Catalytic hydrogenation of quinoline over recyclable palladium nanoparticles supported on tannin grafted collagen fibers

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ABSTRACT

Black wattle tannin (BT), a typical natural plant polyphenol, was grafted onto collagen fiber (CF) to act as the stabilizer and carrier of Pd nanoparticles, and as a result, a recyclable heterogeneous Pd catalyst (Pd-BT-CF) was synthesized. The main physicochemical properties of the Pd-BT-CF catalyst were characterized by Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS), and Transmission Electron Microscopy (TEM). It was found that the catalyst was in an ordered fibrous state, on which Pd nanoparticles with diameter of 4 nm were highly dispersed. Subsequently, the Pd-BT-CF catalyst was employed for the hydrogenation of quinoline. The influences of reaction time, temperature, H_2 pressure and solvent on the catalytic hydrogenation of quinoline were systematically investigated. The experimental results suggested that the Pd-BT-CF catalyst exhibited high catalytic activity and selectivity for quinoline hydrogenation. The average turnover frequency (TOF) of Pd-BT-CF was as high as 165.3 mol mol^{-1} h^{-1}, and the selectivity to 1,2,3,4-tetrahydroquinoline was 100% when the reaction was carried out at 60 °C and 2.0 MPa for 1.0 h. Moreover, the activity and selectivity of Pd-BT-CF catalyst were not significantly reduced after being reused 6 times, exhibiting a satisfied reusability. Further XPS, Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and TEM analyses confirmed that the Pd species were stabilized by the hydroxyls of BT-CF, which prevented the aggregation and leakage of Pd during the reaction.

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1. Introduction

1,2,3,4-Tetrahydroquinoline (py-THQ) is an important organic intermediate for the synthesis of alkaloids, agrochemicals, dyes, and pharmaceuticals [1]. Organic synthesis (such as the Diels–Alder approach) is conventionally used for the preparation of py-THQ [2], but organic synthesis often suffers from the problems of complex synthetic route and/or low product yield. To overcome these disadvantages, catalytic hydrogenation of quinoline is established in order to conveniently obtain py-THQ [3].

Catalytic hydrogenation of quinoline is often carried out using homogeneous precious metal catalysts, such as Rh [4–6], Ir [7–10], Os [11] and Ru [12,13]. Those homogeneous precious metal catalysts exhibit high activity and selectivity during the catalytic reaction, but the separation of metal catalysts from the reaction system is quite difficult, and the resultant product may also be contaminated by the remaining heavy metals. Therefore, the development of heterogeneous precious metal catalysts with superior reusability is one of the most attractive research interests in recent years.

The heterogeneous precious metal catalysts are generally prepared by supporting nanoparticles onto inorganic supports, such as activated carbon, ZrO_2, and Al_2O_3 [14–18]. Compared with homogeneous precious catalysts, the heterogeneous counterparts can be easily recovered by simple filtration, thus exhibiting considerably improved reusability. However, the metal precursors often migrate to the outer surface of the inorganic supports upon drying, which leads to a poor distribution and/or partial expulsion of metal particles after reduction. Furthermore, the metal nanoparticles may be leached out during the recycles, owing to the weak interaction of metal nanoparticles with the supports [19].

