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Mesoporous cross-linked polymer copolymerized with chiral BINAP ligand coordinated to a ruthenium species as an efficient heterogeneous catalyst for asymmetric hydrogenation†

Qi Sun,[a] Xiangju Meng,*[a] Xiao Liu,[b] Xiaoming Zhang,[b] Yan Yang,[b] Qihua Yang*[b] and Feng-Shou Xiao*[a]

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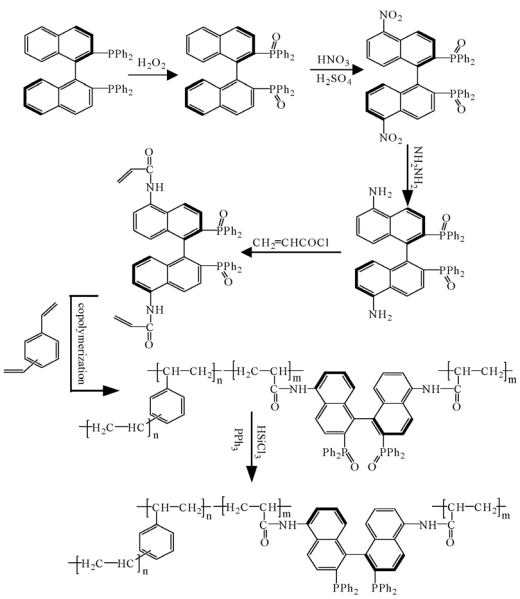
We report here a successful preparation of a heterogeneous chiral catalyst from copolymerization of mesoporous cross-linked polymer with chiral BINAP ligands, followed by coordination of the BINAP with a ruthenium species, which exhibits high activity, excellent enantioselectivity, and extraordinary recyclability in asymmetric hydrogenation.

Porous materials have undergone revolutionary growth in the past decade because of their vital importance in many applications such as catalysis, gas separation, and gas storage.[1] As a typical example, metal–organic-frameworks (MOFs) with unprecedentedly high porosity have been designed and evaluated for a host of applications including gas separation and storage, catalysis and biomedical applications.[2] Inspired by the advances in MOF design, framework materials with more robust linkages such as covalent-organic frameworks (COFs) and porous cross-linked polymers (PCPs) have recently emerged.[3–5] Compared with their MOF counterparts, PCPs show potential advantages over MOFs as heterogeneous catalysts because of their enhanced stability, which greatly facilitates their recovery and reuse. As a result, PCPs can be used as an ideal platform for incorporating molecular catalytic modules into highly stable and recyclable heterogeneous catalyst systems by taking advantage of their permanent porosity and the ability to tune their compositions and properties at the molecular level.[4,5] It is worth noting that most of the research is focused on microporous chiral PCPs, but syntheses of mesoporous chiral PCPs are still scarce.[5] Normally, relatively small micropores influence mass transfer, which limits asymmetric catalytic performance. In addition, relatively bulky reactants make contact with active sites in such small micropores difficult.[1] To solve this problem, the synthesis of mesoporous or macroporous chiral PCPs is strongly desirable.

More recently, a series of unique and stable nanoporous PCPs with superhydrophobicity, hierarchical mesoporosity, high surface area, large pore volume, and extraordinary adsorption capacity for organic compounds has been reported.[6] Herein, we report an alternative route for the preparation of chiral mesoporous PCPs by successful copolymerization of divinylbenzene (DVB) with chiral BINAP [2,2′-bis(diphenylphosphino)-1,1′-binaphthyl] ligands (PCP-BINAP), one of the most important and efficient ligands in asymmetric reactions.[7] The synthesis of PCP-BINAP was begun from 5,5′-diacryloylamino BINAP dioxide, which was synthesized from oxidation of BINAP with H_2O_2, nitration with nitric acid, reduction with hydrazine monohydrate, and acylation with acryloyl chloride. After copolymerization with DVB and reduction with $HSiCl_3$, PCP-BINAP was finally obtained, as illustrated in Scheme 1. Interestingly, PCP-BINAP is porous and insoluble, having a large surface area and good swelling properties (Fig. S1, ESI†), which is quite different from conventional polymer-supported



Scheme 1 Synthesis of the porous and insoluble polymer of (*R*)-BINAP as the backbone (PCP-BINAP).

[a] *Department of Chemistry, Zhejiang University, Hangzhou 310028, China. E-mail: mengxj@zju.edu.cn, fsxiao@zju.edu.cn; Fax: +86 431-8516-8624; Tel: +86 431-8516-8590*
[b] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Dalian 116023, P.R. China*

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BINAP catalysts with soluble features.[8] After loading the ruthenium species, the heterogeneous chiral catalysts exhibited superior catalytic performance in asymmetric hydrogenation.

