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Introduction

Clearfield first prepared and elucidated the layered Zr- $(HPO_4)_2 \cdot H_2O (\alpha - ZrP)^1$ and $Zr(PO_4)(H_2PO_4) \cdot H_2O (\gamma - ZrP)$ ² Subsequently, α - and γ -structured inorganic–organic functional derivatives with different dimensionalities or solubilities,³ ranging from single, linear chains, or layered compounds to open-framework structures, have been extensively studied because of their high structural flexibility and applications in various fields such as adsorption,⁴ membranes,⁵ catalysis,⁶ biotechnologies,⁷ and photochemistry.⁸ Among these compounds, pillared zirconium phosphonates with high and rigid porous structures have received increasing interest during the past decade because of their special physical and chemical properties.9 Generally, pillared zirconium phosphonates are

Anchored [RuCl₂(p-cymene)]₂ in hybrid zirconium phosphate-phosphonate coated and pillared with double-stranded hydrophobic linear polystyrene as heterogeneous catalyst suitable for aqueous asymmetric transfer hydrogenation⁺

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A novel type of phosphonate-containing polystyrene copolymers **1a-e** bearing an N'-alkylated TsDPEN chiral ligand and double-stranded polystyrene chains were prepared for the first time using simple radical copolymerization of 1-phosphonate styrene with (R,R)-N'-4'-vinylbenzyl-N-4-vinylbenzenesulfonyl-1,2diphenylethylene-1,2-diamine. Through the coprecipitation of their supported Ru polystyrene copolymers 2a-e and NaH₂PO₄ with ZrOCl₂, pillared hybrid zirconium phosphate-phosphonate-anchored Ru catalysts 3a-e and $4d_1-d_5$ were obtained as heterogeneous catalysts suitable for aqueous asymmetric transfer hydrogenation. In the aqueous asymmetric transfer hydrogenation of aromatic ketones, the anchored Ru catalysts showed good catalytic activities, chemoselectivities (~100%), and enantioselectivities (73.6% ee to 95.6% ee). The Ru catalysts retained their catalytic properties even at the fifth recycle time (92.2% conv., 92.1% ee). However, corresponding supported Ru catalyst 3d' resulted in disappointing reusability because of the loss of ruthenium in every recycle process. The conversions of aromatic ketones were closely related to the o-, m- or p-positions of the substituents on the aromatic ring caused by shape-selective matching.

> prepared by two different approaches, namely, the coprecipitation of bisphosphonic acid $(H_2O_3P-R-PO_3H_2, R = organic$ group) with Zr⁴⁺ ion and the direct topotactic exchange reaction with a previously formed α -ZrP matrix.¹⁰

> In the field of heterogeneous catalysis, the tailored and pillared cavity, which provides spatial channels for reactants to freely access the inner catalytic sites, is an important, favorable, and essential property. However, the movement of reactants inside the pores is greatly influenced by the interaction between the reactant and the internal wall of the channel as a result of their different polarities. This factor was not given much attention. The majority of the reactants and products in catalytic processes are usually medium- to non-polar. However, the pores constructed by inorganic frames, such as hybrid zirconium phosphate-phosphonate with O3POH moieties, are highly polar. Therefore, modifying the polarity of internal channels constructed by the inorganic frame is necessary to obtain a similar affinity between the channel wall and the reactant to favor the mass transfer of reactants and products inside the pores. Thus, we designed pillared and porous materials, as well as modified the polarity of the inner walls, to achieve better access of reactants to catalytic sites inside inorganic porous backbones.

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[†]Electronic supplementary information (ESI) available: ¹H NMR and ¹³C NMR of monomer 1; GPC spectra; the thermogravimetric curves; IR spectra; SEM images; HRTEM images; the isotherms and distributions of pore diameter; GC spectra. See DOI: 10.1039/c3dt33015j



Scheme 1 The route to Ru catalyst encapsulated in double-stranded polystyrene-pillared hybrid zirconium phosphate-phosphonate.

In this paper, we incorporated the following features to prepare a novel type of double-stranded poly(styrene-1-phosphonate styrene)-pillared hybrid zirconium phosphate–phosphonate suitable for aqueous hydrogenation (Scheme 1): (1) *N'*-alkylated TsDPEN chiral ligand with good complexation for metal ions, such as Ru^{2+} ; (2) inorganic Zr layers coated with double-stranded hydrophobic linear polystyrene pillared by *N'*alkylated TsDPEN to favorably obtain access of substrates to catalytic sites; (3) covalent immobilization of chiral *N'*-alkylated TsDPEN to the Zr layer through anchor points (–PO₃H₂); and (4) encapsulation of supported Ru copolymer by molding hybrid zirconium phosphate–phosphonate to overcome loss of Ru metal by leaching.

