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Synthesis and characterization of mesoporous zirconium phosphonates: A novel supported cinchona alkaloid catalysts in asymmetric catalysis

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ABSTRACT

In this paper, cinchonidine (CD) with the different arm lengths (n = 2-6) was covalently immobolized onto the backbone of zirconium phosphonate to afford a series of mesoporous zirconium phosphonates (**4a–e**) for the first time. It was found that zirconium phosphonates (**4a–e**) were conglomerated with the globular aggregates with the diameters of about 100–150 nm and possessed the surface areas of 20.8–36.2 m² g⁻¹, pore volumes of 0.219–0.498 cc g⁻¹ and average pore sizes of 11.7–41.5 Å. The TEM images of **4a–e** in organic solvent showed that these materials were easily swollen into the filiform structure with the length about several micrometers and thickness about 30–50 nm. In the field of the asymmetric catalysis, the preliminarily enantioselective addition of diethylzinc to various aldehydes catalyzed by **4a–e** (35–62%e.e. in the 68–92% yield) was carried out and can be reused ten times without loss in the yield and enantiomeric excess.

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1. Introduction

Only within the past thirty years cinchona alkaloids emerged as versatile chiral basic catalysts, ligands, chromatographic selectors and NMR discriminating agents. Quite obviously, they conformed to generally accepted requirements: they are commercially available and relatively inexpensive, stable, and their structure can be readily modified for diverse catalytic applications. Especially, the tremendous interest in supported cinchona alkaloids is as a result of rapid development in two main areas: chiral stationary phases in chromatographic separation techniques and chiral polymer-supported catalysts [1–4]. In the field of asymmetric catalysis, Cinchona alkaloids were generally immobilized onto silica gel [5–9] and organic polymer [10–16].

Zirconium phosphate (ZrP) and its derivatives with the layered and porous structure are the important class of compounds in the field of catalysis [17–21], adsorption, ion exchange and/or functional materials [22–26]. Due to the high structural flexibility of these compounds, it is relatively easy to prepare modified inorganic–organic functional derivatives by means of covalently bonding, intercalation and ion–exchange under mild conditions [27–29]. In this paper, cinchonidine (CD) was covalently anchored onto the layered and porous backbone of zirconium phosphate through the quinuclidine olefinic side chain to obtain the functional compounds **4a–e** for the first time (Scheme 1). Furthermore, the enantioselective addition of diethylzinc to various aldehydes under the catalysis of zirconium phosphonates **4a–e** was preliminarily carried out. The experimental results indicated that zirconium phosphonates (**4a–e**) possessed the mesoporous and filiform structure with length and thickness up to several micrometers and 30– 50 nm respectively, which was beneficial for the reactant species to be accessible to the catalytic sites of cinchonidine on the surface or in the internal pores.

2. Experimental

2.1. Materials

Diethyl ω -bromoalkylphosphonates [Br(CH₂)_nP(O)(OEt)₂] (n = 2-6) were synthesized according to the known procedures and well confirmed by ¹H, ¹³C NMR and FT-IR [30]. All the other materials used are of analytical grade obtained from commercial sources without further purification.

2.2. Preparation of the phosphonates 2a-e

In the dried three-necked flask (250 mL) was charged anhydrous K_2CO_3 (16.0 g, 116 mmol), flushed three times with nitrogen at room temperature, added dithioglycol (10.90 g, 116 mmol) and 100 mL of DMF by syringe and cooled to 0–5 °C. 25 mL of DMF solution containing ω -bromoalkylphosphonates **1a–e** (58 mmol) was added dropwise over 1 h and stirred for 30 min. Then the ice-bath was removed and stirred at room temperature for another 48 h with the tracking of TLC. The reaction mixture was added distilled water till the solid K_2CO_3 was dissolved and then separated.



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Scheme 1. The synthetic route to zirconium phosphonates 4a-e.

The water phase was extracted by mixed ethyl acetate/benzene (30 mL × 3, v/v = 3/1). Then the organic phases were combined, washed with distilled water till DMF was removed completely, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to give the pale yellow liquid. The crude products were purified by silica gel column chromatography using petroleum ether (60–90 °C)/ethyl acetate (v/v = $12/1 \rightarrow 10/1 \rightarrow 6/1$) and concentrated under reduced pressure to afford **2a–e** in 60–70% yields.

