of **3** showing the distribution of Si (green) and Rh (yellow).

Table 1 summarized catalytic performances of asymmetric transfer hydrogenation of aromatic ketones without addition of Bu₄NBr in aqueous medium. In general, excellent conversions and high enantioselectivities were obtained for all tested aromatic ketones. Taking acetophenone as an example, the heterogeneous catalyst 3 gave (S)-1-phenyl-1-ethanol with more than 99% conversion and 97% ee value, which were higher than those of Cp*RhTsDPEN without Bu₄NBr (entry 1 versus bracket in entry 1), and even comparable to those (99% conversion and 97% ee) of Cp*RhTsDPEN with Bu₄NBr as a phase transfer catalyst.⁶ Apparently, the catalyst **3** presented a bifunctional feature, in which the residual CTAC (ca. 16%, see ESI† in Fig. S5) acted as a phase transfer catalyst and the Cp*RhTsDPEN functionality acts as a chiral catalyst. Obviously highly catalytic activity could be attributed to the comprehensive effect of the phase transfer function of CTAC in a biphasic reaction system and highly dispersive Cp*RhTsDPEN active centers as confirmed by the TEM chemical mapping. High enantioselectivity should be due to the fact that the Cp*RhTsDPEN active centers within the core of CSSMSS could still keep the original chiral microenvironment, verified by XPS spectra (see ESI[†] in Fig. S4), in which the catalyst 3 had nearly the same Rh 3d_{5/2} electron binding energy as that of Cp*RhTsDPEN (309.3 eV versus 309.4 eV).

One important feature of the design of the catalyst 3 is to obtain high recyclability. In this case, the heterogeneous

 Table 1
 Asymmetric transfer hydrogenation of aromatic ketones^a

	Cp*RhTsDPEN-DMSS (3)		
	Ar CH ₃ Ho	COONa Ar C	H ₃
Entry	Ar	$\operatorname{Conv.}^{b}(\%)$	ee^b (%)
1	Ph	>99(88)	97 (96)
2	4-FPh	>99	95
3	4-ClPh	>99	95
4	4-BrPh	>99	93
5	3-BrPh	98	95
6	4-MePh	>99	92
7	4-OMePh	>99	95
8	3-OMePh	>99	96
9	4-CNPh	>99	89
10	4-CF ₃ Ph	>99	93
11	4-NO ₂ Ph	>99	87
12	2-Naphthyl	>99	95

^{*a*} Reaction conditions: catalysts (25.00 mg, 1.0 μ mol of Rh based on ICP analysis), HCO₂Na (0.13 g, 0.19 mmol), ketone (0.25 mmol) and 2.0 mL water, reaction temperature (40 °C), reaction time (1.0 h). ^{*b*} Determined by chiral GC or HPLC analysis (see ESI in Fig. S6).



Fig. 3 Reusability of 3 using acetophenone as a substrate.



Scheme 2 Asymmetric transfer hydrogenation of the catalyst 4.

catalyst 3 was recovered easily via centrifugation. As shown in Fig. 3, the reused catalyst 3 showed an obviously high recyclability, in which ee values as well as conversions did not decrease obviously after continuous twelve runs using acetophenone as a substrate (ESI[†] in Table S1 and Fig. S7). High recyclability should be due to the fact that the incorporation of the Cp*RhTsDPEN functionality within the silica core of CSSMS could decrease greatly the leaching of Rh due to the protection of the silica shell. An evidence to support the view was derived from a comparable experiment. In this case, the material 2 underwent a similar process of preparation to act as a catalyst. However, after the third recycle, the catalytic activity decreased greatly. ICP analysis showed that the Rh amount after the third recycle for 2 was 3.42 mg per gram catalyst while that after the twelfth recycle was 3.98 mg g^{-1} for the catalyst 3, indicating that the leaching of Rh was 17.0% and 3.4%, confirming that the presence of the silica shell could prevent effectively the leaching of Rh.

More importantly, as a new immobilized strategy, assembling of the various chiral functionalities within CSSMSS materials was convenient. As shown in Scheme 2, chiral 1,2-cyclohexanediamine-derived silica was anchored easily within CSSMSS and Cp*RhTsDACH-CSSMSS (4) was obtained conveniently,⁹ in which the catalyst 4 did also show high recyclability, which could be run fifteen times without affecting obviously its conversion and ee value when acetophenone was used as a substrate (ESI† in Table S2 and Fig. S8). In conclusion, we proposed a facile approach to prepare a core-shell structured heterogeneous chiral catalyst, which exhibited excellent catalytic efficiency and high recyclability in the asymmetric transfer hydrogenation of aromatic ketones in aqueous medium. In particular, the residual surfactant within CSSMSS, which acted as a phase transfer catalyst could enhance greatly the catalytic activity while the presence of the silica shell could prevent effectively the leaching of metals. More importantly, this research did also provide a new immobilized strategy to assemble various chiral functionalities within CSSMSS material for asymmetric catalysis.

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