Experimental

Materials and sample characterization

All chemicals were purchased and used without further purification. Fourier transform infrared spectra were recorded on a Perkin-Elmer Model GX Spectrometer using the KBr pellet method with polystyrene as a standard. Thermogravimetric analysis (TGA) was performed on an SBTQ600 thermal analyzer (USA) with a heating rate of 20 °C min⁻¹ from 40 °C to 800 °C under flowing compressed N₂ (100 mL min⁻¹). ¹H, ¹³C, and ³¹P NMR were performed on a Bruker AV-300 NMR instrument at 300.1, 75.0, and 121.5 MHz respectively, in which all chemical shifts were reported downfield in ppm relative to the H, C, and P resonances of TMS, chloroform-d₁, and H₃PO₄ (85%), respectively. The morphologies of the assynthesized samples were determined by a Hitachi model H-800 transmission electron microscope (TEM) and a Tecnai G2 F20 (HRTEM) operated at 200 kV. N2 adsorption-desorption analysis was conducted at 77 K on an Autosorb-1 apparatus (Quantachrome). The specific surface areas and pore diameters were calculated by the BET and BJH models, respectively. C, H, N, O, and S elemental analyses were obtained from a FLASHEA1112 automatic elemental analyzer instrument (Italy). Gel permeation chromatography (GPC) was performed using a 515 HPCC pump and a Waters styragel HT4 DMF column (M_w 5000 to 600 000) with a 2414 refractive index detector from Waters. Experiments were performed at 35 °C using THF as eluent and a flow rate of 0.7 mL min⁻¹. Molecular weights were reported versus monodispersed polysaccharide standard. The enantiomeric excess (% ee) was determined on GC with a Chiral Cyclodex-B column (30 m × 0.25 nm \times 0.25 μ m, Supelco) at 100 °C for 5 min and 5 °C min⁻¹; and then at 140 °C for 15 min. The retention times of (R) or (S)-1-phenylethanol were $t_R = 8.95$ min and $t_S =$ 9.26 min, respectively. X-ray photoelectron spectroscopy measurements were performed on a Physical Electronics ESCA 5701 instrument, equipped with a multichannel detector and a hemispherical analyzer. Mg K α radiation ($h\nu$ = 1253.6 eV) was used as the excitation source and the instrument was operated at a constant power of 300 W (15 kV, 20 mA). The data were acquired at a take-off angle of 45° and a pass energy of 29.35 eV. The pressure in the analysis chamber was maintained at 8 \times 10⁻⁷ Pa. Charge compensation was conducted with the adventitious C 1s peak at 284.8 eV.

Synthesis of monomer 1: (*R*,*R*)-*N*'-4'-vinylbenzyl-*N*-4-vinylbenzenesulfonyl-1,2-diphenylethylene-1,2-diamine

A dried flask (250 mL) containing K_2CO_3 (2.1 g, 15.0 mmol) and (*R*,*R*)-*N*-4-vinylbenzenesulfonyl-1,2-diphenylethylene-1,2diamine (3.8 g, 10.0 mmol) was flushed thrice with Ar atmosphere. Anhydrous acetonitrile (50 mL) was added from a syringe and stirred at 25 °C until the reaction mixture was completely dissolved. Then, 30 mL of 4-vinylbenzyl chloride (1.5 g, 10.0 mmol) acetonitrile solution was added and stirred at 60 °C for 24 h. The reaction mixture was evaporated under reduced pressure to obtain a yellow solid, purified by flash column chromatography eluted with petroleum ether–chloroform (v/v = 5 : 1) to obtain 3.7 g of white product (76% yield).

$$\begin{split} &\delta_{\rm H} \ (300 \ {\rm MHz}, \ {\rm DMSO-d_6}, \ {\rm Me_4Si}) \ 7.44-6.88 \ (18 \ {\rm H}, \ {\rm m}, \ {\rm Ph-H}), \\ &6.75-6.62 \ (2 \ {\rm H}, \ {\rm m}, \ -{\rm CH}{=}), \ 5.82 \ (2 \ {\rm H}, \ {\rm dd}, \ {}^3J = 19.8, \ 3.0 \ {\rm Hz}, \\ ={\rm CH}_2), \ 5.29 \ (2 \ {\rm H}, \ {\rm dd}, \ {\rm vinyl}, \ {}^3J = 38.9, \ 10.9 \ {\rm Hz}), \ 4.37 \ (1 \ {\rm H}, \ {\rm d}, \ {}^3J \\ = 8.4 \ {\rm Hz}, \ {\rm CHN}), \ 3.78 \ (1 \ {\rm H}, \ {\rm d}, \ {\rm CHN}, \ {}^3J = 8.4 \ {\rm Hz}), \ 3.37 \ (2 \ {\rm H}, \ {\rm s}, \\ {\rm CH}_2). \ \delta_{\rm C} \ (75.0 \ {\rm MHz}, \ {\rm DMSO-d_6}, \ {\rm TMS}) \ 140.6, \ 140.5, \ 140.4, \ 140.2, \\ 139.5, \ 136.7, \ 135.9, \ 135.8, \ 128.5, \ 128.2, \ 127.8, \ 127.7, \ 127.4, \\ 126.9, \ 126.7, \ 126.5, \ 126.3 \ ({\rm Ph}), \ 117.4, \ 114.0 \ ({\rm CH}{=}{\rm CH}_2), \ 67.1, \\ 64.1 \ ({\rm CHN}), \ 50.5 \ ({\rm CH}_2). \ {\rm Anal.} \ {\rm Calcd} \ {\rm for} \ {\rm C}_{31}{\rm H}_{30}{\rm N}_2{\rm O}_2{\rm S}: \ {\rm C}, \ 75.27; \\ {\rm H}, \ 6.11; \ {\rm N}, \ 5.66; \ {\rm O}, \ 6.47; \ {\rm S}, \ 6.48. \ {\rm Found}: \ {\rm C}, \ 75.30; \ {\rm H}, \ 6.14; \ {\rm N}, \\ 5.59; \ {\rm O}, \ 6.53; \ {\rm S}, \ 6.41. \end{split}$$

Synthesis of double-stranded poly(styrene-1-phosphonatestyrene) copolymers 1a–e

A dried flask (25 mL) containing (*R*,*R*)-*N*'-4'-vinylbenzyl-*N*-4-vinylbenzenesulfonyl-1,2-diphenylethylene-1,2-diamine (173.3 mg, 0.35 mmol) was flushed thrice with Ar atmosphere. Then, 5 mL THF was added, and the resulting mixture was stirred for 10 min. Then, 5 mL 1-phosphonate styrene (515.0 mg, 2.8 mmol) and 3 mL benzoyl peroxide (BPO) (20.0 mg, 0.08 mmol) THF solutions were added from a syringe and stirred at 80 °C for 24 h. During the reaction process, the BPO solution (2×20.0 mg) was added at eighthour intervals. The reaction mixture was evaporated under reduced pressure to yield a pale yellow oily liquid. Upon adding 5 mL of ethyl acetate, the white precipitate was filtered off, washed with CH₂Cl₂ (3×5 mL) and acetone (3×5 mL), and dried at 40 °C in a vacuum tank to obtain **1a** (295.6 mg) in 43.0% yield.