2.3. Preparation of the phosphonates **3a-e**

In the dried flask (100 mL) was charged cinchonidine (3.3 g, 11.1 mmol), **2a–e** (44.5 mmol) and AIBN (0.46 g, 2.8 mmol) consecutively, flushed three times with nitrogen at room temperature, added 100 mL of CHCl₃ by syringe and then refluxed for 48 h with the tracking of TLC. The reaction mixture was washed with water (15 mL × 3), the organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure to give the pale yellow liquid. The crude product was purified by silica gel column chromatography using CHCl₃/petroleum ether (60–90 °C) (v/v = 40/1) to remove the side products with poor polarity and then CHCl₃/ methanol (v/v = 80/1 \rightarrow 60/1 \rightarrow 40/1) to afford **3a–e** in 79–98% yields.

2.4. Preparation of zirconium phosphonates 4a-e

A mixture of **3a** (1.0 g, 2 mmol), 45 mL of acetic acid and 15 mL of hydrochloric acid (36%) was stirred at 84 °C for 24 h and concentrated under reduced pressure to 10 mL volume. Zirconium oxychloride (1.7 g, 6 mmol) in 15 mL of deionized water was added dropwise and stirred at room temperature for another 16 h. The white solid was filtered, dispersed in 50 mL of water, adjusted to pH = 6–7 by using sodium carbonate (0.1 mol/L) and filtered again. The mud cake was washed with deionized water till chloride ion was not detected by using ion chromatography, and then dried at 60 °C for 24 h under reduced pressure to afford zirconium phosphonate **4a** in 58% yield. The other zirconium phosphonates **4b–e** were prepared according to the same procedure as **4a** in 50–60% yields.

2.5. Enantioselective addition of Et_2Zn to be nzaldehyde catalyzed by **4a–e**

In the dried flask (10 mL) was charged zirconium phosphonate **4a** (31.8 mg, 0.075 mmol), flushed three times with N₂ atmosphere and sealed, added anhydrous toluene (5 mL) by syringe and stirred for 12 h at room temperature. Then Et_2Zn (1 mL, 1 mol/L in hexane)

was added dropwise at 0 °C under nitrogen atmosphere. After stirring for 1 h, benzaldehyde (50 uL, 0.5 mmol) was added dropwise, stirred for 72 h at room temperature, quenched by a saturated aqueous NH₄Cl solution, filtered and extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed with brine (5 mL × 2), dried over anhydrous Na₂SO₄ and evaporated under reduced pressure to give an oily residue. The residue was purified by silica gel column using ethyl acetate/petroleum ether (60–90 °C) (v/v = 5:1) to give 1-phenyl-1-propanol.

3. Results and discussion

3.1. Characterization of the supported cinchona alkaloid catalysts **4a–e**

3.1.1. IR spectra

The infrared spectra of **4a–e** were recorded in the range 4000–400 cm⁻¹ in order to ascertain whether the attachment of cinchonidine molecule onto the backbone of zirconium phosphate happened. From the IR spectra shown in Fig. 1, it was found that the strong and wide absorption band extending from 3700 to 2500 cm⁻¹ and centered at 3409 cm⁻¹ was assigned to the -O-Hstretching vibration of hydroxyl group in organic moieties and crystal water in the internal or external surface. Due to the increase in the arm chain length of $-(CH_2)_n$ - organic groups (*n* from 2 to 6),



Fig. 1. The infrared spectra of $4\mathbf{a}-\mathbf{e}$ in the 4000–400 cm⁻¹ range.



Fig. 2. Thermal gravimetric curves of zirconium phosphonates 4b-e.

the stronger C–H stretching vibration at 2854 cm⁻¹ was observed. The absorption bands at 1636–1462 cm⁻¹ and 803, 763 cm⁻¹ were attributed to the characteristic absorption and flexural vibration of aryl group in appended organic moieties respectively. Furthermore, the strong and wide absorption bands at about 1031 cm⁻¹ for all the samples **4a–e** indicated that the reaction between the phosphonates **3a–e** and ZrOCl₂ were performed to form the Zr–O–P bonds. Therefore, from FT-IR spectra it was concluded that cinchonidine was successfully anchored onto the framework of zirconium phosphonate by covalently bonding through the different arm lengths of –(CH₂)_n–organic chains (n = 2-6).