A possible way to improve the reusability of heterogeneous precious metal catalysts is to use organic polymers with multifunctional groups as the supports, of which the functional groups are able to stabilize the metal precursors via geometry and/or electron interactions. Sanchez et al. [20] have synthesized heterogeneous Ru catalyst by using 4-vinypyridine polymer as the support. Due to the presence of N-heterocycle in the polymer, the Ru nanoparticles are well stabilized, and as a result, the loss of catalyst activity is
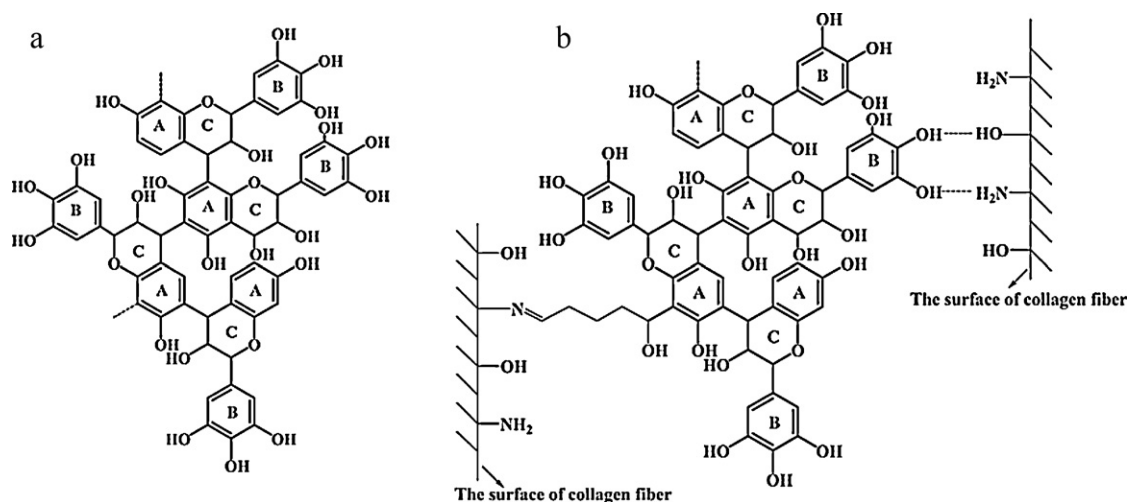
Fig. 1. The structure of BT (a) and the possible grafting mechanism of BT onto the CF (b).

substantially suppressed during the recycles. However, the activity of the catalyst is not satisfied enough and still needs to be improved.

Tannins, one of the most abundant biomasses, are the soluble polyphenols extracted from plants. According to the chemical structures, tannins are classed into condensed tannins and hydrolyzed tannins. Hydrolysable tannins yield gallic acid or ellagic acid when hydrolyzed by acid, base or enzyme. Tannic acid is a representative hydrolysable tannin. Condensed tannins are the polymerized products of flavan-3-ols and/or flavan-3,4-diols. Black wattle tannin is a kind of typical condensed tannins, as shown in Fig. 1a. The general characteristics of tannins are that they are able to chelate with many kinds of metal ions through their dense ortho-phenolic hydroxyls [21]. In our previous researches, tannins were grafted onto collagen fiber using aldehyde as the cross-linking agent to prepare adsorbents, which were able to effectively absorb Pd^{2+} from aqueous solutions [22]. In addition, we also focus on the fibrous morphology of collagen fiber, which is benefit for the catalytic reaction to proceed owing to its better geometrical flexibility and low mass transfer resistance compared with the powder and monolithic counterparts [23]. Based on those results, we make a hypothesis that, if the absorbed Pd^{2+} on tannin-grafted collagen fiber can be reduced by the addition of reductant and stabilized by the phenolic hydroxyls of tannin-grafted collagen fiber, a recyclable heterogeneous Pd catalyst could be prepared for the catalytic hydrogenation of quinoline.

In this study, a recyclable heterogeneous Pd catalyst was prepared by the adsorption of Pd^{2+} onto black wattle tannin grafted collagen fiber, followed by a chemical reduction. Accordingly, the objective of the present research was to investigate the activity and reusability of Pd-BT-CF catalyst for the catalytic hydrogenation of quinoline. For comparison, a commercial Pd-C catalyst was used as control under the same reaction conditions.

2. Experimental

2.1. Materials

Black wattle tannin (BT), a typical condensed tannin, was used in this study, which was purchased from plant of forest product in Guangxi province (China). Cow skin collagen fiber (CF) was purchased from institute of chemical industry of forest product (China). $PdCl_2$, $NaBH_4$, Pd/C (2.0 wt%) and other chemicals were all analytical reagents and purchased from Sigma–Aldrich cooperation.

2.2. Preparation of black wattle tannin grafted collagen fibers (BT-CF)

The typical procedures for the preparation of BT-CF were described as follows. 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 wt%), used as bifunctional cross-linking agent, was added into the above mixture at pH 6.5. 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 BT-CF support was obtained. Based on ultraviolent measurement, the grafting degree of BT on BT-CF was determined to be 60% in weight. Fig. 1b illustrates the preparation mechanism of BT-CF support. The glutaraldehyde acts as a bridge linkage to chemically graft BT onto CF via the Mannich reaction. In addition, the multiple hydrogen bonds may also be formed between BT (–OH) and CF (–OH and $–NH_2$), contributing to the stabilization of BT-CF support.