The other copolymers (1b-e) were prepared under similar conditions as 1a, with only the molar ratios of styrene to 1-phosphonate styrene changed to 1:4, 1:1, 4:1, and 8:1, respectively. 1b: 339.4 mg, 68.9%; 1c: 322.6 mg, 70.6%; 1d: 371.6 mg, 80.0%; 1e: 141.4 mg, 54.6%.

General synthesis of supported Ru complexes 2a-e

A dried flask (25 mL) containing **1a** (20 mg) and $[RuCl_2-(p-cymene)]_2$ (6.0 mg, 9.8 mmol) was flushed thrice with Ar atmosphere. Then, 2 mL anhydrous acetonitrile and 0.1 mL Et₃N were added and stirred at 82 °C for 6 h. Reddish-brown supported Ru complex **2a** (20.8 mg) in 80.1% yield was obtained by filtering, washing with CH_2Cl_2 (3 × 5 mL) and acetone (3 × 5 mL), and drying at 40 °C under reduced

pressure. The other supported Ru complexes **2b–e** were also prepared in 80.0% to 83.4% yields. The supported Ru contents in **2a–e** were in the range of 3.7 wt% to 4.0 wt% according to ICP determination.

General preparation of anchored Ru catalysts 3a-e and 4d1-d5

2d (70.0 mg), Et₃N aqueous solution (5 mL, 10.0 wt%), and NaH₂PO₄·2H₂O (20.0 mg, 0.13 mmol) were added to a dried flask (25 mL). The medium pH 8 to 9 was adjusted to pH 5 using HCO₂H, and the solids were dissolved. Then, ZrOCl₂·H₂O aqueous solution (70.0 mg, 0.22 mmol) was added dropwise and stirred at room temperature (rt) for 24 h. After the pH was adjusted to 6–7 using Et₃N aqueous solution, the reddish-brown solid was filtered off, washed with distilled water (3 × 15 mL), and ethanol (3 × 15 mL), and dried under reduced pressure at 40 °C to yield anchored Ru catalyst **3d** (98 mg). The other catalysts (**3a–e**) (95 mg to 105 mg) were also prepared in similar yields as **3d**. The anchored Ru contents in **3a–e** were in the range of 1.7 wt% to 2.0 wt%, as determined using the ICP method.

The anchored Ru catalysts $4d_1-d_5$ with 1.0 wt% to 1.2 wt% Ru [4d₁: 113 mg; 4d₂: 108 mg; 4d₃ (3d): 98 mg; 4d₄: 95 mg; 4d₅: 93 mg] were prepared under similar conditions, changing only the amounts of NaH₂PO₄·2H₂O used (4d₁: 10.0 mg, 0.064 mmol; 4d₂: 15.0 mg, 0.096 mmol; 4d₃: 20.0 mg, 0.13 mmol; 4d₄: 25.0 mg, 0.16 mmol; 4d₅: 30.0 mg, 0.192 mmol).

Preparation of supported Ru catalyst 3d'

1d (70.0 mg), Et_3N aqueous solution (5 mL, 10 wt%), and NaH₂PO₄·2H₂O (20.0 mg, 0.13 mmol) were added to a dried flask (25 mL). The reaction mixture at pH 8-9 was adjusted to about pH 5 using HCO₂H, and the solid was found to be dissolved. Then, 5.0 mL ZrOCl₂·H₂O aqueous solution (70.0 mg, 0.22 mmol) was added dropwise and stirred at rt for 24 h. The white solids were filtered off, washed with distilled water (3 \times 15 mL), and dried under reduced pressure at 40 °C to yield pillared hybrid zirconium phosphonate-phosphonate. Then, 100.0 mg of [RuCl₂(*p*-cymene)]₂ (30.0 mg, 49.0 mmol) was added to the obtained solid, which was then flushed thrice with Ar atmosphere and added to 2.0 mL of anhydrous acetonitrile and 0.1 mL of Et₃N, then stirred at 82 °C for 6 h. The reddish-brown supported Ru catalyst 3d' (123.1 mg) in 94.7% yield was filtered off, washed with CH_2Cl_2 (3 × 5 mL) and acetone (3×5 mL), and dried at 40 °C under reduced pressure. The supported Ru content in 3d' with 2.5 Ru wt% was determined by ICP.

General procedure for aqueous asymmetric transfer hydrogenation

Anchored Ru catalyst **3d** (1.7 wt%, 15.0 mg, 2.5×10^{-3} mmol), 0.4 mL HCO₂H–Et₃N v/v = 1/3, 1.5 mL water, and 0.1 mL acetophenone (102.8 mg, 0.86 mmol) were mixed in a dried flask (25 mL). The reaction mixture was well dispersed by stirring for 10 min, after which it was heated to 50 °C and stirred for another 10 h. The reaction residue was combined with 5 mL

ethyl acetate and centrifuged. Then, catalyst **3d** was recovered in quantitative yield. The conversion, chemoselectivity of acetophenone, and enantioselectivity of (R) or (S)-1-phenylethanol in the upper organic phase were directly determined by GC. The upper organic phase was concentrated under reduced pressure, and the crude residues were purified by flash column chromatography to obtain pure 1-phenylethanol.