3.1.2. TG analysis

On heating the samples **4a–e**, the similar thermolysis curves over a broad temperature range of 40–1200 °C with a three-step weight loss behavior were observed, which were shown in Fig. 2. The first slope curve of **4a–e** below 200 °C was attributed to the desorption of the surface-bound or intercalated water in the pores with weight losses of 6.8, 5.3, 4.8, 3.7 and 3.5 wt.% respectively, followed by the sharp second curve with a single DTG peak owing to the volatilization of appended organic fragments between 250 °C and 400 °C, while the third stage appeared from 400 °C to

Table 2

The BET surface areas, pore volumes and average pore sizes of 4a-e.

Samples ^a	<i>n</i> = 2	<i>n</i> = 3	<i>n</i> = 4	<i>n</i> = 5	<i>n</i> = 6
$S_{BET} (m^2 g^{-1})^b$	20.8	31.4	34.1	35.9	36.2
Pore volume (cc $g^{-1})^c$	0.219	0.423	0.498	0.280	0.322
Average pore size (Å) ^d	41.5	31.2	28.8	25.3	11.7

^a The samples were degassed at 100 °C for 5 h.

^b Surface based on multipoint BET method.

^c Pore volume based on the desorption data of BJH method.

^d Pore size based on the desorption data using BJH method.

Table 1		
The formulae of 4a-e and	the data of elemental	analysis and TG analysis

Samples	x	n	Elemental analysis calcd [%] (found [%])	The weight loss ^a calcd [%] (found [%])
4a	0.49	2.08	C, 32.05 (31.92); H, 4.34 (4.43), N, 3.26 (3.12)	48.1 (47.0)
4b	0.52	1.62	C, 33.11 (32.98); H, 4.47 (4.56), N, 3.32 (3.16)	48.6 (48.0)
4c	0.59	1.47	C, 37.38 (37.61); H, 4.98 (5.13), N, 3.49 (3.32)	54.8 (54.0)
4d	0.78	1.22	C, 42.49 (42.34); H, 5.50 (5.63), N, 3.80 (3.78)	62.4 (61.3)
4e	0.82	1.15	C, 44.06 (44.0); H, 5.74 (5.90), N, 3.80 (3.69)	64.1 (61.3)

^a The weight loss of organic moieties monitored by TG analysis.

1200 °C corresponding to the oxidation of the cokes generated during the second stage. From Fig. 2, it was found that the total weight

losses of appended organic moieties in 4a-e were 47.0, 48.0, 54.0, 61.3 and 61.3 wt.% respectively and increased with *n* from 2 to 6.



Fig. 3. The nitrogen adsorption-desorption isotherms and pore distribution of 4a-e.



Fig. 4. SEM images of zirconium phosphonates 4b-e.

The pronounced inclination of the less surface-bound or intercalated water from n = 2 to 6 below 200 °C was ascribed to the lower hydrophilicity in the interlayer region owing to the more appended organic moieties (the increasing *x* values from 0.49 to 0.82). In general, the structures of zirconium phosphonates **4a–e** were similar to that of the parent compound α -ZrP, and the organic groups point towards the interlayer region. The free area associated to each organic group is 24 Å² and filled by these organic groups [27]. In the confined areas, due to the increasing arm chain lengths *n* from 2 to 6, the interlayer spacings were expanded and the bulky cinchonidine was more remote to zirconium layer. Therefore, there were the more larger free spaces for zirconium phosphonates with longer arm chain lengths *n* from 2 to 6 to accommodate the more cinchonidines.