Fig. 1A shows N_2 isotherms of PCP-BINAPO and PCP-BINAP samples, exhibiting typical type-IV isotherms with a hysteresis loop at 0.60–0.95, which indicates the presence of mesoporosity in the samples. Correspondingly, pore sizes are mainly distributed around 10–30 nm (Fig. S2 and S3, ESI†). Their BET surface areas and pore volumes are very similar, at 524–585 $m^2\ g^{-1}$ and 0.63–0.65 $cm^3\ g^{-1}$ (Tables S1 and S2, ESI†). Fig. 1B shows a scanning electron microscope (SEM) image of the PCP-BINAP sample, giving direct evidence of abundant mesoporosity (10–30 nm, Fig. S4, ESI†), in good agreement with the results of N_2 sorption isotherms.

Fig. 1C shows the ^{13}C magic angle spinning (MAS) NMR spectrum of PCP-BINAPO, giving a broad peak at 135 ppm assigned to the carbon connected to heteroatoms (P or N) and a very weak peak at 175 ppm assigned to carbonyl groups, which suggest the successful copolymerization of BINAPO with DVB.[9] Fig. 1D shows the ^{31}P MAS NMR spectra of PCP-BINAP and PCP-BINAPO samples. The strong signals confirm the presence of the element P in the samples, which is consistent with its mapping (Fig. S5, ESI†). In addition, PCP-BINAPO exhibits a broad peak centered at about 29.7 ppm assigned to phosphorus of phosphine oxide,[10] while PCP-BINAP gives the signal at −16.5 ppm assigned to the unprotected phosphine. These results indicate the successful transformation from BINAPO to BINAP groups in the sample. Fig. 1E shows IR spectra of PCP-BINAPO and PDVB samples. Compared with PDVB, PCP-BINAPO shows additional new bands at *ca.* 1111, 1201, and 1680 cm^{-1}, which are attributed to P═O, C–N, and C═O, respectively.[11] These results further demonstrate the successful functionalization of BINAPO groups in the sample.

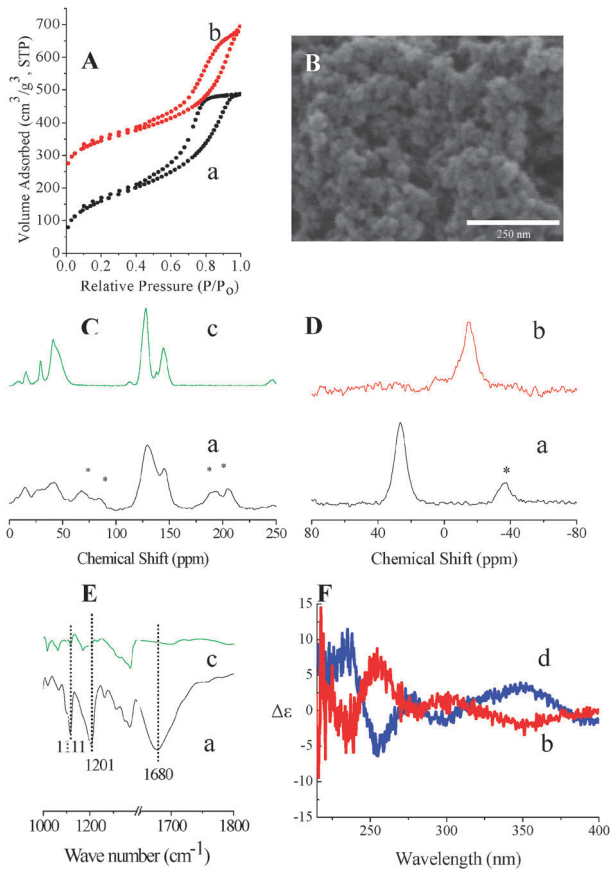


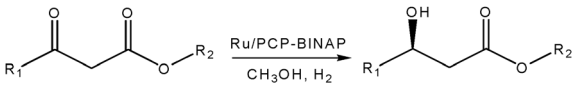
Fig. 1 (A) N_2 isotherms, (B) SEM image, (C) ^{13}C MAS NMR, (D) ^{31}P MAS NMR, (E) IR spectra, and (F) CD spectra of (a) PCP-BINAPO, (b) PCP-(*R*)-BINAP (abbreviation: PCP-BINAP), (c) PDVB, (d) PCP-(*S*)-BINAP. *Side bands. (Line b in A has been offset by 200 $cm^3\ g^{-1}$ along the vertical axis for clarity).

To determine the chirality of the PCP-BINAP sample, the enantiomers of BINAP were used as starting materials. As a result, both PCP-(*S*)-BINAP and PCP-(*R*)-BINAP were obtained. Fig. 1F shows (circular dichroism) CD spectra of PCP-(*S*)-BINAP and PCP-(*R*)-BINAP samples. As expected, both show mirror signals at *ca.* 240, 275 and 335 nm. In addition, UV-visible spectroscopy shows that the PCP-BINAP sample has adsorption peaks at 240, 275 and 335 nm (Fig. S6, ESI†), suggesting that the mirror CD peaks associated PCP-(*S*)-BINAP and PCP-(*R*)-BINAP are not artificial (Fig. S7 and S8, ESI†).[12] As observed from the N_2 sorption isotherm, SEM image, NMR, IR, and CD results (Fig. 1), it is concluded that mesoporous chiral PCP-BINAP was successfully synthesised.