Results and discussion

Synthesis and characterization of double-stranded poly(styrene-1-phosphonatestyrene) copolymer

Double-stranded poly(styrene-1-phosphonatestyrene) copolymer with functional phosphonate group ($-PO_3H_2$) and *N'*-alkylated TsDPEN chiral ligand was utilized to build a chemical and spatial microenvironment suitable for the catalytic process. The phosphonate ($-PO_3H_2$) played a crucial role in anchoring poly(styrene-1-phosphonatestyrene) to the framework of hybrid zirconium phosphate–phosphonate by the coprecipitation of $-PO_3H_2$ and NaH_2PO_4 with $ZrOCl_2$. *N'*-Alkylated TsDPEN had a good coordination of $[Ru(p-cymene)Cl_2]_2$ by the imino group (-NH-). The double-stranded copolymers **1a–e** bearing different amounts of anchor points ($-PO_3H_2$) and *N'*-alkylated TsDPEN chiral ligands were prepared by simple radical copolymerization in THF at 80 °C for 24 h in the presence of BPO as radical initiator.¹¹

The chemical structures and compositions of copolymers **1a–e** could be elucidated by ³¹P NMR spectra. Aside from the ³¹P NMR data of poly(1-phosphonate styrene) at 12.5 (q), 5.1 (s), 1.0 (s) and 0.0 ppm (s), the new and wide ³¹P NMR peaks for copolymers **1a–e** emerged in the range of δ 20 to 30 ppm, which resulted from the ³¹P absorption of chain segments copolymerized by monomer **1** with 1-phosphonatestyrene (Fig. 1-a). The chemical compositions of copolymers **1a–e** with



Fig. 1 The ³¹P NMR and GPC spectra of copolymer 1c

m/n = 1.2, 1.5, 1.8, 3.6, 6.8 were determined by the comparative quantitative ³¹P NMR investigation of **1a–c** and **1a–c** + 85% H₃PO₄ samples, according to eqn (1)–(3) (Fig. 1-b). Based on the quantitative principle of the ³¹P NMR, the peak area is directly proportional to the number of phosphorus atoms. The phosphorus mass in copolymers **1a–e** (m_2) could be calculated according to eqn (1):

$$\frac{S_{\rm p}}{S_{\rm s}} = \frac{\frac{m_1 \times 85.2\%}{M_{\rm H_3 PO_4}}}{\frac{m_2}{M_{\rm p}}} \tag{1}$$

where S_p is the peak area of added H₃PO₄, S_s denotes the total areas of peaks, m_1 denotes the added mass of H₃PO₄, $M_{H_3PO_4}$ is the molar mass of H₃PO₄, and M_p is the molar mass of phosphorus.

Then, *m* and *n* values can be calculated as follows:

$$m = \frac{m_3 - \frac{m_2}{M_{\rm p}} \times M_2}{M_1} \tag{2}$$

$$n = \frac{m_2}{M_{\rm p}} \tag{3}$$

where m_3 is the mass of the sample, M_1 is the molar mass of monomer 1, and M_2 is the molar mass of monomer 2.

The GPC analysis (Fig. 1-c) shows that the weight-average molecular weights (M_w) of **1a–e** were 974.1, 937.4, 883.7, 883.0, and 759.5 kDa, respectively. Narrow polydispersity index (PDI) values between 1.05 and 1.28 were also found. However, these data might be inaccurate since monodisperse polysaccharide standards were used for calibration while the double-stranded copolymers **1a–e** were cross-linked and brushed. The M_w and PDI values of **1a–e** decreased and increased, respectively with increased m/n ratio from 1.2 to 6.8. Relatively narrow PDIs (1.08 to 1.03) were also found for **1a–d** at $m/n \leq 3.6$. Furthermore, from IR spectra, the stretching vibrations of N–H at 3358 cm⁻¹, Ph–H at 3060, 3029 cm⁻¹, C=C at 1631, 1597, 1510 cm⁻¹ and $-PO_3H_2$ at 1091, 1059 cm⁻¹ illustrated that *N*-alkylated TsDPEN ligands were covalently attached to the framework of double-stranded copolymers **1a–e**.

Using **1d** as an example, the porous structure, thermal stability and surface morphology were further characterized by nitrogen adsorption–adsorption isotherm, TGA, SEM, and AFM (Fig. 2). From the TG curves, the thermal decomposition of **1d** occurred in two steps: first, the weight loss of 3.3% between 50 °C and 200 °C corresponded to the surface-bound or intercalated water absorbed in the pores; second, the total weight loss of 62.4% between 200 °C and 800 °C corresponded to the decomposition of organic fragments. The nitrogen adsorption– desorption isotherm, performed at 77 K, was linear to the P/P_0 axis at relatively low P/P_0 range (0–0.8) and convex to the P/P_0 axis in the high range of $P/P_0 = 0.8$ –1.0. From the calculated data, the pore size distribution (PSD) suggested the existence of non-uniform micropores (<2 nm) and mesopores (2 nm to 10 nm), having several representative sharp peaks in the range



Fig. 2 TGA, SEM and AFM of double-stranded copolymer 1d.



of about 0.5 nm to 10 nm (Fig. 3). The average pore diameter, pore volume, and surface area of **1d** were 1.0 nm, 0.2×10^{-2} cm³ g⁻¹ and 2.0 m² g⁻¹, respectively. The AFM images showed that the particles were well dispersed in water (1 mg **1d** in 5 mL water) and had 100.8 nm mean diameter and 10.1 nm mean height (Fig. 2). However, loosely accumulated clusters of **1d** (1 µm to 5 µm) were observed by SEM owing to being badly dispersed in ethanol. Therefore, SEM and AFM images could be considered to mirror the surface morphologies of **1d** in solid state and aqueous medium, respectively.

