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## Magnetic Nanoparticles

# Phenylene-Coated Magnetic Nanoparticles that Boost Aqueous Asymmetric Transfer Hydrogenation Reactions

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**Abstract:** Phenylene-coated organorhodium-functionalized magnetic nanoparticles are developed through co-condensation of chiral 4-(trimethoxysilyl)ethyl)phenylsulfonyl-1,2-diphenylethylene-diamine and 1,4-bis(triethyoxysilyl)benzene onto $Fe_3O_4$ followed complexation with $[\{Cp^*RhCl_2\}_2]$. This magnetic catalyst exhibits excellent catalytic activity and high enantioselectivity in asymmetric transfer hydrogenation in aqueous medium. Such activity is attributed to the high hydrophobicity and the confined nature of the chiral organorhodium catalyst. The magnetic catalyst can be easily recovered by using a small external magnet and it can be reused for at least 10 times without loss of its catalytic activity. This characteristic makes it an attractive catalyst for environmentally friendly organic syntheses.

The use of magnetic materials as immobilized supports for heterogeneous catalysis has attracted much interest because of the merits of magnetic separation.[1] However, intrinsic disadvantages, such as magnetic aggregation and magnetic loss,[2] still hinder the potential applications of such materials. Recently, various surface-coated or otherwise surface-modified magnetic nanoparticles have opened up a variety of possibilities for the immobilization of homogeneous chiral complexes.[3] In particular, many inorganosilica-coated nanoparticles, which are designed to overcome magnetic aggregation and to avoid magnetic loss, have been applied successfully to various asymmetric reactions.[4] However, most of them still suffer from lower catalytic efficiency compared with their homogeneous counterparts owing to the intrinsic nature of inorganosilica.[5] Thus, how to adjust magnet-coat type and to improve catalytic efficiency are still unmet challenges in the design of magnet-supported heterogeneous catalysts for asymmetric catalysis.

Periodic mesoporous organosilica (PMO) materials are known to possess high hydrophobicity owing to their intrinsic organosilicate walls,[6] a property that may facilitate asymmetric reactions in aqueous catalytic systems. More importantly, like general mesoporous materials,[7] PMO materials also possess large surface area/pore volume ratios, tunable pore dimensions, and well-defined pore arrangements, all of which benefit the formation of site-isolated active species and enhance catalytic activity.[6c] Thus, it is reasonable to expect that the design of an organosilica-coated magnetic catalyst would not only enhance catalytic efficiency but would also realize magnetic separation, the applicability of which in asymmetric reactions has not been explored.

To develop silica-based mesoporous heterogeneous catalysts for asymmetric catalysis,[8,9] we recently discovered two inorganosilica-coated magnetic catalysts[9a,b] with high recycling efficiency. However, their reaction rates hardly matched those of their corresponding homogeneous systems. Interestingly, two kinds of chiral organonickel-functionalized periodic mesoporous organosilicas show significantly enhanced catalytic performance in the asymmetric Michael addition of 1,3-dicarbonyl compounds to nitroalkenes owing to the high hydrophobicity of their organosilicate walls.[9c,d] Thus, in this contribution, we utilize the high hydrophobicity of periodic mesoporous organosilica and design a phenylene-coated magnetically separable heterogeneous catalyst. As demonstrated in the present study, the [Cp*RhArDPEN]-functionalized magnetic catalyst (Cp*RhArDPEN[10] = $[(\eta^5\text{-}C_5Me_5)RhC1\{$(l*S*,2*S*)-*N*-4-ethylenephenylsulfonyl-1,2-diphenylethylenediamine}], where Cp* = pentamethylcyclopentadienyl and ArDPEN = *N*-4-ethylenephenylsulfonyl-1,2-diphenylethylenediamine) exhibits excellent catalytic activity and high enantioselectivity in asymmetric transfer hydrogenation in aqueous medium.[10,11] As expected, the high hydrophobicity of the phenylene coating significantly enhances the catalytic activity while retaining high enantiomeric excess (*ee*) values. The catalyst can be recovered easily by using a small magnet; neither filtration nor extraction is necessary. Furthermore, the catalyst can be reused for at least 10 times without loss of its catalytic activity. This characteristic makes it an environmentally friendly catalyst in organic synthesis.

