



## **Using collagen fiber as carrier and stabilizer to prepare heterogeneous palladium (Pd) nanoparticle catalyst and its application in catalytic hydrogenation of olefins**

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### **Abstract**

Collagen fiber (CF) is mainly used as the raw material in leather manufacture. However, collagen fiber, as one of the abundant natural biomass, has a potential application used as carrier and stabilizer to prepare heterogeneous catalysts due to its special chemical structure and spatial structure. Herein, black wattle tannin-grafted collagen fiber was used as carrier and stabilizer to prepare heterogeneous BWT-CF immobilized palladium nanoparticle (Pd-BWT-CF) catalyst. Subsequently, Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS), and Transmission Electron Microscopy (TEM) were used to characterize the as-prepared heterogeneous Pd catalyst. It was found that this novel catalyst exhibited an excellent performance in the heterogeneous hydrogenation of a series of olefins. For example, the initial TOF of the as-prepared Pd-T-CF catalyst for styrene hydrogenation was as high as 1834 mol.mol<sup>-1</sup>.h<sup>-1</sup>. As a consequence, this present investigation suggested that the tannin-grafted collagen fiber is suitable to be used as carrier and stabilizer for preparing heterogeneous Pd catalysts.

**Keywords:** Collagen fiber; vegetable tannin; heterogeneous Pd catalyst; hydrogenation; high activity

### **1. Introduction**

In leather industry, vegetable-tanned leather is generally produced by reacting raw hides with different kinds of vegetable tannins. As we know, the reaction mechanism involved in this manufacturing process was hydrophilic and hydrophobic interactions of raw hides with the vegetable tannins. In details, the raw hides are mainly composed of collagen fibers, which can form multiple hydrogen bonds with the phenolic hydroxyls of vegetable tannins, and also interact with the aromatic backbones of tannins by the formation of hydrophobic bonds.<sup>[1]</sup> Due to the high affinity to collagen fiber, vegetable tannins can react with raw hides to produce various vegetable-tanned leathers.

On the other hand, we also focus on the chemical properties of vegetable tannins. Vegetable

tannins have abundant phenolic hydroxyls on its molecular structures, which are able to chelate with metal ions.<sup>[2,3]</sup> Based on those properties of tannins, vegetable-aluminum combination tanning method has been successfully developed in leather industry to produce high quality leathers.<sup>[4]</sup> In addition to  $\text{Al}^{3+}$ , tannins are actually able to chelate with various metal ions, especially for those with empty orbits, like transition metal ions.

It is well known that transition metals have been widely utilized as catalysts for the synthesis of organic compounds.<sup>[5,6]</sup> At present, the preparation of highly active heterogeneous catalysts is one of the most attracting research interests in catalysis field. To achieve this desirable goal, the choosing of supporting matrix is essentially important because the supporting matrix plays a crucial role in stabilization of metal species and mass transfer of catalytic reaction. As described above, collagen fibers are the main components of raw hides, which have well defined fibrous morphology. According to the literature,<sup>[7]</sup> fibrous catalysts have distinct advantages of geometrical flexibility and low mass transfer resistance when used for liquid-phase or three-phase reactions. Therefore, we presume that, if collagen fiber prepared from raw hides can be used as the supporting matrix to immobilize transition metals, the obtained heterogeneous catalysts would be highly active in catalytic reactions. Fortunately, tannins have high reactivity toward various metals, and high affinity to collagen fibers. Moreover, tannins are able to be chemically bonded with collagen fiber using aldehydes as cross-linking agents.<sup>[8]</sup> Therefore, it is feasible in principle to prepare a novel supporting matrix by the chemical grafting of tannins onto collagen fiber. The resultant tannin-grafted collagen fiber (T-CF) matrix could then be used as carrier and stabilizer to prepare heterogeneous transition metal catalyst.

To confirm our hypothesis herein, black wattle tannin, a typical condensed tannin, was grafted onto collagen fiber by using glutaraldehyde as the cross-link agent. Then,  $\text{Pd}^{2+}$  (a commonly used transition metal catalyst) was absorbed onto the obtained matrix, followed by  $\text{NaBH}_4$  reduction. As a result, a novel heterogeneous Pd catalyst was prepared, which was subsequently characterized by Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS), and Transmission Electron Microscopy (TEM). To evaluate the activity of the as-prepared Pd catalyst, catalytic hydrogenation of a series of olefins were performed. In addition, the reusability of the catalyst was also investigated.

