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RAPID COMMUNICATION

Superhydrophobic, chiral, and mesoporous TsDPEN copolymer coordinated to ruthenium species as an efficient catalyst for asymmetric transfer hydrogenation

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Summary Homogeneous chiral catalysts usually show higher catalytic activities than corresponding heterogeneous chiral catalysts, because of their easy interaction between catalytically active sites with reactant molecules. We demonstrate here superhydrophobic, chiral, and mesoporous catalysts (TsDPEN-Ru) synthesized from copolymerization of N-*p*-styrenesulfonyl-1,2-diphenylethylenediamine (V-TsDPEN) with divinylbenzene and loading of Ru species exhibiting much higher activities in asymmetric transfer hydrogenation (ATH) of ketones in aqueous solution than corresponding homogeneous chiral catalyst. This phenomenon is strongly related to the unique features of high enrichment for the reactants in superhydrophobic TsDPEN-Ru catalysts due to their good wettability, as well as easy transfer of product from the catalyst into water phase. These features open a door for design and developing a wide variety of chiral catalysts for asymmetric catalysis.

Introduction

Homogeneous chiral catalysts play an important role for the synthesis of pharmaceuticals and fine chemicals, but their poor recyclabilities strongly influence their wide applications [1]. Therefore, the development of heterogeneous chiral catalysts has attracted much attention [2], but their performance is normally lower than those of corresponding homogeneous chrial catalysts due to the lower degree of

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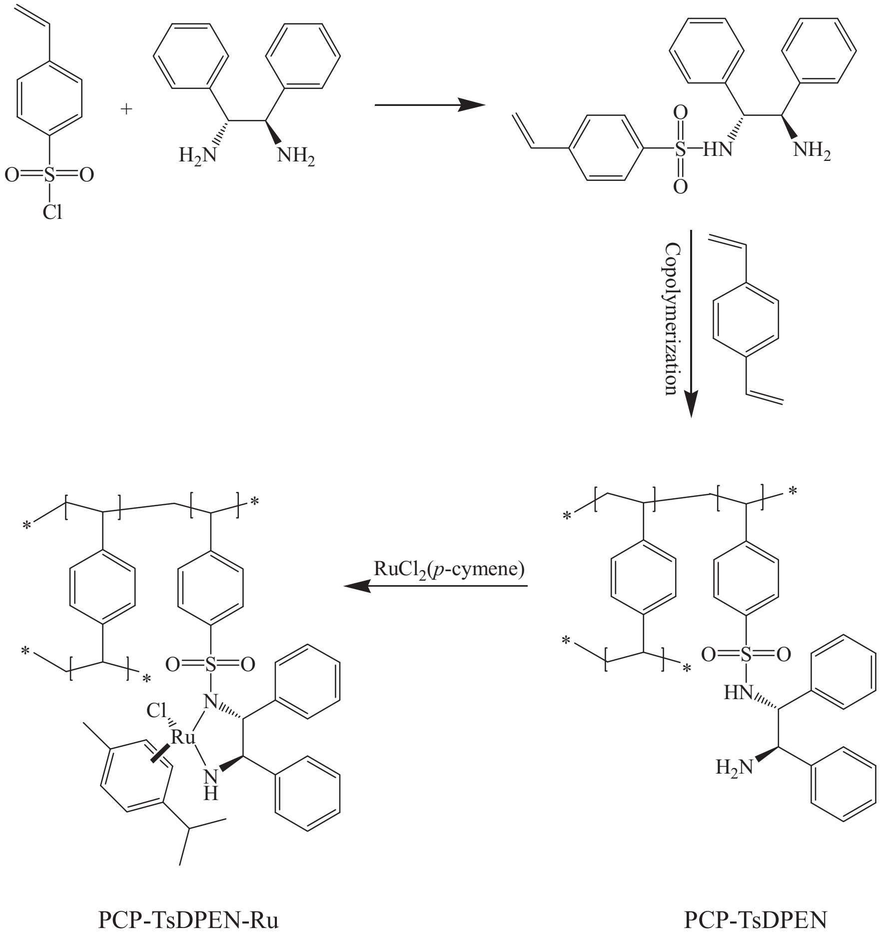
exposure or poorer wettability of active sites to reactants [3].

As a typical homogeneous chiral catalyst, ruthenium-N-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine (TsDPEN-Ru, Noyori-Ikariya catalyst) has been extensively investigated [4]. However, this chiral catalyst immobilized onto insoluble supports shows relatively low yield in asymmetric transfer hydrogenation (ATH) of ketones because of poor wettability of the chiral catalyst to the ketones [5]. To increase the wettability, phase transfer catalysts are introduced into the H_2O—oil—solid system [6].