The phenylene-coated chiral organorhodium-functionalized magnetic catalyst, abbreviated as $Fe_3O_4$@Cp*RhArDPEN-PMO (**3**), was synthesized as outlined in Scheme 1. First, magnetic nanoparticles ($Fe_3O_4$) were obtained according to reported methods.[3a,12] The phenylene layer was then coated onto $Fe_3O_4$ by co-condensation of (*S*,*S*)-4-(trimethoxysilyl)ethyl)phenylsulfonyl-1,2-diphenylethylene-diamine (**1**) and 1,4-bis(triethyoxysilyl)benzene by using cetyltrimethylammonium bromide (CTAB) as a template. This step afforded ArDPEN-functionalized PMO (**2**) in the form of a black powder. Finally, **3** was obtained by the direct complexation of $(Cp^*RhCl_2)_2$ with **2** followed by fur-

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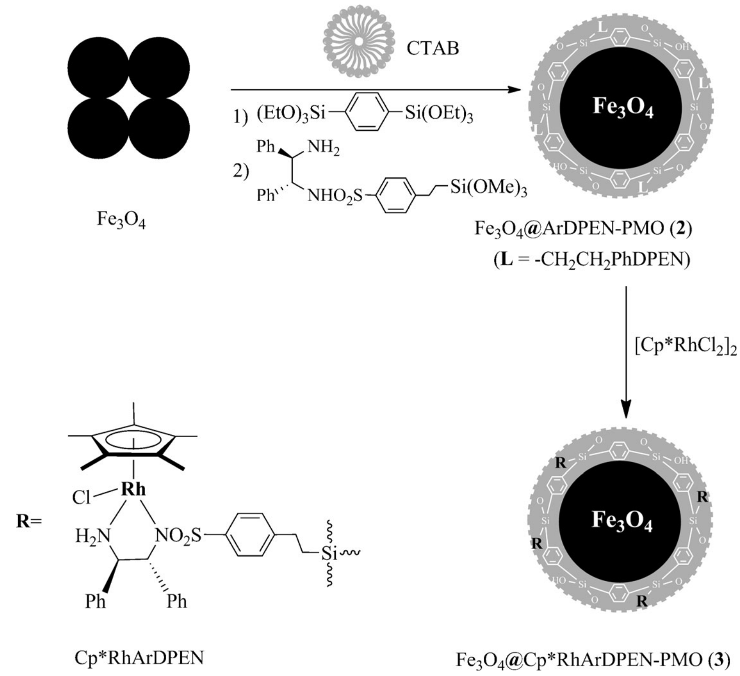


**Scheme 1.** Synthesis of the magnetic catalyst, **3**. CTAB = cetyltrimethylammonium bromide.

ther Soxhlet extraction to clear its nanochannels (see the Supporting Information for additional experimental details, and Figures S1 and S2). To characterize the active species of the magnetic nanoparticles, non-magnetic ArDPEN-functionalized-PMO (ArDPEN-PMO, **2**′) and organorhodium-functionalized-PMO (Cp*RhArDPEN-PMO, **3**′) were also prepared by in situ removal of $Fe_3O_4$[12b] (see the Supporting Information, Figures S1, S3–S6).

Incorporation of well-defined single-site Cp*RhArDPEN active species within the phenylene layer could be confirmed by comparison with ArDPEN-PMO (**2**′) and Cp*RhArDPEN-PMO (**3**′). As shown in their solid-state $^{13}$C MAS NMR spectra (Figure 1), both **2**′ and **3**′ present strong characteristic carbon signals for $SiC_6H_4Si$ and NCH groups around 128 and 47–55 ppm, corresponding to phenylene-bridged organosilica and the ArDPEN moiety, respectively. The peak at 94.8 ppm in the $^{13}$C MAS NMR spectrum of **3**′ was due to the carbon atoms in the Cp* ring, and that at 8.4 ppm originated from the carbon atoms of the $CH_3$ groups attached to the Cp* ring. These peaks were absent in the spectrum of **2**′, suggesting the formation of the Cp*RhArDPEN complex in **3**′. In sharp contrast to the spectra of **2**′ and the homogeneous counterpart of **3**, Cp*RhTsDPEN (TsDPEN = *N*-4-methylphenylsulfonyl-1,2-diphenylethylenediamine),[11d] the chemical shifts in the spectrum of **3**′ were very similar to those of Cp*RhTsDPEN, demonstrating that **3** and **3**′ had the same well-defined single-site active species as those in its homogeneous counterpart. Other peaks, denoted by asterisks in Figure 1, were assigned to the rotational sidebands, which could be distinguished through comparison with peaks of pure phenylene-bridged PMO (Ph-PMO).