3.1.3. The chemical composition of **4a–e**

Because it was difficult for 4a-e to work up single crystals to elucidate the architectural structure, only the chemical composition was determined by using elemental analysis, TG analysis and chemical analysis. According to the reported literature, Cl anion could be topotactically replaced by the inorganic anions such as HO⁻ and Br⁻ [31]. In the preparation process of **4a**–**e** sodium carbonate (0.1 mol/L) and deionized water were used to dealt with the samples enoughly to completely remove the Cl anions, which was confirmed by ion chromatography. In order to detect the zirconium (IV) amount, a mixture of 2 mL of deionized water and 50 mg of **4a–e** in a sealed plastic container was added 4 mL of hydrofluoric acid (30%) and stirred for 6 h at room temperature. Due to the formation of the water-soluble complex ZrF_6^{2-} , **4a–e** were decomposed, and the contents of zirconium (IV) and phosphonic acid with cinchonidine in the resulting solution were determined by ICP-AES and ³¹P NMR respectively. Taking into account the molar ratios (*x*) of the appended organic moieties to zirconium (IV) monitored by ³¹P NMR and ICP-AES and the number (*n*) of crystal water detected by TG curve below 200 °C, the formulae of **4a–e** were given in Table 1, which were in the good agreement with the data by using elemental analysis and TG analysis.

3.1.4. Nitrogen adsorption-desorption isotherms

The textural parameters of **4a–e** calculated by N₂ adsorption and desorption isotherms at 77 K were presented in Table 2. As expected, it was shown that **4a–e** (n = 2-6) were porous solid materials with the surface areas of 20.8–36.2 m² g⁻¹, pore volumes of 0.219–0.498 cc g⁻¹ and average pore sizes of 11.7–41.5 Å. With the increase in arm chain lengths n from 2 to 6, it was observed that the surface areas of **4a–e** increased and average pore sizes decreased respectively, which was related to the bulky size and appended amount of the organic moieties containing cinchonidine.



Fig. 5. TEM images of zirconium phosphonates 4b-e.

A reasonable and plausible explanation of this change in surface area and average pore size was that the longer arm chain lengths n from 2 to 6 made the inorganic zirconium layers more expanded and amorphous, and then the more surface areas were obtained. In the other hand, the organic moieties with the arm chain lengths n from 2 to 6 between the neighbour zirconium layers tended to be more close packing in the interlayer region ascribled to the increase in x values (x = 0.49-0.82) for **4a**–**e** (Table 1), which caused the less free mesopores and the decrease in the average pore sizes from 41.5 to 11.7 Å in solid state.

The nitrogen adsorption–desorption isotherms of all these compounds **4a–e** presented type IV isotherms according to the IUPAC classification with a sharp increase in N₂ adsorption at higher *P*/ *P*₀ value (~0.95) and a distinct hysteresis loop (type H1) possessing an almost parallel adsorption and desorption (Fig. 3). Based on the desorption isotherms of **4a–e**, BJH analysis gave several mesopores in different pore sizes with the non-uniform distribution in the range 20–80 Å. From Fig. 3, it was found that there were three characteristic cavities centered at about 25–28, 30–45 and 55– 70 Å. Especially, it was noted that **4e** with the highest *x* value (0.82), which implied the organic moieties in the interlayer region were crowded, possessed the weakened nitrogen desorption (Dv) in the mesopores, and the micropores below 20 Å strongly appeared.

3.1.5. Surface morphology

Generally, SEM micrographs of metal (IV) phosphonates are spheroid or featureless and submicron in size with a layered crystalline structure in solid state [27–29]. From the SEM images shown in Fig. 4, 4a–e were conglomerated with the globular aggregates with the diameters of about 100–150 nm. It was highlighted that the interaction between two neighbour zirconium layers was greatly weakened owing to the functionalization by the bulky cinchonidine with the different arm chain lengths (n = 2-6), and the conglomerated particles **4a–e** in the smaller size than the parent materials were observed. Interestingly, **4a–e** in the organic solvents were easily swollen, which could be verified by the TEM images. After the samples **4a–e** were dispersed in cyclohexane and stirred for 2 h, their morphologies of the filiform structure with thickness about 30–50 nm and length about several micrometers was observed (Fig. 5).

3.2. The enantioselective addition of diethylzinc to benzaldehyde catalyzed by **4a–e**

Enantioselective addition of diethylzinc to various aldehydes is one of the most studied catalytically asymmetric reactions, which was usually used to evaluate the catalytic activities and enantioselectivities of the chiral ligands. In the homogeneous CD-induced enantioselective addition of diethylzinc to benzaldehyde, 58% e.e. of (R)-1-phenylpropan-1-ol was achieved. Under the catalysis of zirconium phosphonates 4a-e, the enantioselective addition of diethylzinc to benzaldehyde was preliminarily carried out. From Table 3, it was found that the increase of the isolated yields from 64% to 80% and enantiomeric excesses from 19% to 35% e.e. with arm chain lengths (*n*) from 2 to 6 for **4a–e** was observed (Table 3, entries 2–6). In the toluene/hexane mixed solvents (v/v = 1:1) at 20 °C for 84 h, the enantiomeric excess of (R)-1-phenylpropan-1-ol with 49% e.e. in 88% yield for 4e was obtained (Table 3, entry 16), which was 9% e.e. lower than the homogeneous CD-induced enantiomeric excess 58% e.e. in 89% yield (Table 3, entry 1).