Recently, it has been reported that the hydrophobicity of porous catalysts has good wettability to reactant molecules, which is very helpful for the enrichment of organic reactants, significantly enhancing the catalytic performance [7]. In this work, we have successfully synthesized superhydrophobic, chiral, and mesoporous, TsDPEN copolymer (PCP-TsDPEN) from the copolymerization for the first time. After coordination with ruthernium species, the heterogeneous superhydrophobic PCP-TsDPEN-Ru catalyst has significantly enhanced catalytic performance together with easy and excellent recyclability in ATH of ketones compared with the corresponding homogeneous chiral catalyst. This phenomenon is strongly related to the unique features of good enrichment of the reactants and easy product transfer from the catalyst into water phase due to the superhydrophobicity of catalyst.

Results and discussion

PCP-TsDPEN-Ru sample was synthesized from copolymerization of N-*p*-styrenesulfonyl-1,2-diphenylethylenediamine (V-TsDPEN) with divinylbenzene (DVB) under solvothermal conditions (Scheme 1), followed by coordination of $[RuCl_2(p\text{-cymene})]_2$. The V-TsDPEN was synthesized from 1,2-diphenylethylenediamine and *p*-styrenesulfonyl chloride. In the synthesis of PCP-TsDPEN, various mass ratios (*x*) of V-TsDPEN to divinylbenzene have been used, yielding various porous PCP-*x*-TsDPEN samples (Table S1). All the samples exhibit high surface area, large pore volume, and uniform mesopore sizes (Figs. S1 and S2 and Tables S1 and S2). IR spectroscopy (Fig. S3) shows that PCP-1/8-TsDPEN gives additional bands at *ca.* 1095, 1160 and 1345 cm^{-1}, compared with pure PDVB sample. These bands are characteristic of C—N and O═S═O bonds, in good agreement with the presence of V-TsDPEN [8]. Moreover, the intensities of these bands increase with the ratios of V-TsDPEN to DVB (Fig. S4). These results indicate the successful incorporation of V-TsDPEN in the samples.



Scheme 1 The route for synthesizing PCP-TsDPEN-Ru catalyst.

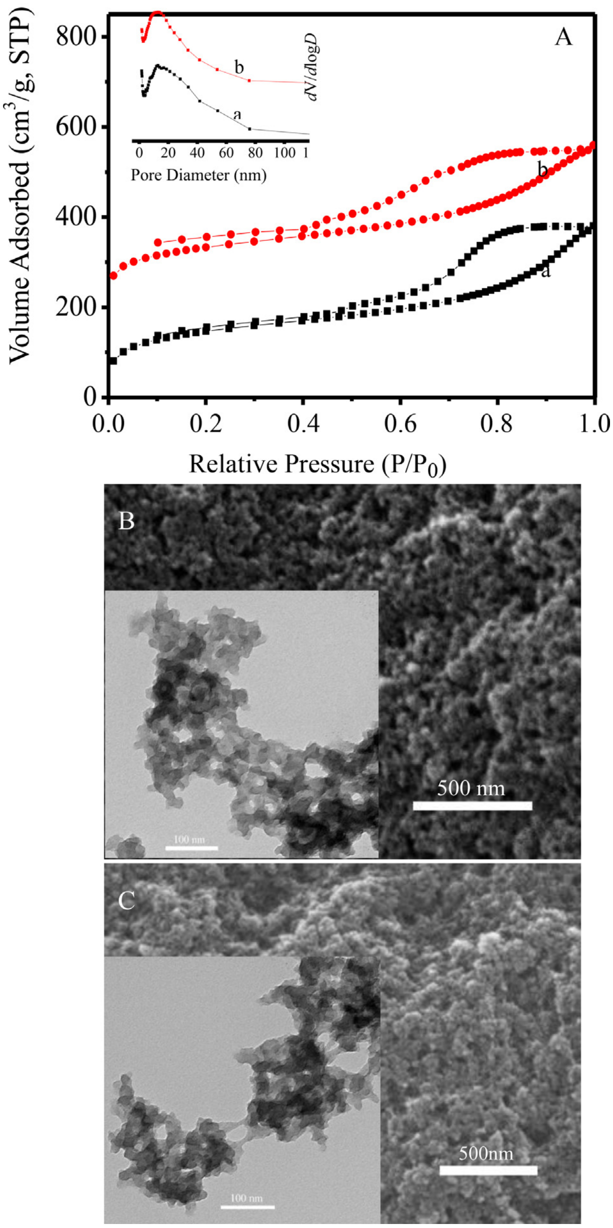


Figure 1 (A) N_2 sorption isotherms of (a) PCP-TsDPEN and (b) PCP-TsDPEN-Ru samples. (b) Isotherms in A have been offset by 200 cm^3/g. Inset: pore size distributions; SEM images of (B) PCP-TsDPEN and (C) PCP-TsDPEN-Ru samples. Inset: corresponding TEM images of the samples.