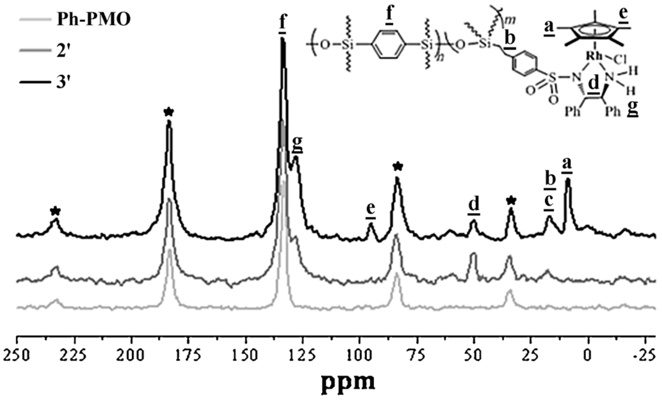


**Figure 1.** $^{13}$C CP MAS NMR spectra of Ph-PMO, ArDPEN-PMO (**2**′) and catalyst **3**′.

Scanning electron microscopy (SEM) demonstrated that catalyst **3** was composed of uniformly dispersed nanospheres with an average size of about 370 nm (Figure 2a). Transmission electron microscopy (TEM) confirmed that the core–shell-structured magnetic nanospheres in **3** were encapsulated by a thin organosilica layer 30 nm thick (Figure 2b). Wide-angle X-ray powder diffraction patterns (Figure 3) clearly show that **3** produced peaks similar to those of pure $Fe_3O_4$ nanoparticles, suggesting that there was no obvious change after the surface coatings. Figure 4 presents the magnetization curves and separation–redispersion process of catalyst **3**. The superparamagnetic behavior of catalyst **3** was 55.1 emu g$^{-1}$ of the magnetization saturation value (Figure 4a). These magnetic nanoparticles could be separated easily by placing a small magnet near the bottle (Figure 4b). As desired, the phenylene-coated magnetic catalyst not only efficiently negated magnetic dipolar attrac-

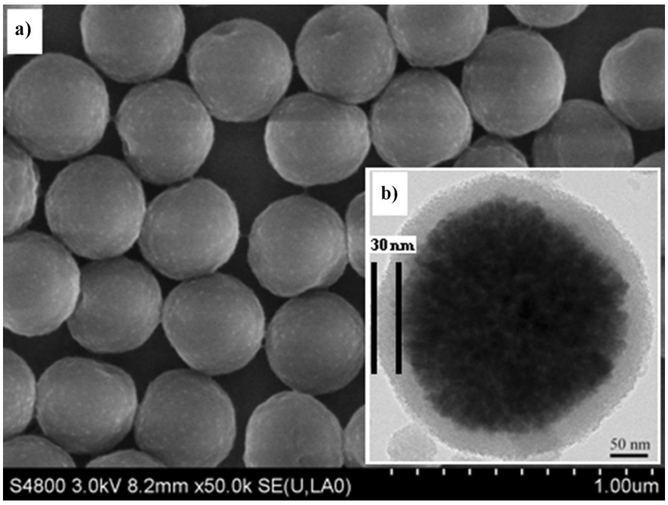


**Figure 2.** a) SEM image, b) TEM image of catalyst **3**.

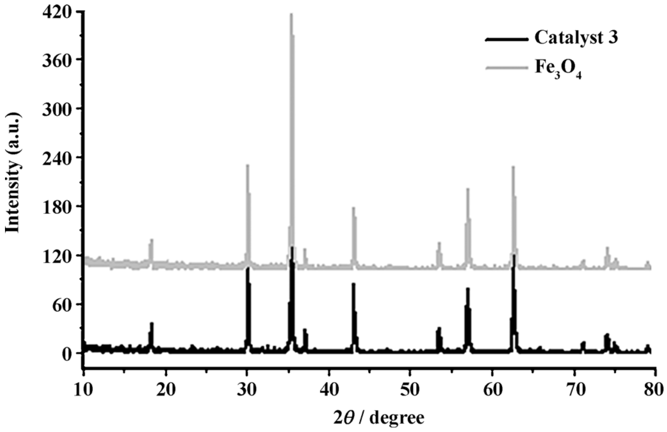


**Figure 3.** Wide-angle powder XRD patterns of pure $Fe_3O_4$ and catalyst **3**.

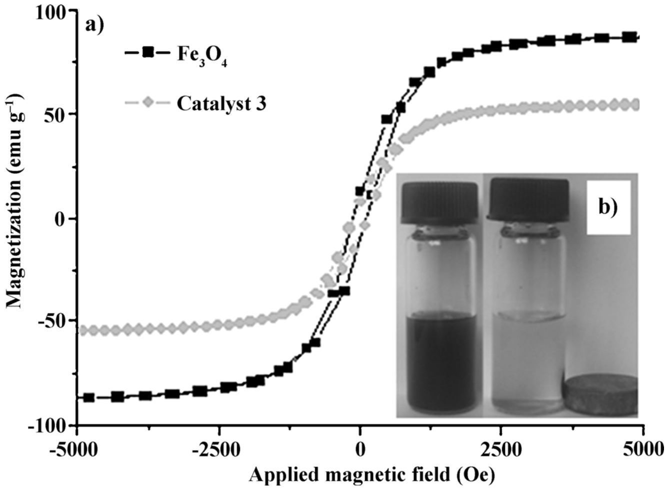
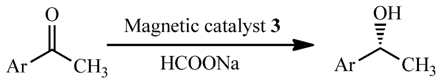