The ligand **4e** was further used as the catalyst for the addition of diethylzinc to the other aromatic aldehydes (Table 3, entries 18–23). Under the optimized conditions at 20 °C in toluene/hexane (v/v = 1:1) for 84 h, the reactions catalyzed by 10 mol% of catalyst **4e** were performed. From the catalytic experimental results, it seemed that the electronic effects of the aromatic ring substituents bearing a strong electron-donating group such as methoxyl or elec-

Table 3

Enantioselective addition of diethylzinc to various aldehydes catalyzed by 4a-e under different solvents^a.

ArCHO + ZnEt ₂	15mol% 4a-e ──────────	H OH Ar
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Entry	Catalyst	Ar	Temperature (°C)	Solvent	Time (h)	Yield (%) ^b	e.e. (%) ^c
1	CD	Ph	20	Toluene	72	89	58(R)
2	4a	Ph	20	Toluene	72	64	19(R)
3	4b	Ph	20	Toluene	72	68	20(R)
4	4c	Ph	20	Toluene	72	70	23(R)
5	4d	Ph	20	Toluene	72	74	31(R)
6	4e	Ph	20	Toluene	72	80	35(R)
7	4e	Ph	20	THF	72	50	15(R)
8	4e	Ph	20	Hexane	72	66	26(R)
9	4e	Ph	20	Toluene/Hexane ^d	72	85	42(R)
10	4e	Ph	0	Toluene/Hexane ^d	72	70	32(R)
11	4e	Ph	-10	Toluene/Hexane ^d	72	62	29(R)
12	4e	Ph	-20	Toluene/Hexane ^d	72	48	25(R)
13	4e	Ph	20	Toluene/Hexane ^d	12	30	25(R)
14	4e	Ph	20	Toluene/Hexane ^d	24	42	28(R)
15	4e	Ph	20	Toluene/Hexane ^d	48	70	32(R)
16	4e	Ph	20	Toluene/Hexane ^d	84	88	49(R)
17	4e (10th)	Ph	20	Toluene/Hexane ^d	72	84	35(R)
18	4e	p-MeO-C ₆ H ₄	20	Toluene/Hexane ^d	84	90	56(R)
19	4e	p-Br-C ₆ H ₄	20	Toluene/Hexane ^d	84	86	48(R)
20	4e	o-Br-C ₆ H ₄	20	Toluene/Hexane ^d	84	78	37(R)
21	4e	p-Cl-C ₆ H ₄	20	Toluene/Hexane ^d	84	92	62(R)
22	4e	p-O ₂ N-C ₆ H ₄	20	Toluene/Hexane ^d	84	74	35(R)
23	4e	p-Me ₂ N-C ₆ H ₄	20	Toluene/Hexane ^d	84	68	43(R)

^a Reaction was carried out with a molar ratio $Et_2Zn/aldehyde/chiral$ ligand of catalyst = 2/1/0.15.

^c Determined by GC (30 m, chiral cyclodex-B column, agilent) for Ar = Ph and HPLC for the other substrates on chiralcel OD, OJ-H and AD-H with hexane-2-propanol as eluant. ^d v/v = 1:1.

^b Isolated yield.

tron-withdrawing groups such as bromo and chloro had a little influence on the yield (86–92%) and great effect on the enantioselectivities varied from 48% to 62%e.e. (Table 3, entries 18, 19, 21). However, the strong electron-donating group p-Me₂N and electron-withdrawing group p-NO₂ decreased the enantioselectivities (43% and 35%e.e. respectively) and yields of the products (68% and 74% respectively) (Table 3, entries 22 and 23). Fortunately, there was no significant loss in the yield and enantiomeric excess after the catalyst **4e** was reused ten times (Table 3, entry 17).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.catcom.2009.10.031.

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