2.3. Preparation of Pd nanoparticles supported on BT-CF (Pd-BT-CF)

1.0 g of BT-CF was suspended in 100.0 mL of $PdCl_2$ solution, of which the concentration of Pd^{2+} was 2×10^{-3} M L^{-1}. After the solution pH was adjusted to 4.5, the mixture was stirred at 303 K for 8.0 h, allowing the chelate adsorption of Pd^{2+} on BT-CF. Subsequently, the mixture was filtrated and fully washed with deionized water. The collected intermediate product was reduced by 20.0 mL of 0.1 M $NaBH_4$ 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 by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, PerkinElmer Optima 2100DV, U.S.).

2.4. Characterization of catalyst

The surface morphology of Pd-BT-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 eV) and a pass energy of 31.5 eV. All of the binding energy peaks of XPS spectra were calibrated by placing the principal C 1s binding energy peak at 284.7 eV. Peaks from all high resolution core spectra were fitted with XPSPEAK 4.1 software, using mixed Gaussian–Lorentzian functions. The size and distribution of Pd

Fig. 2. SEM image of Pd–BT–CF catalyst.

Fig. 3. TEM image of Pd–BT–CF catalyst.

nanoparticles on BT-CF were determined using Transmission Electron Microscopy (TEM, Tecnai G^2 F20 S-TWIN, U.S.) operated at an acceleration voltage of 200 kV. The Pd-BT-CF catalyst was incorporated in liquid epoxy resin, and then cut into thin slices by using an ultramicrotome. These slices were deposited on copper grids for TEM observation.

2.5. Catalytic hydrogenation of quinoline

Catalytic hydrogenations were performed in a 50.0 mL Parr stainless steel autoclave reactor (4597, Parr Instrument Co, U.S.) equipped with a motor-driven stirrer and a Parr 4843 process controller that was able to control the reaction temperature and stirrer speed. Before the reaction, the solvent (H_2O, alcohols, ethers or alkanes), the Pd-BT-CF catalyst and the quinoline were added into the reactor. Subsequently, the reactor was purged with helium at 0.3 MPa three times in order to replace the air in the reactor. The reactor was heated to the reaction temperature, and then the hydrogen was introduced at the set pressure, allowing the starting of the reaction. The reaction mixtures were sampled and analyzed by gas chromatography using SE-30 column (30 m × 0.25 mm × 0.25 μm) and FID detector. Each experiment was repeated at least twice in order to ensure reproducibility, and the corresponding average value was adopted.

3. Results and discussion

3.1. Characterization of catalyst

The SEM image of Pd-BT-CF is shown in Fig. 2. It is clearly observed that the Pd-BT-CF catalyst is in ordered fibrous state. According to the literature [23], fibrous catalysts have better geometrical flexibility and low mass transfer resistance compared with the powder and monolithic counterparts, which make them more suitable for the liquid-phase or three-phase reactions. From this point, a high catalytic activity of the Pd-BT-CF catalyst can be expected. Actually, some fibrous catalysts have been successfully designed in order to improve the activity of the catalyst. For example [24], Lilja et al. used fibrous polymer as the support to prepare supported sulphonic acid catalyst, and the obtained fibrous catalyst exhibited higher activity as compared with conventional non-fibrous catalyst.