Particularly, after coordination of ruthenium species, the band attributed to C—N band of PCP-1/8-TsDPEN-Ru slightly shifts to lower wavenumber, while the bands associated with O=S=O bond almost do not change. These results suggest that the ruthenium species should coordinate with nitrogen atoms rather than sulfur atoms. The measurements of water on the surface of the samples show that the contact angles are higher than 150° when *x* is less than 1/8, indicating their superhydrophobicity (Fig. S5).

As typical samples, PCP-1/8-TsDPEN, and PCP-1/8-TsDPEN-Ru (abbreviation: PCP-TsDPEN and PCP-TsDPEN-Ru) are carefully investigated. Fig. 1A shows N_2 isotherms of PCP-TsDPEN and PCP-TsDPEN-Ru samples, exhibiting typical type-IV sorption isotherms with a hysteresis loop at 0.45—0.95, which indicates the presence of mesoporosity in the samples. Correspondingly, PCP-TsDPEN and PCP-TsDPEN-Ru give the pore size distributions at *ca.* 12.6 and 11.8 nm, BET surface areas at 528 and 481 m^2/g, and pore volumes at 0.59 and 0.55 cm^3/g respectively (Tables S1 and S2). Fig. 1B and Fig. 1C show scanning electron microscope (SEM) and transmission electron microscope (TEM) images of PCP-TsDPEN and PCP-TsDPEN-Ru samples, giving direct evidence of abundant mesoporosity, in good agreement with those of the sample N_2 sorption isotherms. Fig. 2 shows elemental mapping for C, O, S, N, and Ru in the PCP-TsDPEN-Ru, exhibiting very uniform elemental distribution. These results suggest that the PCP-TsDPEN-Ru is a copolymer, rather than a mixture of polydivinylbenzene and polymerized V-TsDPEN.

Fig. 3 shows contact angles of water, 1-phenyl-ethanol, and acetophenone on the sample surface. When a water droplet was contacted with the surface of PCP-TsDPEN, the contact angle (CA) was about 151° (Fig. 3A), indicating that the sample is superhydrophobic. When a water droplet was contacted with the surface of PCP-TsDPEN-Ru, the contact angle was still about 150° (Fig. 3B). This result indicates that the introduction of Ru species in the sample does not influence the sample superhydrophobicity. When a 1-phenyl-ethanol droplet was contacted with the surface of PCP-TsDPEN-Ru, the angle was 16° (Fig. 3C). In contrast, when an acetophenone droplet was contacted with the PCP-TsDPEN-Ru, the acetophenone was momentarily into the sample, giving the swelling surface (Fig. 3D). These results indicate that the wettability of acetophenone into PCP-TsDPEN-Ru is much better than that of 1-phenyl-ethanol. TG curve of PCP-TsDPEN shows that no weight loss occurs below 300 °C (Fig. S6), indicating its good thermal stability.

To determine the chirality of PCP-TsDPEN sample, the enantiomers of 1,2-diphenylethylenediamine were used as starting materials. As a result, both PCP-(*S*)-TsDPEN and PCP-(*R*)-TsDPEN were obtained. Fig. 4 shows CD spectra (circular dichroism spectra) of PCP-(*S*)-TsDPEN and PCP-(*R*)-TsDPEN samples. As expected, both show mirror signals at *ca.* 245, 275 and 365 nm, although there is a peak shift. In fact, the peak shift also can be observed at monomer of V-TsDPEN (Fig. S7). In addition, UV—visible spectroscopy shows that PCP-(*R*)-TsDPEN sample has similar adsorption peaks at *ca.* 245, 290 and 350 nm (Fig. S8), suggesting that the mirror CD peaks associated PCP-(*R*)-TsDPEN and PCP-(*S*)-TsDPEN are not artificial [9].

Based on the results of N_2 sorption isotherm, SEM and TEM images, elemental mapping, IR, contacting angles of water, as well as CD spectra, it can be concluded that the superhydrophobic, chiral, and mesoporous TsDPEN copolymers have been successfully synthesized. After loading Ru species, the Ru species could be coordinated with nitrogen atoms in TsDPEN ligands in the samples.