**Figure 4.** a) Magnetization curves of pure $Fe_3O_4$ and catalyst **3** at 300 K, b) Separation–redispersion process of catalyst **3**.

tion but also retained enough superparamagnetism for magnetic separation.

Table 1 summarizes the catalytic performance of **3** in aqueous asymmetric transfer hydrogenation. Because of its phenylene-coating, catalyst **3** was able to catalyze the asymmetric reaction in the absence of $Bu_4NBr$, which is often necessary to promote catalytic performance in homogeneous catalysis systems.[10] In general, excellent conversions and high enantioselectivities were obtained for all of the aromatic ketones tested. Taking acetophenone as an example, over 99 % conversion was achieved and an *ee* value of 96 % was obtained for (*S*)-1-phenyl-1-ethanol. This conversion was higher than that of the homogeneous counterpart of **3** in the absence of $Bu_4NBr$,[8a] and the *ee* value was comparable to that of its homogeneous counterpart.[10a] Of particular note was that the asymmetric reaction could be performed at a much high ratio of substrate/catalyst without markedly affecting its *ee* value, as exemplified by the asymmetric transfer hydrogenation of acetophenone at a substrate-to-catalyst molar ratio of 500 (entry 1 versus value in brackets).

**Table 1.** Asymmetric transfer hydrogenation of aromatic ketones.[a]



| Entry | R | Conv. [%][b] | *ee* [%][b] |
|---|---|---|---|
| 1 | Ph | > 99 (96[c]) | 96 (95[c]) |
| 2 | Ph | > 99 | 96[d] |
| 3 | 4-FPh | > 99 | 94 |
| 4 | 4-ClPh | > 99 | 93 |
| 5 | 4-BrPh | > 99 | 93 |
| 6 | 3-BrPh | > 99 | 92 |
| 7 | 4-MePh | > 99 | 96 |
| 8 | 4-OMePh | > 99 | 95 |
| 9 | 3-OMePh | > 99 | 96 |
| 10 | 4-CNPh | > 99 | 86 |
| 11 | 4-$CF_3$Ph | > 99 | 93 |

[a] Reaction conditions: catalyst **3** (56.20 mg, 2.00 μmol of Rh based on ICP analysis), $HCO_2Na$ (0.68 g, 10.0 mmol), ketone (0.2 mmol), and water (2.0 mL), 40 °C, 0.5–5.0 h. [b] Determined by chiral GC analysis (see the Supporting Information, Figure S8). [c] With 0.2 mol % of catalyst. [d] Data were obtained by using **2** plus Cp*RhTsDPEN as a catalyst.

To rule out the effect of noncovalent adsorption, a parallel experiment using ArDPEN-functionalized-PMO (**2**) plus the homogeneous catalyst, Cp*RhTsDPEN, was investigated. The result was that the asymmetric reaction of acetophenone afforded (*S*)-1-phenyl-1-ethanol with over 99 % conversion and 96 % *ee* (entry 2), indicating that the homogeneous catalyst added through noncovalent adsorption onto the material also resulted in a good catalytic performance. However, when this catalyst was subjected to Soxhlet extraction, the reused catalyst gave only a small amount of product, demonstrating that the noncovalent physically adsorbed catalyst could be eliminated by Soxhlet extraction. This observation confirmed that the nature of the active catalyst was indeed derived from the magnetic nanoparticles as the catalyst **3** had also undergone this process of Soxhlet extraction, yet remained active.

It is worth mentioning that the asymmetric reactions catalyzed by **3** have markedly higher reaction rates relative to those obtained with general inorganosilica-based mesoporous heterogeneous catalysts,[8d] and they are even higher than those obtained with the homogeneous counterpart, Cp*RhTsDPEN.[10a] Taking 4-methylacetophenone as an example, the asymmetric reaction of 4-methylacetophenone catalyzed by **3** could be completed within 1.5 h, whereas 4.0 h was needed with the homogeneous catalyst system. To confirm this result, kinetic profiles of the asymmetric reactions of 4-methylacetophenone were compared (see the Supporting Information, Figure S7). It was found that catalyst **3** showed initial activity higher than that of Cp*RhTsDPEN; the initial turnover frequency (TOF) values were 480.0 and 362.5 mol $mol^{-1}\,h^{-1}$ for **3** and Cp*RhTsDPEN, respectively.