The TEM image of Pd-BT-CF catalyst is shown in Fig. 3. The Pd nanoparticles are well dispersed in the catalyst without any aggregation, where the average d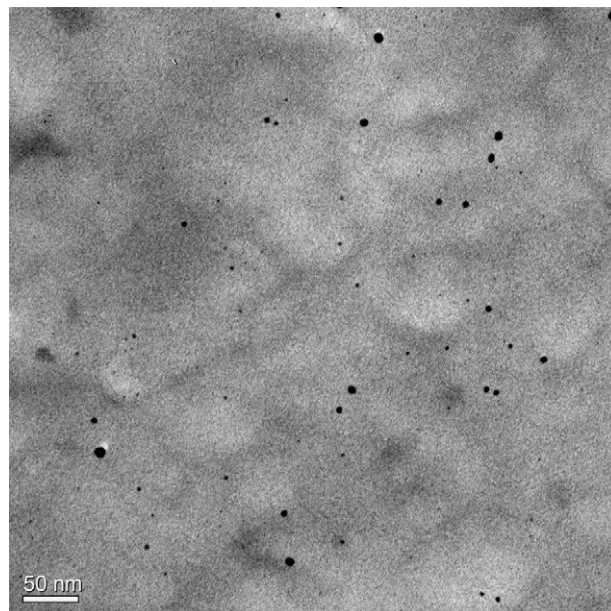iameter of the Pd nanoparticles is about 4.0 nm. By assuming that these Pd nanoparticles are spherical, the dispersion of Pd nanoparticles can roughly be calculated by the following equation [25]

$$\text{Pd dispersion} = \frac{1.12}{\text{diameter of Pd nanoparticles (nm)}}$$

Accordingly, the dispersion value of Pd nanoparticles in Pd-BT-CF catalysts was determined to be 28.0%, which suggested that the Pd nanoparticles in Pd-BT-CF have a large number of active surface Pd atoms for the H_2 chemisorption. Therefore, a high catalytic activity of Pd-BT-CF catalyst for quinoline hydrogenation can also be expected when considering the high dispersion of Pd nanoparticles.

The obtained Pd-BT-CF catalyst was then characterized by XPS analysis. As shown in Fig. 4, the Pd 3d XPS spectra of Pd-BT-CF shows two pairs of doublets from the spin-orbital splitting of the 3d 7/2 and 3d 5/2. The doublets observed at 335.4 and 341.5 eV are attributed to Pd(0) while those at 338.2 eV and 343.1 eV are assigned to Pd(II) [26]. These results indicate that the Pd nanoparticles observed in the TEM image of the Pd-BT-CF catalyst should
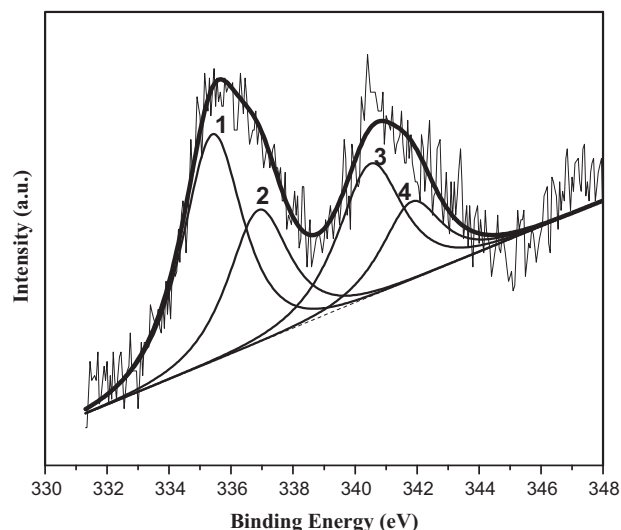

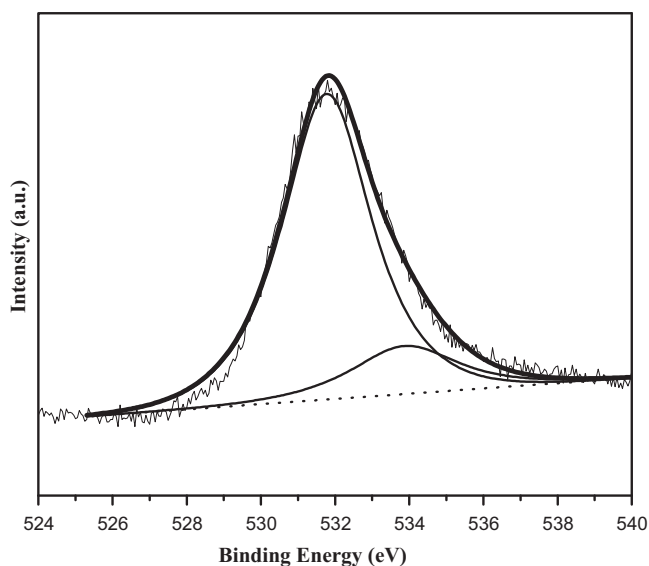**Fig. 4.** Pd 3d XPS spectra of Pd-BT-CF catalyst.