## 2. Materials and method

### 2.1 Materials

Collagen fiber (CF) and black wattle tannin (BWT) were purchased commercial supplier and used without further purification.  $\text{PdCl}_2$ ,  $\text{NaBH}_4$ , and other chemicals were all analytical reagents.

### 2.2 Preparation of black wattle tannin grafted collagen fibers (BWT-CF) and Pd nanoparticles supported on BT-CF (Pd-BWT-CF)

The typical procedures for the preparation of BWT-CF were described as follows. 3.0 g of BWT 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 wt%), used as bifunctional cross-linking agent, was added into the above mixture at pH 6.5. The reactions proceed at 318 K for 6 h. Subsequently, the product was filtrated, fully washed with deionized water and dried in vacuum at 308 K for 12 h, and then the BWT-CF supports

were obtained. The grafting degree of BT on BWT-CF is determined to be 60% in weight according to ultraviolet measurement.

1.0 g of BWT-CF was suspended in 100.0 mL of  $\text{PdCl}_2$  aqueous solution, of which the concentration of  $\text{Pd}^{2+}$  was  $2.0 \times 10^{-3} \text{ M.L}^{-1}$ . After the solution pH was adjusted to 4.5. The mixture was stirred at 303 K for 8 h, allowing the chelating adsorption of  $\text{Pd}^{2+}$  on BWT-CF. Subsequently, the mixture was filtrated and fully washed with deionized water. The collected materials were reduced by 20.0 mL of 0.1 M  $\text{NaBH}_4$  aqueous solution, filtrated, and successive washed with deionized water and ethanol. Finally, the Pd-BWT-CF catalyst was obtained. The Pd amount on catalyst was determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, PerkinElmer Optima 2100DV, U. S.).

### 2.3. Characterization of the catalyst

The surface morphology of Pd-BWT-CF was observed by Scanning Electron Microscopy (SEM, JEOL LTD JSM-5900LV). X-ray Photoelectron Spectroscopy (XPS, Kratos XSAM-800, UK) analyses were conducted by employing Mg Ka Xradiation ( $h\nu = 1253.6 \text{ eV}$ ) and a pass energy of 31.5 eV. The observation of Pd nanoparticles on BWT-CF was conducted using Transmission Electron Microscopy (TEM, Tecnai G<sup>2</sup> F20 S-TWIN, U.S.) operated at an acceleration voltage of 200 kV.

### 2.4. Catalytic hydrogenation of olefins

Catalytic hydrogenations of olefins were performed in a 50 mL stainless steel autoclave reactor equipped with a motor-driven stirrer. 25.0 mL of methanol was added into the reactor, and then a proper amount of the Pd-BWT-CF catalyst was added into the reactor, followed by the addition of determined amount of substrate. Subsequently, the reactor was purged with helium at 0.3 MPa three times in order to replace the air in the reactor. After the reactor was heated to the reaction temperature, the hydrogen was introduced at the set pressure and the reaction started. The reaction products were analyzed by gas chromatography.

## 3. Results and discussion

### 3.1 Characterization of catalyst

Fig. 1a shows the SEM image of the Pd-BWT-CF catalyst, which appear as fiber bundles with a diameter of  $10 \pm 2.0 \text{ }\mu\text{m}$ . This observation suggested that the fibrous morphology of natural collagen fiber is well preserved in the Pd-BWT-CF catalyst. As we know, fibrous catalysts are more suitable than powder and monolithic counterparts in liquid-phase or three-phase reactions due to their better geometrical flexibility and low mass transfer resistance.<sup>[7]</sup> Therefore, a high catalytic activity of the Pd-BWT-CF catalyst can be expected in the following catalytic hydrogenation of olefin. Fig. 1b is the TEM image of the Pd-BWT-CF catalyst. It can be observed that due to the stabilization effect of BWT, spherical Pd nanoparticles are well dispersed in the catalyst without any aggregation, of which the average diameter is about 4.0 nm. Hence, it is reasoned that the well dispersion and small particle size of the Pd nanoparticles can also ensure a high catalytic activity of the Pd-BWT-CF catalyst.<sup>[9]</sup>