To evaluate the efficiency of the mesoporous PCP-BINAP with chiral BINAP ligands, the asymmetric hydrogenation of methyl methacrylate as a model was chosen. Notably, the ruthenium species $[RuCl_2(benzene)]_2$ was effectively coordinated with PCP-BINAP in methanol at room temperature for 2 h, as evidenced by an obvious shift in UV-visible spectra between PCP-BINAP and Ru/PCP-BINAP (Fig. S9, ESI†). Interestingly, a number of different β-keto esters could be completely converted into the corresponding chiral alcohols on Ru/PCP-BINAP with very high enantioselectivity in the range of 94–99% under a very high S/C (substrate/catalyst) ratio of 2000 (Table 1, entries 1–8). For example, in the hydrogenation of methyl acetoacetate, the catalyst shows a full conversion with 94.6% *ee* (entry 1). Moreover, even if the S/C ratio was increased to 5000, methyl acetoacetate could still be completely transformed into methyl-3-hydroxybutyrate with 90.1% *ee* (entry 10). Heterogeneous asymmetric catalysts with such high enantioselectivities at very high S/C ratios (*e.g.* 5000) have not been reported yet.[10,14] The high enantioselectivity could be attributed to the following unique features of the catalyst: (1) chiral BINAP ligands are incorporated into the polymer backbones rather than grafted onto the surface of the supports, which offers a more uniform distribution for catalytically active sites;[13] (2) the ruthenium species could be effectively coordinated with chiral BINAP ligands in the PCP-BINAP sample, which is quite similar to the case in homogeneous catalysts. In contrast, the hydroxyl groups in silica-based heterogeneous catalysts strongly influence the coordination of ruthenium species with BINAP ligands.[10] Moreover, the effect of various parameters (*e.g.* Ru/BINAP molar ratio, the amount of solvent, H_2 pressure and S/C ratio) on *ee* values have been systemically investigated (Fig. S10–S13, ESI†).

Furthermore, it is observed that Ru/PCP-BINAP has extraordinary recyclability in the hydrogenation of methyl acetoacetate (Table S3, Fig. S14, ESI†). Very importantly, the Ru/PCP-BINAP catalyst is not only limited to the use of asymmetric hydrogenation of β-keto esters. Other reactions, such as asymmetric isomerization, transfer hydrogenation of ketones, and hydrogenation of olefins, could be also applied.[7,14]

Table 1 Asymmetric hydrogenation of β-keto esters catalyzed by Ru/PCP-BINAP catalyst[a]



Entry	R	S/C [b]	Conv.[c] (%)	Sel.[c] (%)	*ee*[c] (%)
1	$R_1 = R_2 = Me$	2000	>99.5	>99.5	94.6
2	$R_1 = Me$, $R_2 = Et$	2000	>99.5	>99.5	95.1
3	$R_1 = 4'$-OMe–Ph, $R_2 = Et$	2000	>99.5	>99.5	97.7
4	$R_1 = CH_2Cl$, $R_2 = Me$	2000	>99.5	>99.5	94.3
5	$R_1 = {}^iPr$, $R_2 = Me$	2000	>99.5	>99.5	95.3
6	$R_1 = Me$, $R_2 = PhCH_2$	2000	>99.5	>99.5	95.4
7	$R_1 = Me$, $R_2 = {}^tBu$	2000	>99.5	>99.5	99.0
8	$R_1 = Me$, $R_2 = {}^iPr$	2000	>99.5	>99.5	97.0
9	$R_1 = R_2 = Me$	3000	>99.5	>99.5	91.3
10[d]	$R_1 = R_2 = Me$	5000	>99.5	>99.5	90.1
11[e]	$R_1 = R_2 = Me$	2000	>99.5	>99.5	99.0
12[f]	$R_1 = R_2 = Me$	2000	>99.5	>99.5	94.3
13[g]	$R_1 = R_2 = Me$	2000	>99.5	>99.5	95.3

[a] The reaction was carried out under a hydrogen pressure of 2 MPa in 2.0 mL methanol at 50 °C for 20 h (the use of 0.005 mmol of Ru with BINAP/Ru at 1.01). [b] Molar ratio of substrate to catalyst. [c] Determined by GC on a Supelco γ-DEX 225 capillary column. [d] The use of 2.5 mL of methanol. [e] The use of homogeneous Ru/BINAP catalyst. [f] Reuse. [g] Recycled 6 times.

More importantly, this methodology is not limited to BINAP. Other chiral ligands such as 1,2-diaminocyclohexane and 1,2-diphenylethylenediamine groups (Fig. S15 and S16, ESI†) could also been copolymerized into the mesoporous PCPs as highly efficient heterogeneous chiral catalysts. For example, mesoporous PCP containing chiral 1,2-diphenylethylenediamine coordinated with a ruthenium species gives complete conversion with an *ee* value at 94% in asymmetric transfer hydrogenation of 1-phenyl-ethanone using water as a green solvent. This method might open a door for designing and preparing highly efficient heterogeneous chiral catalysts in the future.

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