Fig. 5. O 1s XPS spectra of Pd-BT-CF catalyst.

be Pd(0) nanoparticles and/or Pd(0)-Pd(II) hybrid nanoparticles. Although the Pd(II) species in Pd-BT-CF catalyst was not so highly active for the hydrogenation reaction to proceed, the quite small Pd nanoparticles should still be effective in catalytic hydrogenation of quinoline owing to their well dispersion. In Fig. 5, the O 1s XPS spectra of Pd-BT-CF catalyst exhibits a major peak at 531.7 eV and a shoulder at 533.9 eV. The major peak can be attributed to the hydroxyl groups of BT-CF while the shoulder peak should belong to the hydroxyl oxygens that stabilize the Pd nanoparticles by donating their electrons [27].

3.2. Catalytic hydrogenation of quinoline

3.2.1. Effects of reaction time

As presented in Fig. 6, the conversion yield of quinoline significantly increases with the increase of reaction time, and gradually reaches the equilibrium at 60 min. The average turnover frequency (TOF) of the catalyst is as high as 165.3 mol mol^{-1} h^{-1}, which is higher than that of commercial Pd-C catalyst (130.0 mol mol^{-1} h^{-1}). Compared with other reported polymer stabilized precious metal catalyst, the activity advantage of as-prepared Pd-BT-CF catalyst is still obvious [20], which may be attributed to the fibrous morphology of the catalyst and the quite small Pd nanoparticles. On the other hand, the obtained hydrogenation product was py-THQ while no other hydrogenation products of quinoline (bz-THQ and DHQ)
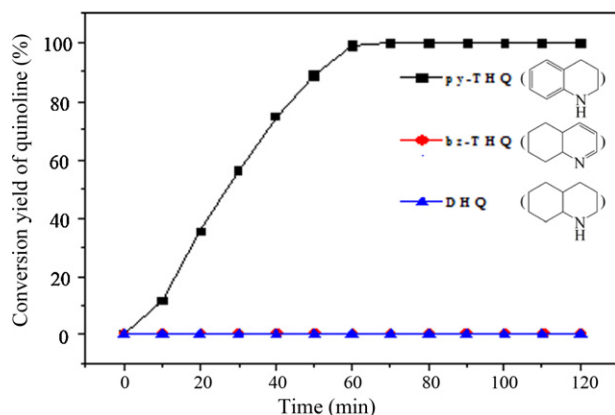

Fig. 6. Effect of reaction time on the catalytic activity and selectivity of Pd-BT-CF.

were detected, which suggested the high selectivity of Pd-BT-CF catalyst, thus avoiding the complex separation of final products. On the contrary, the selectivity of commercial Pd-C catalyst to py-THQ is quite poor, which is as low as 84%.

Based on Fish's researches [28–32], the product of quinoline hydrogenation is depended on the adsorption types of quinoline over precious metal catalyst. The py-THQ would be the target hydrogenated product if the quinoline molecule is adsorbed on the metal catalyst through its N-heterocycle while the bz-THQ should be the major hydrogenation product once the quinoline molecule is absorbed on the catalyst via its benzene ring. As for our catalyst prepared herein, the py-THQ is the only hydrogenation product, which suggests that the quinoline molecule should be exclusively absorbed on the Pd nanoparticles of Pd-BT-CF catalyst via its N-heterocycle. To specifically explain the exclusive adsorption behaviors is difficult, but one reasonable explanation is possible when considering the micro-environment of Pd nanoparticles stabilized by BT molecule. The phenolic hydroxyls of BT molecule are interact with Pd nanoparticles via the electron donating/accepting, which leads to a relatively high concentration of phenolic hydroxyls on Pd nanoparticles. As a result, the adsorption of N-heterocycle of quinoline onto the Pd nanoparticles is significantly promoted by the formation of multiple hydrogen bonds between the N-heterocycle of quinoline molecule and the phenolic hydroxyls of BT around Pd nanoparticles. Subsequently, those quinoline molecules are interacted with the actived H produced over Pd nanoparticles, resulting in the formation of py-THQ (Fig. 7b and c). Actually, other researchers also found that the N-heterocycle of quinoline can interact with the hydroxyls of support via the formation of hydrogen bond [17], and our FTIR data (Supporting information 1) also showed that the hydrogen bonds were indeed formed between the quinoline and the hydroxyls of BT in Pd-BT-CF due to that the hydroxyl peak of Pd-BT-CF located at 3342.2 cm^{-1} was broaden after mixed with quinoline [33]. Based on above explanations, it is understandable for the relatively poor selectivity of commercial Pd-C catalyst to py-THQ, which should be attributed to the diverse adsorption types of quinoline molecules over commercial Pd-C catalyst, owing to the lack of phenolic hydroxyls.