To evaluate the catalytic performance of the superhydrophobic, chrial, and mesoporous PCP-TsDPEN-Ru, ATH of acetophenone as a model was chosen, and the catalytic results are presented in Table 1. Notably, PCP-TsDPEN-Ru catalyst shows a full conversion with 94.0% *ee* in 1.5 h at 40 °C (entry 1, Table 1). This activity is even higher than that of TsDPEN-Ru species in the nanocages containing phase

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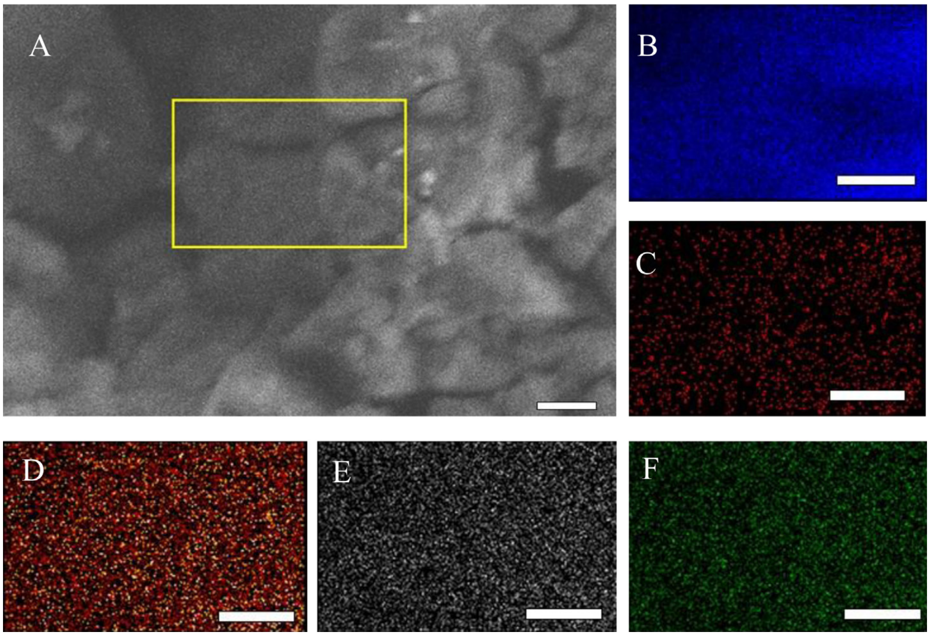

Figure 2 (A) SEM image of PCP-TsDPEN-Ru; (B), (C), (D), (E), and (F) elemental mapping for C, O, S, N, and Ru in the yellow rectangle of PCP-TsDPEN-Ru, respectively. The bars in the samples are 60 μm.

transfer catalyst, one of the best hetergeneous catalysts in ATH reactions [6c]. This result suggests that the superhydrophobic and mesoporous PCP-TsDPEN-Ru catalyst is very active. When the reaction temperature is increased to 70 °C, the full conversion takes for only 0.5 h (entry 2, Table 1). The reaction can be also performed at room temperature, but required longer reaction time 8 h (entry 3, Table 1). Interestingly, even if the S/C ratio is increased to 500, the conversion of acetophenone could still reach 98% with 93.1% *ee* (entry 4, Table 1).

