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Recoverable organorhodium-functionalized polyhedral oligomeric silsesquioxane: a bifunctional heterogeneous catalyst for asymmetric transfer hydrogenation of aromatic ketones in aqueous medium†

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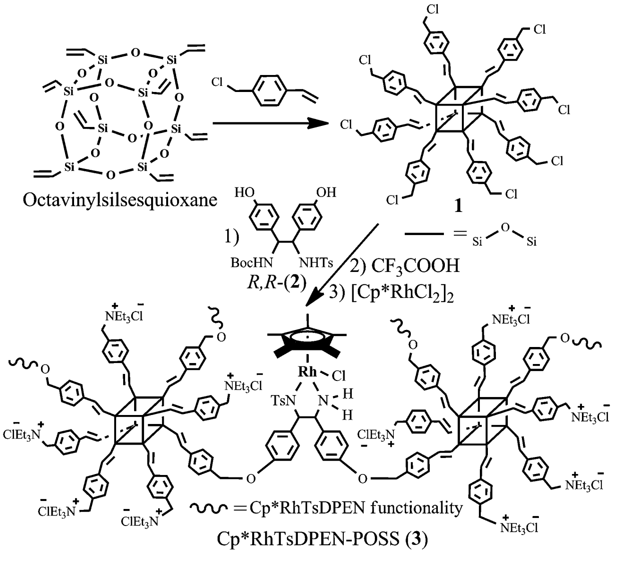
A bifuctional heterogeneous chiral rhodium catalyst exhibited excellent catalytic activity and enantioselectivity in asymmetric transfer hydrogenation of aromatic ketones and their analogues in aqueous medium, which could be recovered easily and used repetitively without affecting obviously its enantioselectivity.

Developments of silica-supported heterogeneous catalysts for asymmetric catalysis have led to significant achievements.[1] In particular, various self-assemblies of chiral-functionalized inorganosilanes or organosilanes have dominated the preparation of heterogeneous catalysts.[2] However, intrinsic limits, such as uncontrollable hydrolysis of the silane resource and complicated compatibility of functionalities, often make chiral functionalities anchor randomly within frameworks, resulting in difficulty to form precisely site-directed frameworks. Thus, searching for well-defined silica-based building blocks to control the arrangement of chiral functionalities within materials is still a scientific and technological challenge. Octavinylsilsesquioxane $(CH_2CH)_8Si_8O_{12}$, as a well-defined molecular building block, shows some salient features. Octavinylsilsesquioxane, as one of the cubic silsesquioxanes family,[3] is readily prepared in large quantity, and with vinyl groups at each vertex is easily functionalized, in which various hydrosilylations, alkyl, epoxy, isocyanate and acrylate groups have been introduced.[4] Furthermore, self-assemblies of these functional silsesquioxane units are convenient to construct various polyhedral oligomeric silsesquioxane (POSS) materials.[5] In particular, potentially site-directed multifunctionality of octavinylsilsesquioxane within POSS is beneficial for forming frameworks bearing desired chiral functional groups. However, practical self-assembly of chiral-fuctionalized silsesquioxane units for asymmetric catalysis is still rare.

We are interested in mesoporous silica-supported heterogeneous Catalysts.[6] In this contribution, we utilize the potentially site-directing vinyl groups in octavinylsilsesquioxane and report a bifunctionalized polyhedral oligomeric silsesquioxane for the first time, in which a quaternary ammonium salt functionality as a phase transfer catalyst and a chiral Cp*RhTsDPEN functionality [(Cp* = pentamethyl cyclopentadiene and TsDPEN = 4-(methylphenylsulfonyl)-1,2-diphenylethylenediamine)] as a chiral catalyst[7] are combined successfully together within POSS. This bifunctional heterogeneous catalyst not only controls the dispersibility of bifunctionality, but also promotes significant catalytic efficiency, showing an obvious superiority in asymmetric transfer hydrogenation of aromatic ketones and their analogues. Meanwhile, an investigation of its reusability is also discussed in detail.

The Cp*RhTsDPEN-functionalized polyhedral oligomeric silsesquioxane, Cp*RhTsDPEN-POSS (**3**), was prepared according to the procedure illustrated in Scheme 1. First, the octavinylsilsesquioxane-derived **1** with benzyl chloride groups at each vertex was synthesized readily *via* Grubbs coupling method.[4a] The condensation of **1** with (*R*,*R*)-**2** (Fig. S1, ESI†)



Scheme 1 Preparation of catalyst **3**.