Coordination of [RuCl₂(*p*-cymene)]₂ into poly(styrene-1-phosphonatestyrene) copolymer

In order to shed light on the coordination reaction of Ru^{2+} ions with *N*'-alkylated TsDPEN ligands, double-stranded copolymer **1d** and its supported Ru complex **2d** as a pair of comparative examples were monitored by XPS, N₂ adsorption– desorption analysis and TGA. From XPS spectra, the C1s, O1s, N1s, P2p and S2p binding energies in **1d** were 284.7, 532.1, 401.2, 133.3, and 168.2 eV, respectively. Upon the immobilization of $[RuCl_2(p\text{-cymene})]_2$ into copolymer **1d**, the N1s binding energy decreased from 401.2 to 399.8 with a 1.4 eV decrement. However, there were only 0.1 eV to 0.3 eV changes for the other binding energies. On the other hand, the Ru3p (462.7 eV) and Cl2p (197.8 eV) binding energies with 1.4 At% and 0.6 At% contents were detected in supported Ru complex

2d. Furthermore, as can be seen from nitrogen adsorptiondesorption isotherms (Fig. 3), some sized nanopores below 10 nm in 2d disappeared, and surface area and pore volume decreased from 16.3 m² g⁻¹ and 0.8×10^{-2} cm³ g⁻¹ to 2.0 m² g^{-1} and 0.1×10^{-2} cm³ g⁻¹, respectively, which demonstrated that [RuCl₂(*p*-cymene)]₂ particles occupied those nanopores. Crucially, it was very important that the remaining mesopores in 2d at about 0.5, 1.0, 1.8, and 5.0 nm provided the diffusional channels for substrates to smoothly access the catalytic sites of entrapped $[RuCl_2(p-cymene)]_2$ in the catalytic process. Compared with copolymer 1d, TGA of the corresponding supported Ru complex 2d showed that organic weight loss between 150 °C and 800 °C increased from 62.6 wt% to 77.0 wt%. Therefore, $[RuCl_2(p-cymene)]_2$ species exclusively and successfully complexed with chiral imino (-NH) functional groups in the framework of poly(styrene-1-phosphonatestyrene) copolymers 2a-e.

Anchoring of Ru complex into hybrid zirconium phosphate-phosphonate

Although double-stranded poly(styrene-1-phosphonatestyrene) copolymer had good coordination with $[RuCl_2(p-cymene)]_2$, the Ru(II) ions escaped from the porous backbone of 2a-e owing to the flexibility of the polystyrene chain, especially in the catalytic process. To reduce the loss of Ru(II) ions, 2a-e were further anchored into the rigidly porous backbone of hybrid zirconium phosphate-phosphonate through the easy coprecipitation of mixed NaH₂PO₄ and 2a-e containing phosphonate (-PO₃H₂) with Zr⁴⁺ ions. Two strategies were formulated to encapsulate $[RuCl_2(p-cymene)]_2$ into the porous framework of hybrid zirconium phosphate-phosphonate. The first approach was the coprecipitation of NaH₂PO₄ and 2a-e bearing different amounts (m/n) of anchor points $(-PO_3H_2)$ as precursors with $ZrOCl_2$ at a molar ratio of $Zr^{4+}/H_2PO_4^{-} = 2$ to afford anchored Ru catalysts 3a-e. The second approach was the coprecipitation of different molar ratios of supported Ru copolymer 2d to NaH₂PO₄ with ZrOCl₂ to yield anchored Ru catalysts $4d_1-d_5$. The Ru contents in 3a-e and $4d_1-d_5$ were detected by ICP to be 1.7 wt% to 2.0 wt% and 1.0 wt% to 1.2 wt%, respectively. Their properties were characterized in detail by TGA, IR, SEM, TEM, AFM, and nitrogen adsorptiondesorption isotherms.

Anchoring of 2a–e into hybrid zirconium phosphate–phosphonate. The TG curves (see ESI[†]) show that the 29.0%, 37.7%, 40.3%, 44.4%, and 48.1% weight losses for **3a–e** between 150 °C and 800 °C corresponded to the thermal decomposition of appended organic fragments in the framework of hybrid zirconium phosphate–phosphonate. The amounts of **2a–e** into **3a–e** externally appeared to increase with increasing *m/n* values from 1.2 to 6.8. In fact, *m/n* values in **2a–e** also exemplified the amount of anchor points (–PO₃H₂). The more the *m/n* values were, the fewer anchor points (–PO₃H₂) existed. However, the phosphonate –PO₃H₂ moieties were difficult to thermally decompose below 800 °C. Therefore, the thermal weight losses of **3a–e** increased with the decreasing number of –PO₃H₂ moieties from **3a** to **3e**. On the other hand,



Fig. 4 IR spectra of copolymer-supported Ru 2b and hybrid zirconium phosphonate-anchored Ru catalyst 3d.

4d₁–**d**₅, prepared at various $Zr^{4+}/H_2PO_4^-$ molar ratios, possessed 35.2, 40.6, 44.4, 43.5, and 44.5% total weight losses, respectively over the 150 °C to 800 °C temperature range, implying that similar amounts of **2d** with 40.3% to 44.5% weight losses were found to be immobilized into the framework of hybrid zirconium phosphate–phosphonate at Zr^{4+}/NaH_2PO_4 (molar ratio) < 2.3.

The successful covalent attachment of double-stranded copolymer supported Ru complexes 2a-e onto the inorganic frame of hybrid zirconium phosphate-phosphonates 3a-e and $4d_1-d_5$ was verified by infrared spectroscopy. The characteristic peaks of -Ph and -CH2- moieties in 2a-e could also be observed in the infrared spectra of 3a-e and 4d1-d5. For example, the spectrum of 3d had two main differences compared with that of 2d (Fig. 4). One variation was the stronger absorption bands from 3700 cm^{-1} to 2500 cm^{-1} and 1700 cm⁻¹ to 1500 cm⁻¹ assigned to the O-H stretching vibration of adsorbed waters in 3d. The other variation was the stronger and wider absorption band from 1150 cm⁻¹ to 900 cm⁻¹ caused by the newly formed Zr-O-P stretching vibration through the anchor points $(-PO_3H_2)$ with Zr^{4+} ions. Based on the characteristic peaks of -Ph, -CH₂-, and Zr-O-P moieties in 3d, double-stranded copolymer-supported Ru 2d was covalently attached into the inorganic framework of 3d. Similar infrared spectra to that of 3d were also observed for 4d₁-d₅. However, there were different absorption intensities of Zr-O-P stretching vibration. The smaller the molar ratios of Zr⁴⁺ to NaH₂PO₄ in the preparation, the stronger the absorbing intensities of Zr-O-P stretching vibration were found at 1150 cm^{-1} to 900 cm⁻¹ (see ESI⁺).