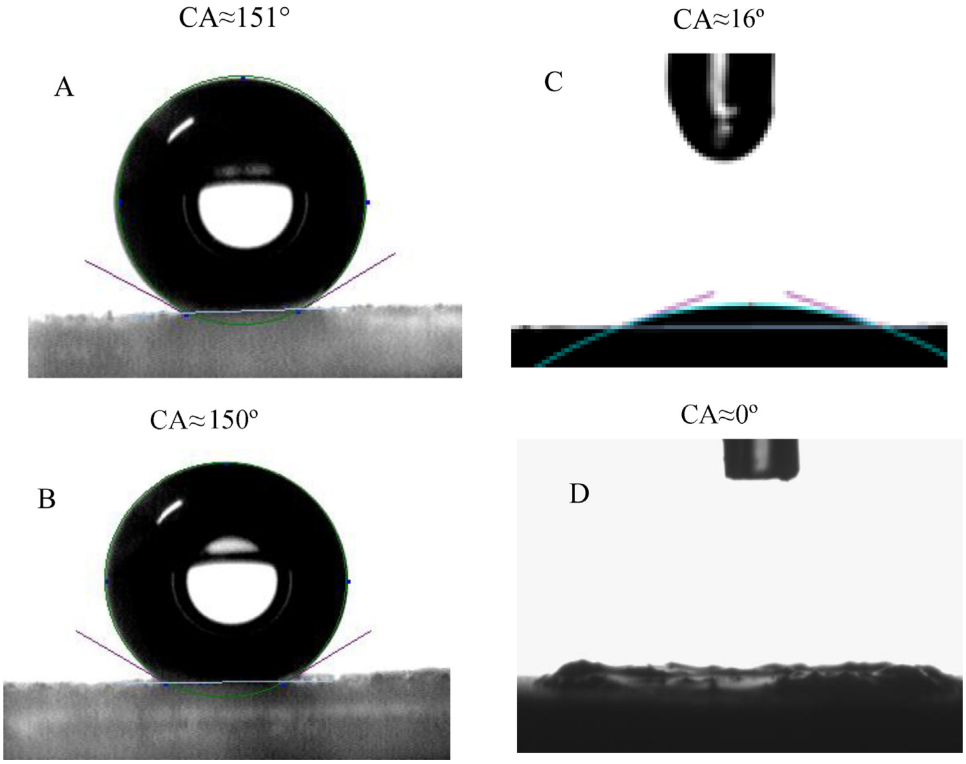

Figure 3 (A) Contact angle of water on the surface of PCP-TsDPEN; (B), (C), and (D) contact angles of water, 1-phenyl-ethanol, and acetophenone on the surface of PCP-TsDPEN-Ru, respectively.

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Table 1 Asymmetric transfer hydrogenation of ketones catalyzed by PCP-TsDPEN-Ru[a].

Entry	R_1	R_2	Time (h)	Conv. [%][b]	Sel. [%][b]	*ee* [%][b]
1	CH_3	H	1.5	>99.5	>99.5	94.0
2[c]	CH_3	H	0.5	>99.5	>99.5	90.1
3[d]	CH_3	H	8	>99.5	>99.5	94.3
4[e]	CH_3	H	9	98	>99.5	93.1
5[f]	CH_3	H	1.5	81	>99.5	95.1
6[g]	CH_3	H	1.5	52	>99.5	93.1
7[h]	CH_3	H	1.5	>99.5	>99.5	94.2
8[i]	CH_3	H	1.5	94	>99.5	92.9
9	CH_3CH_2	H	1.5	>99.5	>99.5	92.8
10	CH_3	*p*-CH_3O	2	>99.5	>99.5	95.2
11[j]	CH_3	*m*-CH_3O	2	>99.5	>99.5	98.4
12	CH_3	*p*-CH_3	3	>99.5	>99.5	94. 8
13	CH_3	*p*-Cl	1.5	>99.5	>99.5	94. 3
14	CH_3	*p*-Br	2.5	>99.5	>99.5	93. 2
15[k]	CH_3	H	1.5	>99.5	>99.5	93.7
16[l]	CH_3	H	1.5	5.1	>99.5	94.2

[a] Reactions were carried out under N_2 atmosphere at 40°C, using 0.5 mmol of ketones, 2.5 mmol of HCOONa, and a S/C ratio of 100 in 5 mL degassed water.
[b] Determined by GC on a Supelco γ-DEX 225 capillary column.
[c] Reaction at 70 °C.
[d] Reaction at RT.
[e] Acetophenone (2.5 mmol), HCOONa (12.5 mmol), water (20 mL) and a S/C ratio of 500.
[f] TsDPEN-Ru as catalyst.
[g] Using 3 mL of H_2O and 3 mL of DMF as solvent.
[h] Reused.
[i] Recycles for 14 times.
[j] Determined by GC on a Agilent CycloSil-B.
[k] PCP-(1/8)-*(S)*-TsDPEN-Ru was used as catalyst.
[l] PS-TsDPEN-Ru without nanoporosity was used as catalyst.

To understand the high activities in this work, the dependences of acetophenone conversion on reaction time over heterogeneous PCP-TsDPEN-Ru and homogeneous TsDPEN-Ru catalysts are compared, as shown in Fig. 5A. Notably, when the reaction time is less than 30 min, both catalysts exhibit similar reaction rate. However, when the reaction time is over 40 min, PCP-TsDPEN-Ru catalyst shows much higher reaction rate than TsDPEN-Ru catalyst. The PCP-TsDPEN-Ru catalyst gives the conversion at 97% for 70 min, while TsDPEN-Ru catalyst shows the conversion at only 81% for 90 min (entry 5, Table 1). To explain this phenomenon, the percentage of the reactant (acetophenone) and product (1-phenyl-ethanol) in the catalyst and water has been measured, and the results (Fig. 5B) show that the heterogeneous catalyst of PCP-TsDPEN-Ru has a strong ability for enrichment of reactant in the catalyst and transfer of product from the catalyst to water phase. This phenomenon is obviously related to the superhydrophobicity of the catalyst. The adsorption of acetophenone on the superhydrophobic catalyst is much easier than that of 1-phenyl-ethanol, in good agreement with that the wettability of acetophenone into PCP-TsDPEN-Ru is much better than that of 1-phenyl-ethanol (Fig. 3C and D). In this case, when the reaction time is over 40 min, about 60% acetophenone is converted, but the residual reactant (>80%) is still enriched in the catalyst, and a large amount of product (>90%) are transferred from the catalyst to the water phase (Fig. 5B). This feature leads to very high activity in ATH over PCP-TsDPEN-Ru catalyst. The phenomena of reactant enrichment in the catalysts such as carbon nanotube [7b,c], amphiphilic polymer-based catalyst [7d,e], and superhydrophobic catalysts [7a], have been reported, which plays an important role for enhancing catalytic activities.