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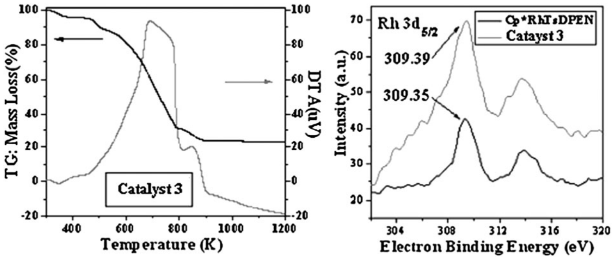


Fig. 1 (a) TG/DTA curves of **3** and (b) XPS spectra of Cp*RhTsDPEN and **3**.

Table 1 Asymmetric transfer hydrogenation of aromatic ketones[a]

Entry	Ar	Conv.[b] (%)	Ee[b] (%)	TOF[f]
1	Ph	>99 (88)[c]	96 (96)[c]	248
2	Ph	93	92[d]	232
3	Ph	84	96[e]	209
4	4-FC_6H_4	99	93	250
5	4-ClC_6H_4	>99	92	250
6	4-BrC_6H_4	>99	92	250
7	3-BrC_6H_4	>99	95	250
8	4-MeC_6H_4	97	91	245
9	4-OMeC_6H_4	>99	94	248
10	3-OMeC_6H_4	>99	93	250
11	2-Naphthyl	>99	92	248

[a] *Reaction conditions*: catalyst (10.58 mg, 8.00 μmol of Rh based on ICP analysis), HCO_2Na (0.68 g, 10.0 mmol), ketone (2.0 mmol) and 2.0 mL water, reaction temperature (40 °C), reaction time (1.0 h). [b] Determined by chiral GC or HPLC analysis (see Fig. S6,m ESI†). [c] Data were obtained using the homogeneous Cp*RhTsDPEN catalyst. [d] Data were obtained using (*R*,*R*)-TsDPEN-modified POSS plus $[Cp^*RhCl_2]_2$ as a catalyst. [e] Data were obtained using (*R*,*R*)-TsDPEN-modified POSS plus RhTsDPEN as a catalyst. [f] Turnover frequency (TOF = mole of substrate converted per mole of Rh complex per hour).

under basic conditions afforded the (*R*,*R*)-TsDPEN-modified POSS material. Finally, the heterogeneous catalyst **3** was successfully obtained *via* the deprotection of Boc groups followed by the complexation with $[Cp^*RhCl_2]_2$ (see ESI†). Thermal gravimetric (TG) analysis (Fig. 1a) showed that a new exothermic peak around 850 K with weight loss of 8% could be assigned to the oxidation of rhodium chloride when compared to the TG of (*R*,*R*)-TsDPEN-modified POSS (Fig. S2, ESI†), which was consistent with 77.88 mg (0.76 mmol, 7.78%) of Rh loading per gram catalyst as detected by inductively coupled plasma (ICP) analysis. Elemental analysis disclosed N and S at 2.78 and 0.76 mmol per gram of catalyst as calculated from mass% of N and S atoms (N 3.89, S 2.42%), in which a 3.66 mole ratio of N to S suggested that five functionalities of each octavinylsilsesquioxane within the POSS formed the quaternary ammonium units.

The incorporation of the chiral Cp*RhTsDPEN functionality within POSS could be confirmed by solid-state NMR spectra. From the ^{13}C CP MAS NMR spectrum (Fig. S4, ESI†), typical peaks of the TsDPEN moiety (21 ppm for Ar*C*H_2, 70–72 ppm for N*C*HPh and 126–136 ppm for C_6H_5) and of the $CpMe_5$ moiety (94 ppm for C_5 and 8 ppm for Cp*C*H_3) could be observed clearly. These observations were similar to those of homogeneous Cp*RhTsDPEN,[8] proving that the heterogeneous catalyst **3** possessed the same single-site well-defined active centers as Cp*RhTsDPEN. This behavior could be further confirmed by XPS spectra (Fig. 1b), in which the heterogeneous catalyst **3** had the same Rh $3d_{5/2}$ electron binding energy as Cp*RhTsDPEN (309.39 *vs.* 3309.35 eV). In addition, the ^{29}Si MAS NMR spectrum (Fig. S5, ESI†) showed that catalyst **3** possessed an organosilicate framework, in which the exclusively characteristic T^3 signal at −77.5 ppm corresponding to T^3 [C–$Si(OSi)_3$] suggested that the structure of cubic silsesquioxane was preserved and all Si species were covalently attached to carbon atoms.[9]

Table 1 summarizes the catalytic performances of asymmetric transfer hydrogenation of aromatic ketones[10] without Bu_4NBr additive. In general, excellent conversions and high enantioselectivities were obtained for all tested aromatic ketones. Taking acetophenone as an example, it was found that >99% conversion and 96% ee value of (*R*)-1-phenyl-1-ethanol were obtained, in which the conversion was obviously higher than that of the homogeneous Cp*RhTsDPEN while the ee value was comparable to that of Cp*RhTsDPEN (entry 1 *vs.* entry 1 in parentheses). The excellent catalytic activity could be attributed to the phase transfer function of the quaternary ammonium salt in a two-phase reaction system while similar enantioselectivity ascribed to the unchanged chiral microenvironment was verified by XPS spectra.