3.2.2. Effects of reaction temperature and hydrogen pressure

The effect of reaction temperature on quinoline hydrogenation was investigated, and the corresponding results were summarized in Table 1. In the temperature range of 20–60 °C, the TOF of the catalyst considerably increases along with the increase of reaction temperature, from 57.7 to 165.3 mol mol^{-1} h^{-1}. The higher temperature is beneficial for the activation of the catalyst and substrate molecule. However, the promoting effect of temperature to catalyst activity is not obvious when the reaction temperature is beyond 60 °C. Consequently, the following experiments were conducted at 60 °C. It should be noted that the TOF of Pd-BT-CF catalyst is 165.3 mol mol^{-1} h^{-1} at 60 °C and 2.0 MPa, which is much higher than those of catalysts conducted at much harsh reaction conditions [34,35].

The effect of hydrogen pressure on the activity of the Pd-BT-CF catalyst is shown in Table 2. Similar with the effect of reaction temperature, the increase of H$_2$ pressure from 1.0 to 2.0 MPa is able to promote the catalytic activity of the catalyst while no significant change of the catalyst activity is observed when further increasing the H$_2$ pressure from 2.0 to 4.0 MPa,. These facts can be explained by the influence of H$_2$ pressure to the dissolved H$_2$ in solvent. The increase of H$_2$ pressure promotes the dissolution of molecular H$_2$ in solvent, which increases the number of active atomic H produced over the Pd nanoparticles. As a result, the quinoline is easily hydrogenated, resulting in the increased TOF of the Pd-BT-CF catalyst. However, the dissolved molecular H$_2$ is limited in a given solvent, and thus, the TOF of the catalyst will not be
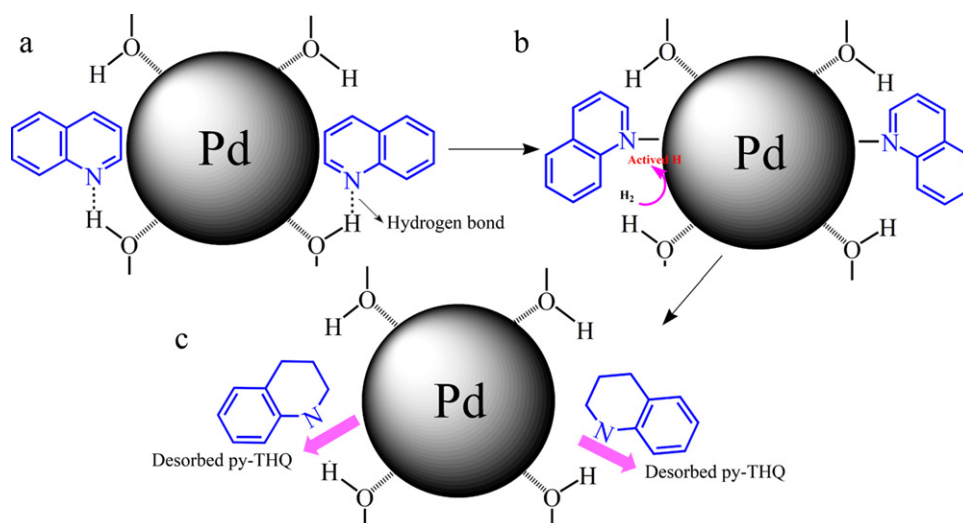
Fig. 7. The possible catalytic mechanism of quinoline over Pd-BT-CF catalyst.