An important design feature of magnetic catalysts is their easy separation by application of an appropriate magnetic field. Ideally, the recovered catalyst should retain its catalytic activity and enantioselectivity after multiple cycles. In this case, upon completion of the reaction, magnetic catalyst **3** was recovered quantitatively by using a small external magnet (Figure 4b). As shown in Figure 5, the recycling of magnetic catalyst **3** in ten consecutive reactions still afforded (*S*)-1-phenyl-1-ethanol with 97% conversion and 96% *ee* (see the Supporting Information, Table S1 and Figure S9).

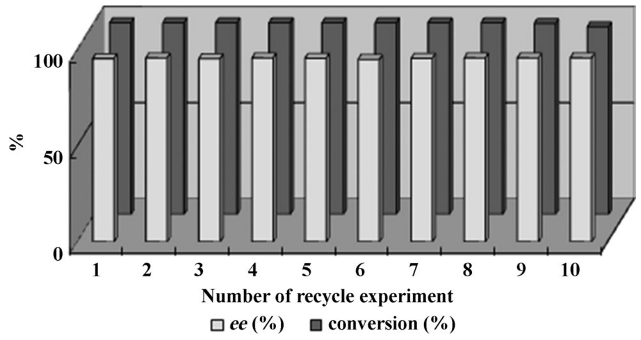


**Figure 5.** Reusability of catalyst **3** using acetophenone as the substrate.

In conclusion, phenylene-coated organorhodium-functionalized magnetic nanoparticles were prepared and their use in asymmetric transfer hydrogenations of aromatic ketones in aqueous medium were investigated. As desired, the magnetic catalyst has a greatly enhanced catalytic performance because of the hydrophobic nature of the phenylene-coated organosilicate layer. Furthermore, the magnetic catalyst can be recovered and reused at least 10 times without loss of its catalytic activity. This outcome offers a general approach to coat magnetic nanoparticles and to achieve enhanced catalytic activity in aqueous media.

## Experimental Section

### Typical preparation of heterogeneous catalyst 3

[{Cp*$RhCl_2$}$_2$] (0.50 g, 0.08 mmol) was added to a stirred suspension of $Fe_3O_4$@ArDPEN-PMO (**2**; 0.50 g) in dry $CH_2Cl_2$ (20 mL) at room temperature (25 °C) . The resulting mixture was stirred at room temperature for 12 h. The mixture was then separated by a small magnet. After Soxhlet extraction in $CH_2Cl_2$ for 24 h to remove the starting materials, the solid was dried overnight (12 h) at 60 °C in vacuo to afford catalyst **3** as a black powder. Inductively coupled plasma (ICP) optical emission spectrometer analysis shows that the Rh loading is 11.58 mg (0.11 mmol) per gram of catalyst. IR (KBr): $\tilde{\nu}$ = 3426.8 (s), 3062.3 (w), 2916.6 (w), 2852.8 (w), 1586.8 (s), 1441.1 (s), 1149.4 (s), 1076.6 (s), 930.9 (w), 858.1 (w), 575.8 (s) $cm^{-1}$; elemental analysis found (%): C 12.41, H 0.49, N 0.31, S 0.36.

### General procedure for asymmetric transfer hydrogenation of aromatic ketones

Heterogeneous catalyst **3** (2.00 μmol of Rh based on ICP analysis), $HCO_2Na$ (0.68 g, 10.0 mmol), ketone (0.2 mmol), and water (2.0 mL) were added in a 10 mL round-bottomed flask. The mixture was allowed to react at 40 °C for 0.5–4.0 h. During that time, the reaction was monitored constantly by TLC. After completion of the reaction, the catalyst was separated from the mixture by a small magnet being placed near the flask in order to be used for the recycling experiments. The aqueous solution was extracted by $Et_2O$ (3× 3.0 mL). The combined $Et_2O$ washings were washed with brine twice and dried with $Na_2SO_4$. After evaporation of $Et_2O$, the residue was purified by silica gel flash column chromatography to afford the desired product. The conversion and *ee* values were determined by chiral GC using a Supelco β-Dex 120 chiral column (30 m × 0.25 mm (i.d.), 0.25 μm film).

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**Keywords:** asymmetric transfer catalysts · heterogeneous catalysis · magnetic nanoparticles · magnetic separation · mesoporous materials

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