To gain better insight into the nature of this heterogeneous catalysis and to eliminate the effect of non-covalent adsorption during the catalytic process, two comparable experiments were carried out using (*R*,*R*)-TsDPEN-modified POSS plus $[Cp^*RhCl_2]_2$ and (*R*,*R*)-TsDPEN-modified POSS plus Cp*RhTsDPEN as heterogeneous catalysts. It was found that the former afforded the corresponding alcohol with 93% conversion and 92% ee value (entry 2), while the latter gave the alcohol with 84% conversion and 96% ee value (entry 3). The former suggested that the catalyst synthesized by an *in situ* complexation method could result in a catalytic performance. Lower catalytic activity and enantioselectivity than those of **3** should be due to the fact that a small part of $[Cp^*RhCl_2]_2$ had not been coordinated during the catalytic process (and loss of Rh was detected by ICP analysis in solution). The latter system indicated that the chiral microenvironment had not been changed a result of non-covalent adsorption. Lower conversion than that of **3** suggested that part of catalyst did not participate in the reaction due to blockage from physical absorption.[6b–d] However, when both the above catalysts were subjected to Soxhlet extraction, the reused catalysts were essentially inactive. These facts ruled out the role of non-covalent adsorption, demonstrating that the nature of heterogeneous catalysis was derived from the catalyst **3** itself.

An important feature of design of the heterogeneous catalyst **3** was its easy separation *via* simple filtration and the reused catalyst could still retain its catalytic activity and enantioselectivity over multiple cycles. As shown in Fig. 2, the catalyst **3** was quantitatively recovered *via* nanofiltration. It was to be noted that, in twelve consecutive reactions, the recycled catalyst **3** still afforded 96.2% conversion and 92.8% ee value (Fig. S7, ESI†).

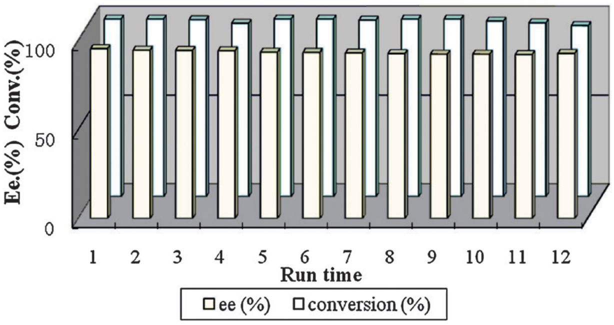
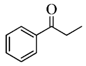
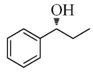
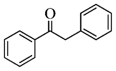
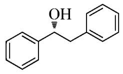
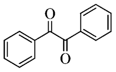
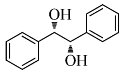
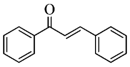
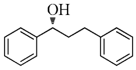
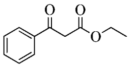
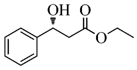


Fig. 2 Reusability of **3** using acetophenone as a substrate.

Table 2 Asymmetric transfer hydrogenation of ketones and analogues[a]

Entry	Substrate	Product	Conv.[b] (%)	Ee[b] (%)
1			>99	92
2			99	94
3			>99	99
4			99	92
5			>99	97

[a] *Reaction conditions*: catalyst (10.58 mg, 8.00 μmol of Rh based on ICP analysis), HCO_2Na (0.68 g, 10.0 mmol), ketone (2.0 mmol) and 2.0 mL water, reaction temperature (40 °C), reaction time (1.0 h). [b] Determined by chiral HPLC analysis (Fig. S8, ESI†).

Also, the bifunctional heterogeneous catalyst **3** could be applied to the asymmetric transfer hydrogenation of ketones and analogues (Table 2). The results showed that all tested ketones and analogues gave excellent conversions and good enantioselectivities, with yields obviously higher than those of Cp*RhTsDPEN without Bu_4NBr, and with similar enantioselectivities.[10a]

In conclusion, we employed a facile approach to prepare a bifunctional octavinylsilsesquioxane-based heterogeneous chiral catalyst, which exhibited excellent catalytic activities and high enantioselectivities in the asymmetric transfer hydrogenation of aromatic ketones and analogues. In particular, the anchoring of the quaternary ammonium salt onto POSS significantly enhanced the catalytic efficiency in a two-phase reaction system. More importantly, the heterogeneous catalyst could be recovered easily and reused repeatedly. The recycled catalyst (reused 12 times) still showed high catalytic efficiency without affecting obviously its enantioselectivity, thus showing good potential in industrial application.

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