



# Preparation of Pd/C designed for chiral modified catalyst: Comparison with Pd/TiO<sub>2</sub> in enantioselective hydrogenation of $\alpha$ -phenylcinnamic acid

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## ABSTRACT

Enantioselective hydrogenation of  $\alpha$ -phenylcinnamic acid was investigated on Pd/C catalysts prepared in our laboratory to compare activity and selectivity with those on commercial Pd/C and Pd/TiO<sub>2</sub> catalysts. The Pd/C catalysts after the 353 K-H<sub>2</sub>-pretreatment exhibited satisfactory and comparable performances obtained with commercially available best ever Pd/C by optimizing catalyst preparation. In contrast to Pd/TiO<sub>2</sub>, a high loading of Pd is not necessary with Pd/C, but only 5% loading on a certain activated carbon was found to result in high e.e. It is suggested that the optimum size or size-distribution of Pd metal particle are different between the two supports, suggesting a support effect of this catalyst system.

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## 1. Introduction

Cinchonidine (CD)-modified palladium catalyst is an asymmetric heterogeneous catalyst for hydrogenation of olefins, and has been studied with Pd/TiO<sub>2</sub> as the best catalyst for the modification since Nitta introduced it in 1994 [1]. Among several different types of applicable substrates,  $\alpha$ -phenylcinnamic acid (PCA) is a representative substrate, and the catalyst and hydrogenation conditions were fine tuned with this substrate to result in 72% enantiomer excess (e.e.) of (2S)-2,3-diphenylpropionic acid [2].

Recently, the highest e.e. was renewed with a high metal-loaded 38%Pd/TiO<sub>2</sub> prepared by the modified method, and under specific conditions (high CD/substrate ratio at 288 K) the e.e. value reached 91% [3]. Detailed study on the Pd/TiO<sub>2</sub> catalysts indicated that low metal dispersion (5–10%) or a large Pd metal particle size (up to 3 nm) is a key factor to obtain the product in high e.e.

**Abbreviations:** Pd/C, palladium supported on activated carbon; Pd/TiO<sub>2</sub>, palladium supported on rutile titania; CD, cinchonidine; PCA, phenylcinnamic acid; % e.e., enantiomer excess of product in percent;  $r_0$ , reaction rate evaluated by the hydrogen uptake at a 25% conversion of PCA (hydrogen consumption in mmol per gram catalyst and per reaction time in hour); G-60, activated carbon supplied by Darco; CGSP, activated carbon supplied by Norit; S-51, activated carbon supplied by Darco; Pd/C-A, powder type activated carbon supplied by Nacalai Tesque; Pd/C-B, granular type activated carbon supplied by Nacalai Tesque; wet dioxane, 2.5% (v/v) water-containing dioxane.

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Another choice of Pd catalysts is commercial Pd/C catalysts, which generally have higher catalytic activity than Pd/TiO<sub>2</sub> due to their higher metal dispersion [4], and of course, their use is advantageous in its handiness and reproducibility. Pd/C was first reported to give only 30.5% e.e. [5], but later on, the e.e. was improved to 49% by using an eggshell type Pd/C [6]. Addition of sub-stoichiometric benzylamine to the reaction mixture was another finding to obtain the higher e.e. [7]. An important progress in dealing with the poor product e.e. with Pd/C was made by the discovery of a pretreatment method; that is, an H<sub>2</sub>-pretreatment at 353 K in a solution prior to the CD-modification [8]. The pretreatment was effective irrespective of different types of Pd/C to give the improved e.e. values of 82%, 81%, and 76% with STD type 5%Pd/C, AER type 5%Pd/C (both supplied by N.E. Chemcat), and 10%Pd/C (Aldrich), respectively [9,10].

Although CD-modified Pd/C and Pd/TiO<sub>2</sub> catalysts both show high selectivity for the enantioselective hydrogenation of PCA, the characteristics of these Pd/C catalysts are apparently different from those of Pd/TiO<sub>2</sub>; especially, the dispersions of Pd metal are very high with Pd/C (76% and 67% for STD and AER, respectively [9,10]), while the dispersion on Pd/TiO<sub>2</sub> catalysts is considerably low, 5–20% to show comparable selectivity [3,11–13]. To understand the different characteristics between Pd/C and Pd/TiO<sub>2</sub>, Pd/C catalysts have not been sufficiently studied up to now. Rather, commercial Pd/C catalysts are designed to have specific properties for certain reactions, but not for the enantioselective hydrogenation of PCA. The present report deals with the enantioselective hydrogenation of PCA with Pd/C catalysts prepared in our laboratory (prepared Pd/C), which were also expected to reach or even exceed the best commercial Pd/C as well as Pd/TiO<sub>2</sub>.