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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 $m^2\ g^{-1}$, 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.

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 $[Br(CH_2)_nP(O)(OEt)_2]$ (*n* = 2–6) were synthesized according to the known procedures and well confirmed by ^1H, ^{13}C 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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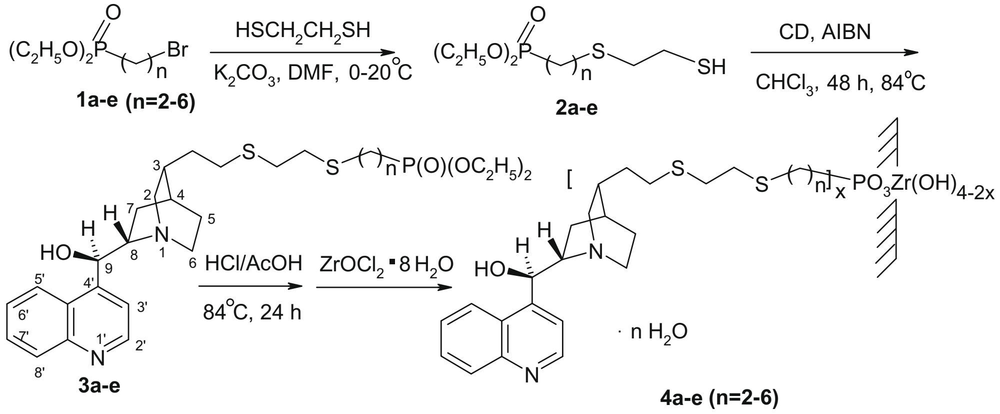

Scheme 1. The synthetic route to zirconium phosphonates **4a**–**e**.

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 Na_2SO_4 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 → 10/1 → 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 $CHCl_3$ 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 Na_2SO_4 and concentrated under reduced pressure to give the pale yellow liquid. The crude product was purified by silica gel column chromatography using $CHCl_3$/petroleum ether (60–90 °C) (v/v = 40/1) to remove the side products with poor polarity and then $CHCl_3$/methanol (v/v = 80/1 → 60/1 → 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 benzaldehyde 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 N_2 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 NH_4Cl solution, filtered and extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed with brine (5 mL × 2), dried over anhydrous Na_2SO_4 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—H stretching 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),

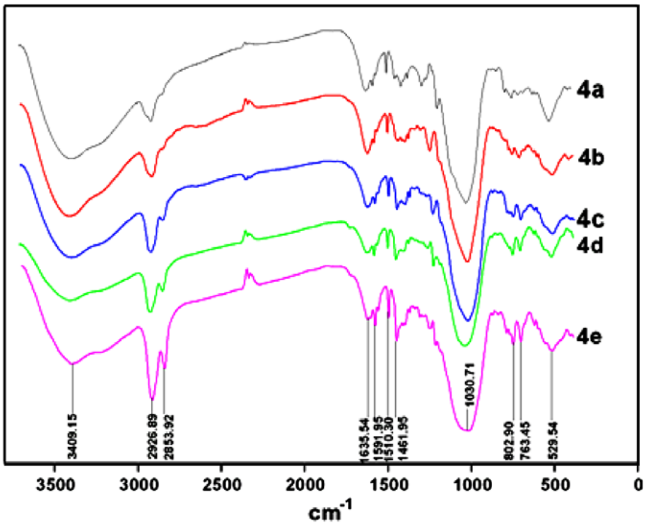

Fig. 1. The infrared spectra of **4a**–**e** in the 4000–400 cm^{-1} range.