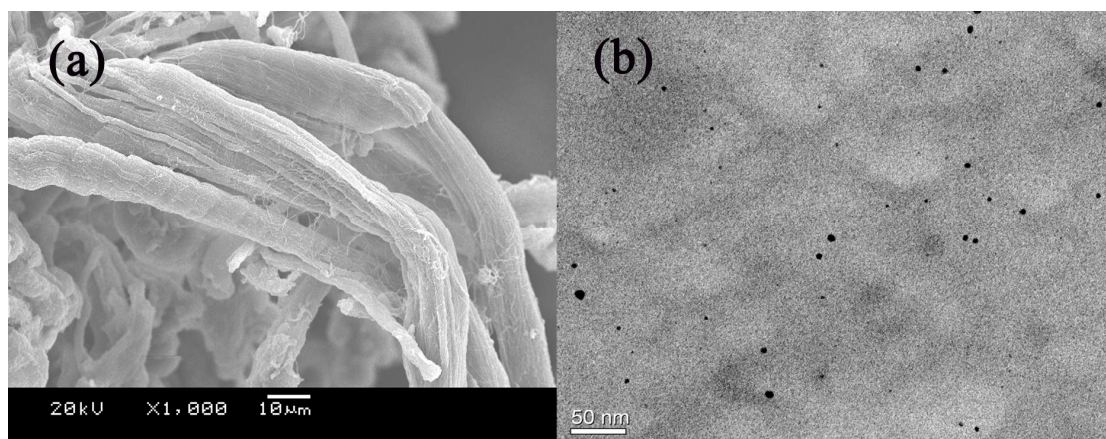


Fig. 1. SEM image (a) and TEM image (b) of the Pd-BWT-CF catalyst

Subsequently, the Pd-BWT-CF catalyst was analyzed by XPS technology. It was found that the Pd 3d peaks of Pd-BWT-CF show two pairs of doublets. A pair of doublets are located at 335.4 and 341.5 eV, which are attributed to Pd(0), and another pair of doublets are located at 338.2 and 343.1 eV, which are assigned to Pd(II).<sup>[10]</sup> These facts indicate that the Pd nanoparticles observed in the TEM image of the Pd-BWT-CF catalyst should be Pd(0) nanoparticles and/or Pd(0)-Pd(II) hybrid nanoparticles. In addition, the O 1s XPS spectra of Pd-BWT-CF catalyst exhibit a major peak at 531.7 eV and a shoulder at 537.3 eV. The major peak should be attributed to hydroxyl groups of BWT-CF support while the shoulder peak should belong to the hydroxyl oxygens that stabilize with the Pd nanoparticles. Based on the XPS analyses, the preparation mechanism of the Pd-BWT-CF catalyst is understandable, which can be expressed by the schematic graph in Fig. 2. After BWT-CF was prepared, it was able to chelate with the Pd<sup>2+</sup> via its adjacent phenolic hydroxyls. Then, the chelated Pd<sup>2+</sup> was reduced by using NaBH<sub>4</sub> as the reducing agent, which allows the formation of Pd nanoparticles. Meanwhile, the formed nanoparticles were still stabilized by the phenolic hydroxyls of BWT.

### 3.2. Catalytic hydrogenation of olefins

In general, the hydrogenation of olefins is often carried out using Pd species as the catalyst.<sup>[11]</sup> Accordingly, the catalytic hydrogenation of the Pd-BWT-CF catalyst to a series of olefins was performed, which includes allyl alcohol, acrylic acid, styrene and cyclohexene. The turnover frequency (TOF) of the Pd-BWT-CF catalyst to olefins is summarized in Table 1. It can be seen that the Pd-BWT-CF catalyst shows much higher catalytic activity for all substrates. For example, the TOF of styrene over Pd-BWT-CF catalyst is as high as 1874 mol·mol<sup>-1</sup>·h<sup>-1</sup>. In view point of practical application, it is quite necessary to evaluate the reusability of the catalyst. Thus we investigated the reusability of the Pd-BWT-CF catalyst for catalytic hydrogenation of styrene. Much to our delighted, the catalyst can be easily collected by filtration, and the TOF of the catalyst was still as high as 1402 mol·mol<sup>-1</sup>·h<sup>-1</sup>, which suggested a satisfied reusability.