Very interestingly, when the mixed solvent of water and DMF is used, the conversion is very low at only 52% (entry 6, Table 1). This result is well interpreted by the absence of the product transfer from the catalyst to water solution. Notably, catalyst recyclability is very important for practical applications. As observed in Table 1 (entries 7 and 8) and Table S3, even recycling for 14 times, the conversion and *ee* value still remained at 94 and 92.9%, respectively. The leaching of the catalyst is not detected by ICP-MS analysis. These results indicate that the PCP-TsDPEN-Ru is a very efficient and recyclable catalyst in ATH reactions using water as solvent.

Encouraged by superior performance in ATH of acetophenone, other ketones have been intensively expended. Table 1 also presents the catalytic data in ATH of electron-rich and electron-deficient aromatic ketones over the mesoporous superhydrophobic PCP-TsDPEN-Ru catalyst (entries 9—14). The results show that various ketones are efficiently converted into chiral alcohols with high *ee* values (92.8—98.4%) using HCOONa as the reductant and water as the solvent. The substitution position of the ketones has

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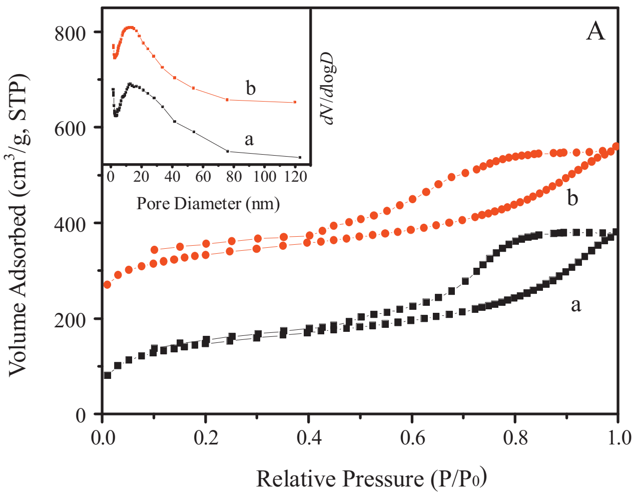

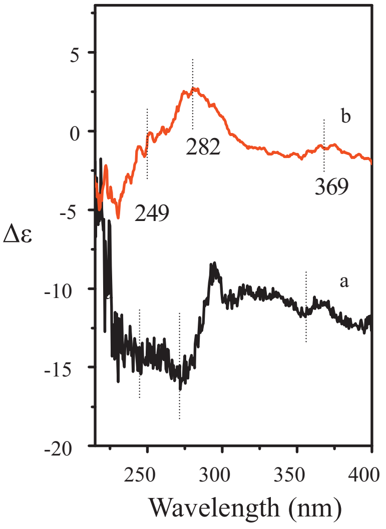

Figure 4 CD spectra of (a) PCP-(*R*)-TsDPEN and (b) PCP-(*S*)-TsDPEN.