The chemical compositions (m/n) of **1a–e** were elucidated by ³¹P NMR to be 1.2, 1.5, 1.8, 3.6, and 6.8, respectively. The higher the m/n values, the fewer phosphonates $(-PO_3H_2)$ were contained in **2a–e**, implying that fewer anchor points $(-PO_3H_2)$ could be utilized to anchor **2a–e** into the frameworks of hybrid zirconium phosphate–phosphonates. Surprisingly, upon encapsulation of **2a–e** with the anchor points $(-PO_3H_2)$, the BET surface areas and pore volumes of **3a–e** and **4d₁–d₅** were found to have sharply increased from 2.0 m² g⁻¹ and 0.1 × 10^{-2} cm³ g⁻¹ to 15.2 m² g⁻¹ and to 52.1 m² g⁻¹, and to 0.8 cm³

Table 1 Porous properties of zirconium phosphonate-anchored Ru catalysts $3a{-}e$ and $4d_1{-}d_5\,^{\rm a}$

Entry		Surface area ^{<i>b</i>} $[m^2 g^{-1}]$	Average pore diameter ^c [Å]	Pore volume ^c [×10 ⁻² cm ³ g ⁻¹]
1	1d	16.3	10.3	0.8
2	2d	2.0	10.2	0.1
3	3a	15.2	10.5	0.8
4	3b	30.3	10.5	1.6
5	3c	31.1	10.9	1.7
6	3d	37.2	11.5	2.1
7	3e	34.6	10.4	1.8
8	$4d_1$	34.1	10.7	2.7
9	$4d_2$	35.0	10.7	2.1
10	$4d_{3}(3d)$	37.2	11.5	2.4
11	$4d_4$	52.1	10.6	2.8
12	$4d_5$	33.4	10.3	1.7

^{*a*} The samples were degassed at 100 °C for 5 h. ^{*b*} Based on multipoint BET method. ^{*c*} Based on the desorption data using BJH method.



Fig. 5 The nitrogen adsorption-desorption isotherms of 3a, b, d and 4d₅.

 g^{-1} and to 2.8×10^{-2} cm³ g^{-1} , as a result of the pillaring of double-stranded copolymers. No significant change in average pore diameters (1.03 nm *vs.* 1.15 nm) was noted (Table 1). The quantity of the anchor points (-PO₃H₂) in **3a**–e had a great influence on the PSDs (Fig. 5). In the anchoring effect, at high content of anchor points (-PO₃H₂) in **3a** (*m*/*n* = 1.2), a single micropore size at 1.8 nm was constructed owing to the reinforcements of anchor points (-PO₃H₂). With an increase in the *m*/*n* values from 1.2 to 6.8 for **3a–e**, the micropores in the range of 0.5 nm to 5.0 nm emerged because of the weakening anchorage of fewer anchor points (-PO₃H₂). However, upon altering molar ratios of Zr⁴⁺/H₂PO₄⁻ using **2d** as a pillar, **4d₁-d₅** possessed similar PSDs with non-uniform pores like **3d** (Fig. 5).

Surface morphology. Taking into account the close relationship between the surface property of the catalyst and its catalytic performance, the anchored Ru catalysts **3a**, **d** were assigned as examples to understand the surface morphologies in different states by SEM and TEM.



Fig. 6 (a) SEM; (b) TEM; (c) HRTEM of 3a and 3d.

The powders of anchored Ru catalysts **3a**, **d** in the solid state primarily consisted of approximately 1 μ m to 10 μ m particles (Fig. 6a). After being well dispersed in water (5 mg in 10 mL), the TEM images showed that water medium was an effective swelling system suitable for anchored Ru catalysts **3a**, **d**, and the particles obviously became smaller in size (100 nm to 300 nm) owing to the hydrophilicity of O₃POH moieties (Fig. 6b). Due to the bonds between compolymers and the flexibility of double-stranded polystyrene copolymers, randomly wavy strips, in which Zr and P elements were detected by EDS, were observed in the surfaces of anchored Ru catalysts **3a**, **d** under HRTEM (Fig. 6c), illustrating the pillaring of double-stranded polystyrene copolymers.

Porous structure. The BET surface areas, average pore diameters, and pore volumes of hybrid zirconium phosphate–phosphonate anchored Ru catalysts 3a-e and $4d_1-d_5$ in the solid state are summarized in Table 1, and the representative nitrogen adsorption–adsorption isotherms of 3a, b and $4d_1$, d_2 are shown in Fig. 5.

Application in aqueous asymmetric transfer hydrogenation

From the viewpoint of green chemistry, reactions in which water is used as a solvent have attracted much attention because water is an environmentally friendly and safe

Table 2 The catalytic performances of anchored-Ru 3a-e and $4d_1-d_5$ in aqueous ATH reaction^a

			$\frac{\text{a-e, }4\text{d}_{1-5}}{\text{CO}_2\text{H/Et}_3\text{N}}$	H ₃ C H R OH	
Entry	Cat.	S/C	$\operatorname{Conv.}^{b}(\%)$	Yield (%)	(% ee) ^c
1	2a	246	7.3	_	82.8
2	2b	246	18.0	15.0	82.7
3	2c	246	46.8	45.3	92.3
1	2d	246	81.3	79.8	94.9
5	2e	246	48.4	46.1	91.2
5	3a	400	10.9	_	94.3
7	3b	400	27.3	24.4	94.9
3	3c	400	36.9	33.6	94.6
Ð	3d	400	58.0	56.2	95.2
10	3e	400	45.2	42.5	95.2
11	$4d_1$	400	49.8	47.4	94.6
12	$4d_2$	400	48.8	45.1	95.0
13	4d ₃ (3d)	400	61.4	58.9	94.8
14	4d ₄	400	45.7	43.6	94.9
15	$4d_5$	400	20.0	15.6	95.0

