



A new non-cinchona chiral modifier immobilized on Pt/SiO₂ catalysts for enantioselective heterogeneous hydrogenation

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ABSTRACT

Pt heterogeneous catalysts were prepared by the covalent immobilization of (4*R*,5'*S*)-4',5'-dihydro-4',5'-diphenyl-2-(6-cyanopyridyl)imidazoline (Pylm) as the asymmetric modifier. These novel series of catalysts were studied in the 1-phenyl-1,2-propanodione (PPD) hydrogenation. The effects of the Pylm surface concentration, hydrogen pressure, solvent nature and recycles on the reaction were studied. These modified catalysts represent the first effective immobilized chiral non-Cinchona-type modifier of Pt for the enantioselective hydrogenation. The enantio-differentiation was attributed to the substrate–modifier interactions involving hydrogen bonding between the keto-carbonyl O atom and the NH moiety Pylm. The results confirmed that the variations in the H₂ pressure and the solvent affect the activity and the enantioselectivity due to the substrate adsorption on the active sites of the metal. Additionally, this heterogeneous catalyst can be conveniently reused at least five times without loss of its catalytic efficiency, but the enantioselectivity decreased, which may be due to the leaching of the modifier.

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1. Introduction

Asymmetric synthesis is a rapidly growing field in chemistry. Among the various strategies for the synthesis of optically pure compounds, asymmetric catalysis offers the advantage of using small amounts of a chiral catalyst to produce large quantities of the desired chiral product [1–3]. Heterogeneous enantioselective catalysis is of special interest for industrial application because of its advantages over homogeneous reactions in separation and reuse of the catalyst [2,4]. However, only a few heterogeneous enantioselective catalytic systems have been investigated in detail because they require a chiral auxiliary molecule to induce the desired enantiomer [2,5,6]. Therefore, a chiral auxiliary must be readily available and inexpensive, indicating that the fewer steps required from the natural molecule to the auxiliary will result in a higher probability of its application. Historically, natural chiral modifiers have played an important role in the prospects of using organic chemistry to mimic nature [7,8]. Cinchona modified supported Pd catalysts have been successfully used in the enantioselective

hydrogenation of several types of prochiral olefinic substrates [9–12]. The two chirally modified metal catalysts most effective in the hydrogenation of ketones are Ni modified with tartaric acid [13,14] for β -diketones and Pt modified with cinchona alkaloids [15–19] to hydrogenate α -diketones. The mechanistic studies of cinchona-modified Pt, including the systematic variation of the structure of cinchonidine and certain other chiral amine modifiers and their derivatives, have revealed that the crucial structural parts of the modifiers, in addition to the stereogenic center(s), are the size of flat aromatic ring for anchoring onto the catalyst surface and the basic aliphatic nitrogen function for interacting with the substrate [20–23]. In addition to amines and amino alcohols, several other types of chiral compounds have been tested as modifiers in the Pt-catalyzed hydrogenation of ketones, but none of them can compete with cinchonidine or its O-methyl derivative [8,16,24].

The wealth of the results reported in the literature tempted us to perform a simple structure analysis. Therefore, we selected a relatively unusual approach. Instead of analyzing the structural effects of the related auxiliaries with high and low enantioselectivity, we compared only the highly efficient auxiliaries. Because most of the used chiral auxiliaries possess N and/or O atoms for enantioselective metal-based catalysts or reagents, we concentrated on this class of chiral agents to find the following

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common structural elements: ligand atom, chelate size, type of backbone, and number and location of asymmetric centers. In our previous results, (4'R,5'S)-4,5-dihydro-4,5-diphenyl-2-(6-cyanopyridyl)imidazoline (Pylm) has shown an excellent performance as a chiral modifier in the enantioselective hydrogenation of 1-phenyl-1,2-propanodione (PPD) [25]. In this case, the modifier was employed as a stabilizer in the synthesis of the Pt nanoparticles and in the subsequent dispersion on the ZrO₂ nanotubes as supports of the heterogeneous catalysts. However, to date, no attempt has been performed to immobilize the modifier to generate a more efficient catalytic system.

The modifier concentration played an important role in the activity and enantioselectivity in most of the heterogeneous catalytic reactions. The modifier Pylm possesses a structure similar to the other chiral amines tested in the hydrogenation of activated ketones, primarily ethyl or methyl pyruvate. The useful modifiers of Pt include 2-(1-pyrrolidinyl)-(1-naphthyl)ethanol [26] and other similar chiral 1,2-aminoalcohols [10,12], 1-(1-naphthyl)ethylamine and their derivatives [9,11], anthryl- and phenanthryl-ethylamines [27], vinca alkaloid derivatives [28], L-tryptophan derivatives [22], and isocinchona alkaloids [15].

In this study, our goal was to demonstrate that the covalent anchorage of Pylm on the Pt/SiO₂ catalysts could provide a reusable system for application in the PPD heterogeneous hydrogenation. In addition to our previous studies [29–31], we attempted to gain insight into the role of the chiral immobilized modifier on the activity and selectivity of PPD heterogeneous hydrogenation in semi-batch systems. The study focused on the direct immobilization using a top-down approach of Pylm with previous heterogenized trimethoxysilane-SiO₂ supports. The synthetic procedure towards the supports synthesis and modification is shown in Scheme 1. Certain important reaction parameters, such as the surface modifier concentration, PPD concentration, H₂ pressure and cycles, which have been studied less frequently in the literature, were investigated in detail to optimize the enantioselectivity and catalytic performance.

