



Short Communication

Highly active and selective catalytic transfer hydrogenolysis of α -methylbenzyl alcohol catalyzed by supported Pd catalystHui Mao^a, Xuepin Liao^{a,b,*}, Bi Shi^{a,b,*}^a Department of Biomass Chemical and Engineering, Sichuan University, Chengdu, 610065, PR China^b National Engineering Laboratory of Clean Technology for Leather Manufacture, Sichuan University, Chengdu, 610065, PR China

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ABSTRACT

A novel supported Pd catalyst was synthesized by using plant tannin grafted collagen fiber as the supporting matrix. The as-prepared Pd catalyst was subsequently used for the catalytic transfer hydrogenolysis of α -methylbenzyl alcohol. Due to the fibrous morphology of collagen fiber and the well dispersed Pd nanoparticles anchored by tannins, the as-prepared Pd catalyst showed superior activity for the catalytic transfer hydrogenolysis of α -methylbenzyl alcohol when compared with the Pd catalyst supported on inorganic oxides. Moreover, the as-prepared Pd catalyst can be reused at least 6 times without significant loss of activity and selectivity, suggesting a satisfied reusability.

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1. Introduction

Catalytic transfer hydrogenolysis (CTH) is an important synthetic technique, which has been widely used in biomass conversion [1–3], pharmaceutical production [4,5] and organic synthesis [6–8]. By using organic compound as hydrogen donor, CTH can be conveniently carried out under mild conditions, which exhibits distinct advantages over the conventional hydrogenolysis methods that need to be performed with molecular hydrogen at high pressure. In addition, CTH is available for various functional groups including alcohol, halo, nitro and benzyl [9–13], thus providing an environmental benign synthetic route for a large number of organic compounds.

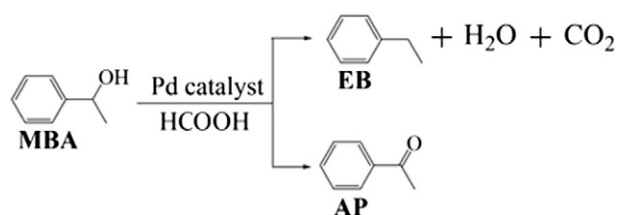
In general, noble metals, such as palladium [6,7], platinum [14] and nickel [15], have been employed as the catalysts in CTH, and those metals were often immobilized onto insoluble matrices to improve their reusability. Inorganic oxides with high specific surface area are commonly used as the supporting matrices, including active carbon, γ -alumina and silica etc. [16]. Unfortunately, those immobilized metal species often suffered from a reduced catalytic activity due to their poor distribution with aggregation. Furthermore, the metal species may also be leached into the solvent during reaction owing to the weak association with supporting matrices, which inevitably leads to a decreased activity when the catalyst was recycled. Ideally, the metal species should be stably immobilized onto the supporting matrix via

suitable interaction, and the metal species are also need to be highly dispersed on the surface of supporting matrix. As a consequence, the design of supporting matrix becomes the crucial factor for preparing noble metal catalyst with high activity and stability for CTH reaction.

Our previous research showed that collagen fiber was able to react with plant tannins to prepare adsorbents, which were highly effective for the adsorptive recovery of Pd²⁺ and Pt²⁺ from aqueous solutions [17]. Moreover, Pd²⁺ and Pt²⁺ absorbed by the adsorbent can be desorbed using diluted acid solution, indicating that the interaction of Pd²⁺/Pt²⁺ with tannin is mild. In addition, the fibrous morphology of collagen fiber can considerably decrease the mass transfer resistance, resulting fast adsorption rate. Based on unique characteristics of the fibrous adsorbent, we proposed herein a feasible strategy for synthesis of highly active and recoverable heterogeneous Pd catalyst for CTH reaction, that is the use of plant tannins grafted collagen fiber as the supporting matrix to prepare heterogeneous supported Pd nanoparticles catalyst. In this supporting matrix, the phenolic hydroxyls of plant tannins act as the anchors of Pd nanoparticles, thus ensuring a high dispersion and stability of Pd nanoparticles. Additionally, the low mass transfer resistance nature of the fibrous supporting matrix should be also beneficial for the CTH reaction performance, resulting in a higher catalytic activity. At present investigation, α -Methylbenzyl alcohol (MBA) was employed as model compound to study the activity and selectivity of the as-prepared Pd catalyst in CTH reaction of alcohol (C—OH bond). As shown in Scheme 1, the target product in CTH of MBA was ethylbenzene (EB) while acetophenone (AP) may also be formed as the by-product. We therefore systematically investigated the effects of various experimental conditions on the

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Scheme 1. The disproportionation-type reaction of MBA during the CTH process.

activity and selectivity of the as-prepared Pd catalyst in CTH of MBA, such as water content in reaction medium, type of hydrogen donor and reaction temperature. For comparison, Pd/C, Pd/SiO₂, and Pd/Al₂O₃ catalysts were also used in CTH of MBA under the same conditions.

2. Experimental

2.1. Materials

PdCl₂, formic acid, NaBH₄, and other chemicals were all analytical reagents and purchased from Sigma-Aldrich Corporation, which were used as received without further purification. Pd/C (2.0%) and MBA (97%) was purchased from Alfa Aesar. Collagen fiber (CF) was purchased from Institute of Chemical Industry of Forest Product (China). Black wattle tannin (BT), a typical condensed tannin, was

provided by the plant of forest product in Guangxi province (China). Pd/SiO₂, and Pd/Al₂O₃ were prepared by conventional impregnation methods (see supporting information).