^{*a*} Reaction conditions: acetophenone (0.1 mL, 0.86 mmol), HCO_2H-Et_3N (0.5 mL, v/v = 1:3), 2 mL H₂O, 50 °C, 16 h. ^{*b*} Monitored by GC. ^{*c*} Determined by chiral GC, Chiral Cyclodex-B (30 m × 0.25 nm × 0.25 µm, Supelco).

medium, preventing the problems of pollution that are inherent with organic solvents.¹² In this paper, considering the hydrophilicity and good dispersal of O_3POH moieties in **3a–e** and **4d₁–d₅** in water, aqueous asymmetric transfer hydrogenation (ATH) of aromatic ketones was used as a model reaction to investigate their catalytic performances.

The Ru(II) complex of N-tosyl-1,2-diphenylethane-1,2diamine (TsDPEN) is one of the most famous chiral ligands and showed excellent catalytic performance in ATH reaction.¹³ However, N'-alkylated TsDPEN-derived Ru(II) catalysts proved to be ineffective until 2009.14 Although the double-stranded polystyrene copolymer supported Ru catalysts 2a-e were isolated as N'-alkylated TsDPEN-derived Ru(II) complexes, they led to moderate to poor yields and satisfactory enantioselectivities in ATH reactions at S/C = 246 (7.3% ee to 81.3% ee, 82.8% ee to 94.9% ee, Table 2, entries 1–5). Among them, 2d (m/n = 3.6)possessed the best catalytic performance (81.3% ee, 94.9% ee). Upon anchoring 2a-e in the framework of hybrid zirconium phosphate-phosphonate, **3a-e** with different amounts (m/n)of anchor points (PO₃H₂) yielded decreased conversions of acetophenone like other heterogeneous catalysts (10.9% to 58.0%, Table 2, entries 6-10). Anchored Ru catalyst 3a possessed a single pore size distribution at 1.8 nm and the lowest surface area (15.2 $\text{m}^2 \text{g}^{-1}$), and the poorest conversion (10.9%) of acetophenone was obtained. However, their enantioselectivities increased slightly as a result of the confinement effect of the pores (94.3% ee to 95.2% ee). Anchored Ru catalysts 4d₁-d₅ with similar pillars of double-stranded polystyrene 1d showed similar catalytic properties except for $4d_5$ (45.1% to 58.9%, 94.6% ee to 95.0% ee, Table 2, entries 11 to 15).

Table 3 The catalytic performances of anchored Ru 4d₃ in different conditions^a

		$ \begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $				
Entry	S/C	Solvent (mL)	Conv. ^{b} (%)	Yield (%)	(% ee) ^c	
1	400	CH ₃ OH (2.0)	14.1	_	95.0	
2	400	$CH_3CN(2.0)$	11.9	_	93.9	
3	400	THF (2.0)	12.0	_	94.0	
4	400	$CHCl_{3}(2.0)$	12.9	—	95.0	
5	400	DMF(2.0)	10.6	—	94.0	
6	400	$H_2O(0.5)$	46.0	44.4	95.6	
7	400	$H_2O(1.0)$	74.3	72.3	94.0	
8	400	$H_2O(1.5)$	75.2	73.8	94.2	
9	400	$H_2O(2.0)$	58.0	57.8	95.0	
10	400	$H_2O(5.0)$	44.3	41.7	94.7	
11	100	$H_2O(1.5)$	>99	98.0	94.9	
12	200	$H_2O(1.5)$	86.9	85.9	93.3	
13	800	$H_2O(1.5)$	52.2	50.7	94.5	

Table 4 The catalytic performances of anchored-Ru 4d₃ in different conditions^a

	R	$\frac{4d_3}{HCO_2H/Et_3N}$	R R OH	
Entry		$\operatorname{Conv.}^{b}(\%)$	Yield (%)	(% ee) ^c
1	<i>m</i> -OCH ₃	90.4	88.9	91.9
2	p-OCH ₃	36.0	34.6	86.0
3	o-Br	>99	98.5	94.8
4	<i>m</i> -Br	98.5	97.8	90.7
5	<i>p</i> -Br	96.6	95.1	90.4
6	o-Cl	97.7	95.4	89.8
7	<i>m</i> -Cl	>99	97.9	95.6
8	p-Cl	98.3	96.4	90.1
9	$m-NO_2$	>99	97.6	73.6
10	$p-NO_2$	94.9	92.2	74.5
11	m-CH ₃	98.2	96.7	95.2
12	<i>p</i> -CH ₃	72.8	70.8	56.4

 a Reaction conditions: acetophenone (0.1 mL, 0.86 mmol), HCO₂H–Et₃N (0.5 mL, v/v = 1 : 3), 50 °C, 16 h. b Monitored by GC. c Determined by chiral GC, Chiral Cyclodex-B ($30 \text{ m} \times 0.25 \text{ nm} \times 0.25 \mu \text{m}$, Supelco).