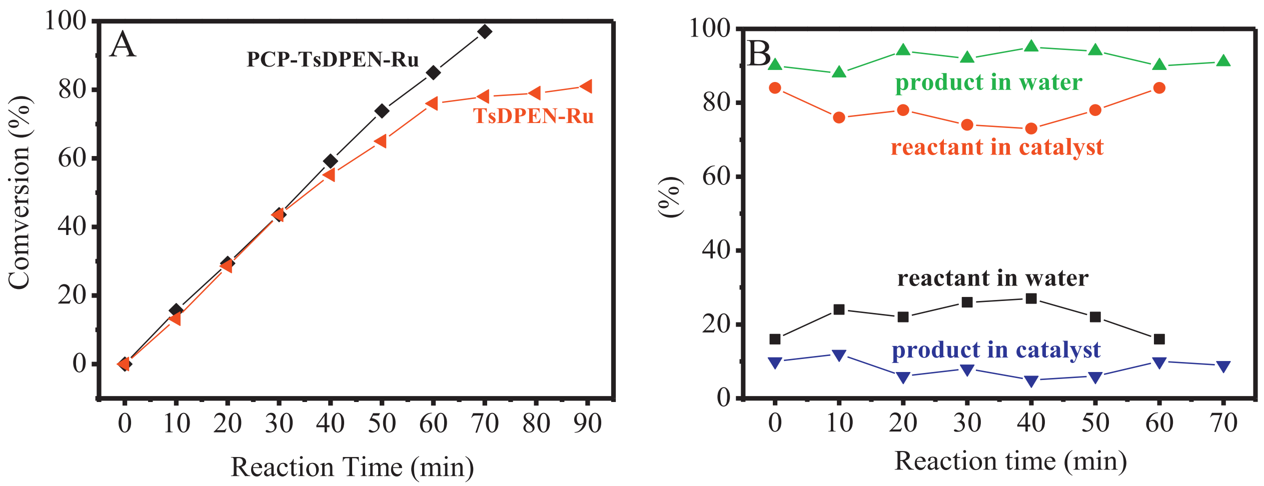

Figure 5 (A) ATH catalytic kinetics over PCP-TsDPEN-Ru and TsDPEN-Ru catalysts; (B) percentage of ATH reactant and product in PCP-TsDPEN-Ru catalyst and water at various reaction time. Reaction conditions: acetophenone (0.5 mmol), HCOONa (2.5 mmol), H_2O (5 mL), S/C = 100, N2, 40 °C.

no significant influence on the reaction time for obtaining high conversion (entries 9—14, Table 1). The solid reactant of 4-bromoacetophenone (melting point 48—53 °C) can be also reduced to corresponding chiral alcohol (entry 14, Table 1) with high activity and *ee* value, although a longer time is needed, compared with liquid reactant of 4-chloroacetophenone (entry 13, Table 1). Notably, when the substrate with hydrophilic hydroxyl group (*o*-acetylphenol) was used, the heterogeneous PCP-TsDPEN-Ru gives similar activity to the homogeneous TsDPEN-Ru, which indicates that the PCP-TsDPEN-Ru is favorable for the hydrophobic substrates (Table S3).

Conclusion

In summary, TsDPEN-functionalized copolymers (PCP-TsDPEN) with the features of superhydrophobicity, high surface area, large pore volume, abundant mesoporosity, good thermal stability, and obvious chirality have been successfully synthesized from a copolymerization of divinylbenzene with V-TsDPEN ligands. After coordination of Ru species, the PCP-TsDPEN-Ru catalysts show superior performance in ATH reactions using water as green solvent. The enrichment of the reactant in the catalyst and the product transfer from the catalyst to the water phase in the reaction system would be responsible for the superior catalytic performance. This feature should be potentially important for designing and preparing novel catalysts for organic synthesis in the future.

Experimental

Catalysts preparation

Synthesis of p-styrenesulfonyl chloride

p-styrenesulfonyl chloride was synthesized according to the literature [10]. As a typical run, 15 g of sodium *p*-styrenesulfonate was dissolved in 80 mL of anhydrous DMF (dried over CaH_2) under N_2 and cooled to 0 °C, followed by addition of 30 mL of $SOCl_2$. After stirred at 0 °C for 30 min, the mixture was stirred at room temperature for another hour, and then poured into ice. The resulting aqueous layer was extracted with diethyl ether. Finally, the collected organic phase was combined, dried over $MgSO_4$ and evaporated to obtain a light yellow liquid, which was *p*-styrenesulfonyl chloride.

Synthesis of (1R, 2R)-N-p-styrenesulfonyl-1,2-diphenylethylenediamine

(1*R*, 2*R*)-N-*p*-styrenesulfonyl-1,2-diphenylethylenediamine was synthesized as follows: 1 g of (1*R*, 2*R*)-1,2-diphenylethylenediamine (4.71 mmol) was dissolved in 20 mL of CH_2Cl_2 in the presence of excessive of triethylamine and cooled to 0 °C, followed by the slow addition of 5 mL of CH_2Cl_2 solution containing 1 g of *p*-styrenesulfonyl chloride (4.78 mmol), and stirred at room temperature overnight. The solution was washed with 5% NaOH aqueous solution, dried with $MgSO_4$, and evaporated under vacuum to remove the solvent. The obtained solid was dissolved in diethyl ether, followed by the addition of 1 mL of concentrated HCl (37 wt%). The formed white precipitated was filtrated, treated with 5% NaOH aqueous, and then extracted with CH_2Cl_2 for 3 times. The combined organic phase was washed thoroughly with brine and dried over with $MgSO_4$. The solvent was removed under vacuum and 1.28 g of light yellow solid (72% yield) was obtained, which was denoted as V-TsDPEN [11]. ^{1}H NMR (400 MHz, DMSO-d6, 298 K, TMS): δ 6.64–7.38 (m, 14H), 6.64–6.67 (m, 1H), 5.87 (d, 1H, *J* = 16.8 Hz), 5.35 (d, 1H, *J* = 11.2 Hz), 4.33 (d, 1H, *J* = 7.2 Hz), 3.95 (d, 1H, *J* = 6.6 Hz) ppm.