2.2. Preparation and characterization of Pd nanoparticles supported on black wattle tannin grafted collagen fiber (Pd–BT–CF)

3.0 g of BT was dissolved in 100.0 mL of deionized water, and then 5.0 g of CF was added. The resultant mixture was stirred at 298 K for 2.0 h. Then, 50.0 mL of glutaraldehyde solution (2.0%), used as bifunctional cross-linking agent, was added into the above mixture at pH 6.5, and the reaction proceeded at 318 K for 6.0 h. Subsequently, the product was filtrated, fully washed with deionized water and dried in vacuum at 308 K for 12.0 h, and then the black wattle tannin grafted collagen fiber (BT–CF) supporting matrix was obtained. Based on ultraviolet measurement, the grafting degree of BT on BT–CF was determined to be 60% by weight.

Subsequently, 1.0 g of BT–CF was suspended in 100.0 mL of PdCl₂ solution, of which the concentration of Pd²⁺ was 2.0 × 10^{−3} mol/L. After the solution pH was adjusted to 4.5, the mixture was stirred at 303 K for 8.0 h, allowing the chelating adsorption of Pd²⁺ on BT–CF. Then, the mixture was filtrated and fully washed with deionized water. The collected intermediate product was reduced by 20.0 mL of 0.1 M NaBH₄ aqueous solution, filtrated, and successively washed with deionized water and ethanol. The loading amount of Pd on BT–CF was determined to be 2.0% in weight.

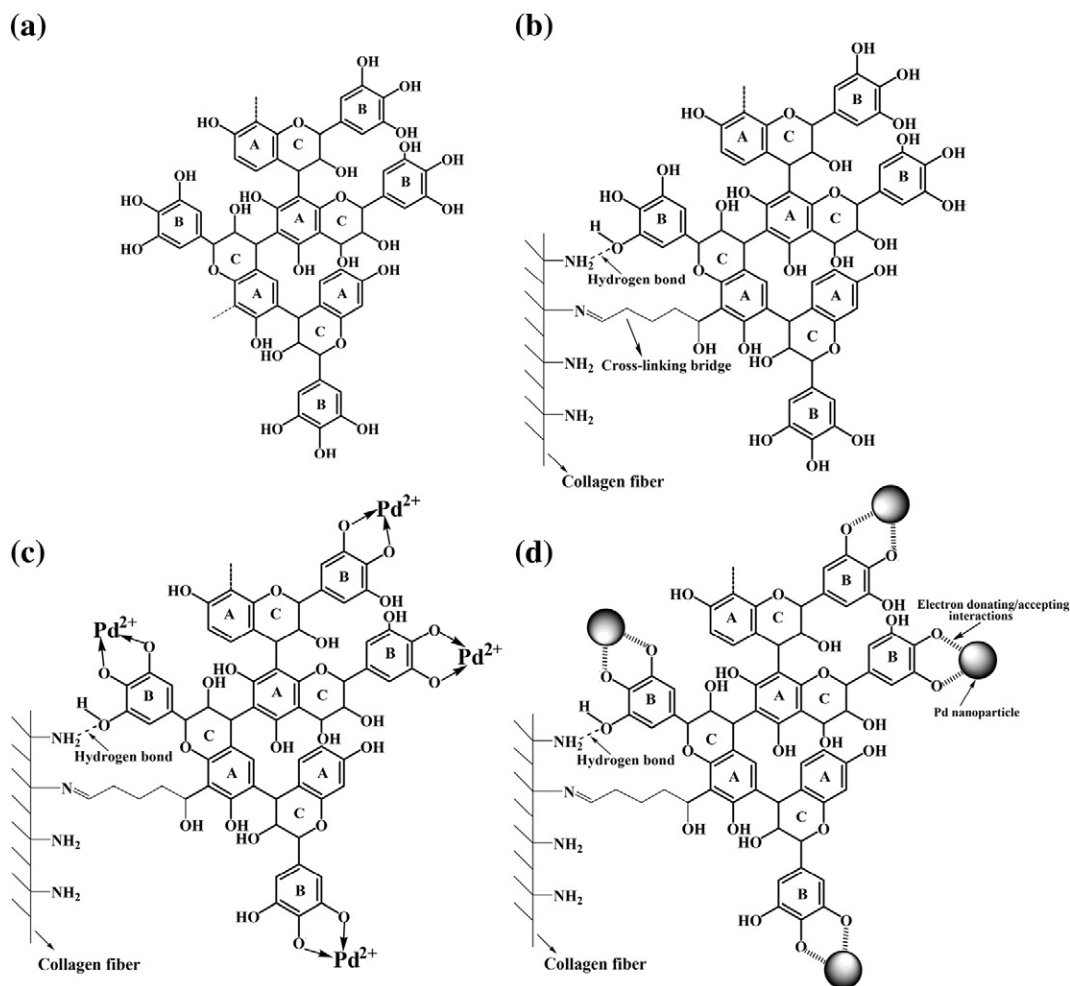


Fig. 1. The molecular structure of BT, and the proposed preparation mechanism of the Pd–BT–CF catalyst.

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