The effects of solvents and substrate/catalyst molar ratios on the catalytic performance were further investigated using anchored Ru catalyst $4d_3$ (3d) as an example. Significantly reduced conversions of acetophenone (10.6% to 14.1%) in organic solvents were observed as expected as a result of the poor swelling properties of $4d_3$ in organic solvents, such as ethanol, and even the contraction in THF, CH₃CN, and CHCl₃ (Table 3, entries 1–5). To improve the catalytic activity of $4d_3$, the effects of temperature, amount of water consumed, and substrate/catalyst molar ratio (S/C) on reactivity, and enantioselectivity were also investigated and screened out. Table 3 entries 6-10 shows that the conversion of acetophenone was a function of used water volume. At the lowest amount of water used (0.5 mL), a strong inhibiting influence on the conversion of acetophenone was found (46.0%) because of its poor mass diffusion. At a higher amount of water volume used (5.0 mL), the poor conversion (44.3%) was caused by the diluted concentration of acetophenone and catalyst. The best catalytic performance (73.8%, 94.2% ee) was found at 1.5 mL water. Molar ratios of substrate/catalyst (S/C) played a great role in catalytic performance. The excellent conversion of acetophenone (>99%) was observed at S/C = 100 (Table 3, entry 11). Hence, the optimum catalytic properties of acetophenone (>99% conv., 94.9% ee) catalyzed by 4d₃ was obtained under the following conditions: 1.0 mol% Ru (S/C = 100), 50°, 0.86 mmol acetophenone in 1.5 mL water for 16 h. The specifically selective hydrogenation of C=O to C-O bond was observed without side reactions such as further hydrogenolysis of benzyl alcohol to ethylbenzene and aromatic ring to cyclohexane, which are generally found in Pd,Rh-catalyzed hydrogenation reaction.¹⁵

The optimized protocol was expanded to various aromatic ketones. Any electron-rich (OCH₃ and CH₃) or -poor (NO₂ and X) aromatic ketones could yield excellent conversions

^a Reaction conditions: acetophenone (0.1 mL, 0.86 mmol), HCO₂H- Et_3N (0.5 mL, v/v = 1:3), S/C = 100, 1.5 mL H₂O, 50 °C, 16 h. Monitored by GC. ^c Determined by chiral GC, Chiral Cyclodex-B (30 m × 0.25 nm × 0.25 µm. Supelco).

(Table 4). However, these conversions were closely related to the o-, m- or p-positions of the substituents on the aromatic ring. When the substituents of OCH₃ and CH₃ were in the *p*-position of the aromatic ketones, the conversions sharply decreased from 90.4% and 98.2% to 36.0% and 72.9%, respectively (Table 4, entries 2, 12) caused by the mismatch between the bulkier spatial volumes of the substrates and the microporous spaces in $4d_3$. In addition, decreased enantioselectivities (86.0% ee and 56.4% ee) were also found. Similar shape-selective catalyses were observed for Br, Cl, and NO₂ substituents in the *p*-position, although they yielded excellent conversions (94.9% to 98.3%, Table 4, entries 5, 8, 10).

The recovery and reuse of anchored Ru catalyst

At the end of the catalytic reaction, the anchored Ru 4d₃ was readily recovered from the reaction mixture by simple centrifugal separation, washed with ethyl acetate and water, and reused without any other further treatment. To investigate the reused catalytic properties of the anchored Ru catalyst $4d_3$, the supported Ru catalyst 3d' as a reference catalyst was prepared first by precipitation of double-stranded polystyrene copolymer 1d with Zr⁴⁺ ion to form the framework of hybrid zirconium phosphate-phosphonate and then by complexation of $[\operatorname{RuCl}_2(p\text{-cymene})]_2$ (Scheme 2).

Considering the different preparation sequences of anchored Ru catalyst $4d_3$ (3d) and supported Ru catalyst 3d', these catalysts had significant differences in conversions of acetophenone in the recycled catalytic reactions (Fig. 7). Fig. 7 shows that the activity of supported Ru catalyst 3d' decreased sharply upon repeated recycling (only 52.3% conv. at the fifth recycled time). However, anchored Ru catalyst 3d retained its catalytic properties even at the fifth recycled times (92.2% conv., 92.1% ee). To determine the reason for this difference,



Scheme 2 The synthetic route to supported Ru catalyst 3d'



Fig. 7 The catalytic properties of recycled anchored Ru catalyst $\mathbf{3d}$ and supported-Ru $\mathbf{3d'}$ in aqueous recycled transfer hydrogenation.

the resulting centrifugate was collected, and the loss of Ru(n) in the centrifugate was monitored by ICP method. However, the supported Ru catalyst 3d' lost $[RuCl_2(p\text{-cymene})]_2$ particles easily from the anchored pores, resulting in the contamination of the product by Ru metal. However, $[RuCl_2(p\text{-cymene})]_2$ in 3d cannot escape from the anchored pores because of the embedded effect of hybrid zirconium phosphate–

phosphonate. Therefore, the preparation strategy through the first complexation of $[RuCl_2(p-cymene)]_2$ and final molding of hybrid zirconium phosphate-phosphonate was particularly important for anchored Ru $4d_3$ to inhibit Ru from escaping from the anchored pores.

Conclusions

A series of double-stranded polystyrene copolymers bearing N'alkylated TsDPEN chiral ligands and phosphonate (-PO₃H₂), with good coordination for [RuCl₂(p-cymene)]₂ by imino functional groups, were prepared by simple radical copolymerization using different monomer molar ratios. Through the anchor points of phosphonate $(-PO_3H_2)$, the pillared and anchored Ru hybrid zirconium phosphate-phosphonates coated with hydrophobic linear polystyrene over the inner surface of the Zr layers were obtained by the coprecipitation of polystyrene copolymer-supported Ru complexes and NaH₂PO₄ with ZrOCl₂. Compared with the copolymer-supported Ru catalyst, zirconium phosphate-phosphonate-anchored Ru catalyst was suitable for aqueous asymmetric transfer hydrogenation and had good catalytic properties after recycling because of the minimal loss of Ru. The preparation procedure known as the "first complexation of ruthenium and then molding of inorganic backbone" was essential to prevent Ru from escaping from the anchored pores. Given the shape-selective restriction of porous and pillared zirconium phosphatephosphonate, the substituents in the *p*-position of the aromatic ketones showed relatively poor conversions in the ATH reaction.

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