(1*S*, 2*S*)-N-p-styrenesulfonyl-1,2-diphenylethylenediamine was synthesized as the same method except that (1*S*, 2*S*)-1,2-diphenylethylenediamine was used.

Synthesis of PCP-TsDPEN with various amount of V-TsDPEN (PCP-*x*-TsDPEN)

PCP-*x*-TsDPEN (*x* stands for the mass ratios of V-TsDPEN to divinylbenzene) was synthesized *via* solvothermal synthesis according to the literature [12]. As a typical run, 2 g of divinylbenzene and 0.25 g of V-TsDPEN were dissolved in 20 mL of DMF, followed by addition of 0.05 g of azobisisobutyronitrile (AIBN). After stirring for 3 h at room temperature, the mixture was transferred into an autoclave at 100 °C for 24 h. After extraction of solvent with ethanol, a light yellow solid product was obtained, which was designated as PCP-1/8-TsDPEN.

Synthesis of PS-TsDPEN

PS-TsDPEN was synthesized as follows: 0.95 g of styrene, 0.05 g of divinylbenzene, and 0.125 g of V-TsDPEN were dissolved in 1 mL of DMF, followed by addition of 0.02 g of azobisisobutyronitrile (AIBN). After heating at 80 °C for 36 h, a light yellow solid product was obtained and denoted as PS-1/8-TsDPEN (abbreviation: PCP-TsDPEN).

Synthesis of PCP-TsDPEN-Ru catalyst

PCP-TsDPEN-Ru was synthesized as follows: In a typical run, 1 g of PCP-TsDPEN was dried at 80 °C under vacuum for 6 h before a certain amount of $[RuCl_2(p\text{-cymene})]_2$ and CH_2Cl_2 was added. The mixture was stirred at 40 °C under N_2 for 2 h, filtered off and washed with excess of CH_2Cl_2 in order to remove physical adsorbed Ru species. The catalyst was dried at room temperature under vacuum.

Characterization

Nitrogen sorption isotherms at the temperature of liquid nitrogen were measured using Micromeritics ASAP 3020M and Tristar system. The samples were outgassed for 10 h at 100 °C before the measurements. ICP analysis was measured with a Perkin-Elmer plasma 40 emission spectrometer. ^{1}H NMR spectra were recorded on a Bruker Avance-400 (400 MHz) spectrometer. Chemical shifts are expressed in ppm downfield from TMS at δ = 0 ppm, and J values are given in Hz. Diffuse reflectance ultraviolet–visible (UV–vis) spectra were measured with spectrometer of PE Lambda 20, and $BaSO_4$ was an internal standard sample. CD spectra were performed on MOS-450. XPS spectra were performed on a Thermo ESCALAB 250 with Al Kα irradiation at $\theta = 90°$ for X-ray sources, and the binding energies were calibrated using the C1s peak at 284.9 eV. FTIR spectra were performed on IFS 66 V (Bruker) IR spectrometer in the range 400–4000 cm^{-1}. Scanning electron microscope (SEM) images were performed using a Hitachi SU 1510. Transmission electron microscope (TEM) images were performed using Hitachi HT-7700. Contact angles of water and organic compunds were measured on a contact angle measuring system SL200KB (USA KNO Industry Co.), equipped with a CCD camera. The static contact angles were measured in sessile drop mode.

Catalytic tests

In the asymmetric transfer hydrogenation of aromatic ketones, all reactions were carried out under a nitrogen atmosphere by using standard Schlenk-type techniques. As a typical run, a desired amount of PCP-TsDPEN-Ru, $HCOONa \cdot 2H_2O$ (2.5 mmol) and ketones (0.5 mmol, S/C = 100) were added into degassed water (5 mL) in a Schlenk tube and the mixture was stirred at 40 °C for a desired time. After the reaction, the mixture was extracted with ethyl acetate and catalyst was taken out from the system by centrifugation and the liquid was passed through a short column before analyzed by gas chromatography (GC-1690 Kexiao Co. equipped with a flame ionization detector and a Supelco γ-DEX 225 capillary column). Dodecane was added as internal standard.

The recyclability of PCP-TsDPEN-Ru was studied using acetophenone as substrate. For recycling the catalyst, the catalyst was separated by centrifugation, washed with water (5 mL × 5 mL), then another portion of acetophenone (0.5 mmol), $HCOONa \cdot 2H_2O$ (2.5 mmol) and degassed H_2O (5 mL) were added. The reactions were conducted at 40 °C for 1.5 h.

Acknowledgements

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.nantod.2013.07.002.

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