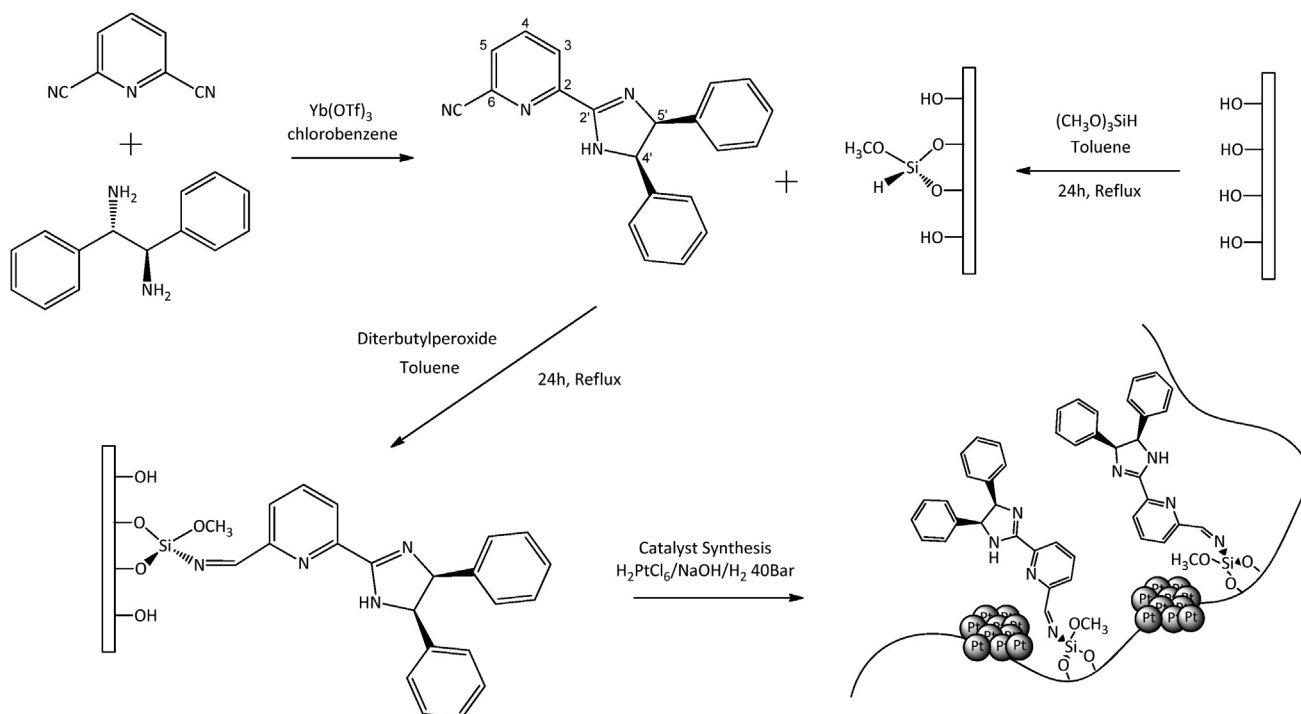
2. Experimental

2.1. Synthesis of the chiral modifier

2,6-Dicyanopyridine (100 mg, 0.77 mmol) was treated with meso-1,2-diphenylethylenediamine (164 mg, 0.77 mmol) in chlorobenzene (5 mL) in the presence of ytterbium(III) trifluoromethanesulfonate (46 mg, 0.14 mmol). The mixture was stirred for 24 h under reflux. The desired product was separated from the bis-imidazoline product [32] by column chromatography in a 20% yield. $R_f = 0.41$ (hexane/ethyl acetate 1:2). ¹H NMR (300 MHz, CDCl₃, RT): $d = 8.46$ (d, $3J = 7.8$ Hz, 1H; H5), 7.91 (t, $3J = 7.8$ Hz, 1H; H4), 7.85 (d, $3J = 7.8$ Hz, 1H; H3), 7.01 ± 6.93 (m, 10H; Ph), 6.49 (s, 1H; NH), 5.50 ppm (br, 2H; H4', H5'); ¹³C NMR (75 MHz, CDCl₃, RT): $d = 162.5$ (s, C2'), 150.0 (s, C2), 138.4 (s, C4), 130.2 (s, C3 ± C5 ± C6), 130.0 (s, C3 ± C5 ± C6), 127.9 ± 127.1 (Ph), 126.2 (s, C3 ± C5 ± C6), 117.0 (s, CN), 67.0 ppm (br, C4', C5'); elemental analysis calcd (%) for C₂₁H₁₆N₄ (324.4): C 77.76, H 4.97, N 17.27; found: C 77.56, H 4.91, N 17.33.

2.2. SiO₂ activation and silanization

The procedure for the SiO₂ activation and silanization was similar to that reported by Matyska et al. [33,34] in which 5.00 g SiO₂ was placed in a 250 mL three-neck round-bottom flask equipped with a condenser, an addition funnel with an equalizing tube, a heating mantle, and a magnetic stirrer. To this flask, 100 mL 1,4-dioxane was added followed by 7 mL of an (aqueous) 3.1 mol L⁻¹ HCl solution. The mixture was heated to approximately 70–80 °C, and then 45 mL of a 0.50 mol L⁻¹ TMS/1,4-dioxane solution was added dropwise over a period of 15–20 min. The mixture was then gently refluxed for approximately 1 h, and the product was centrifuged and washed consecutively with 50 mL portions of 20/80 water/THF, THF, and diethyl ether (twice with each solvent). The final product was dried at room temperature and then in a vacuum oven at 110 °C for 6 h or more.



Scheme 1. Synthetic route for Pylm, immobilization and preparation of the catalysts.

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