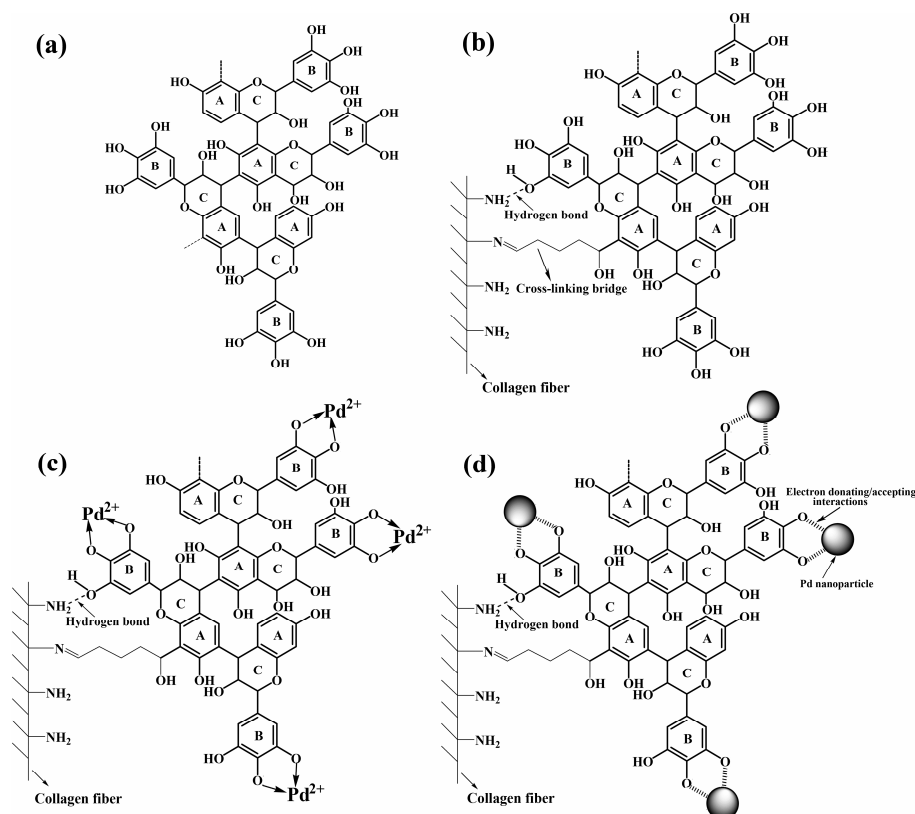


Fig. 2. The molecular structure of BT (a), and the proposed preparation mechanism of the Pd-BWT-CF catalyst (b-d).

Table 1. The activity of the Pd-BWT-CF catalyst on catalytic hydrogenation of different olefins

Substrate	Product	Molar ratio substrate/Pd	TOF ( $\text{mol} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$ )
Allyl alcohol ( <chem>C=CCO</chem> )	<chem>CCCO</chem>	1000:1	768
Acrylic acid ( <chem>C=CC(=O)O</chem> )	<chem>CCC(=O)O</chem>	1000:1	1332
Styrene ( <chem>C=Cc1ccccc1</chem> )	<chem>CCC1=CC=CC=C1</chem>	1000:1	1874
Cyclohexene ( <chem>C1=CCCCC1</chem> )	<chem>C1CCCCC1</chem>	200:1	310

#### 4. Conclusions

In this study, a novel heterogeneous Pd catalyst was prepared by using black wattle tannin-grafted collagen fiber (BWT-CF) was used as carrier and stabilizer. The as-prepared heterogeneous Pd catalyst was found to highly active in heterogeneous hydrogenation of a series of olefins. Furthermore, the catalyst can be reused without significant loss of the activity. In conclusion, collagen fiber extracted from raw hides can be used as carrier and stabilizer for

preparing heterogeneous Pd catalysts.

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