Table 1
Effects of reaction temperature on the activity and selectivity of the Pd-BT-CF catalyst.[a]

Temperature (°C)	TOF (mol mol^{-1} h^{-1})	Conversion (%)	Selectivity (%)		
			py-THQ	bz-THQ	DHQ
20	57.5	34.5	100	0	0
40	124.7	74.8	100	0	0
60	165.3	99.2	100	0	0
80	166.5	99.9	100	0	0

[a] Reaction conditions: 3.0 mL H$_2$O; 2.0 MPa H$_2$ pressure; 0.032 g Pd-BT-CF (6×10^{-3} mmol Pd); 1 mmol quinoline.

Table 2
Effect of hydrogen pressure on the activity and selectivity of the Pd-BT-CF catalyst.[a]

H$_2$ pressure (MPa)	TOF (mol mol^{-1} h^{-1})	Conversion (%)	Selectivity (%)		
			py-THQ	bz-THQ	DHQ
1	131.2	78.7	100	0	0
2	165.3	99.2	100	0	0
3	166.5	99.9	100	0	0
4	166.5	99.9	100	0	0

[a] Reaction conditions: 3.0 mL H$_2$O; 60 °C; 0.032 g Pd-BT-CF (6×10^{-3} mmol Pd); 1 mmol quinoline.

changed with the increase of H$_2$ pressure once the molecular H$_2$ dissolved in solvent is saturated.

More importantly, py-THQ is the only catalytic product of quinoline, and no DHQ is formed at high H$_2$ pressure, which confirms the high selectivity of the as-prepared Pd-BT-CF catalyst. Based on the above results, the following experiments were performed under 2.0 MPa of H$_2$ pressure.

3.2.3. Effects of solvent

To investigate the effect of solvent on the activity of the Pd-BT-CF catalyst, H$_2$O, alcohol, ether and alkane were used as the solvent for quinoline hydrogenation. As shown in Table 3, the catalyst activity is significantly influenced by the use of solvent, which follows the sequence: H$_2$O > alcohol > ether > alkane. These results suggest that the solvent with stronger polarity promotes the hydrogenation of quinoline over the Pd-BT-CF catalyst, which is consistent with other reported researches [16,17,20].

3.2.4. Reusability of the Pd-BT-CF catalyst

The reusability of the Pd-BT-CF catalyst in quinoline hydrogenation was investigated. For comparison, a commercial Pd–C catalyst was used under the same conditions. After each cycle, the catalyst was recovered by filtration and washed with ethanol, and then
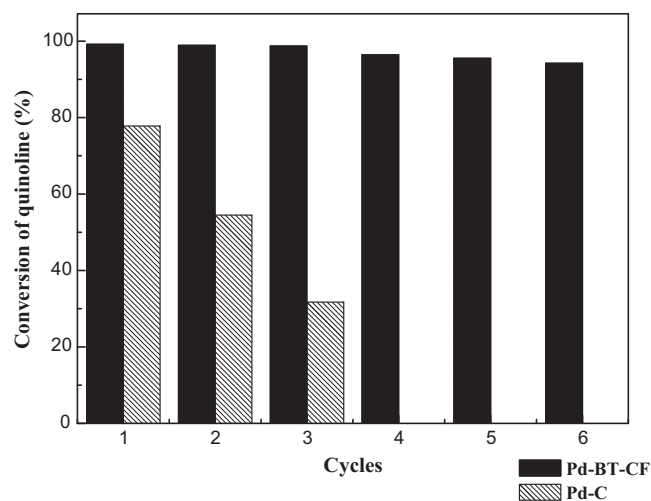

Fig. 8. Reusability of Pd-BT-CF and Pd–C in hydrogenation of quinoline (2.0 MPa H$_2$ pressure; 60 °C; 0.032 g Pd-BT-CF; 1 mmol quinoline).

Table 3
Effect of solvent on the conversion and selectivity.[a]

Solvent	TOF (mol mol^{-1} h^{-1})	Conversion (%)	Selectivity (%)		
			py-THQ	bz-THQ	DHQ
H_2O	165.3	99.2	100	0	0
CH_3OH	142.3	85.4	100	0	0
i-PrOH	92.2	55.3	100	0	0
THF	41.0	24.6	100	0	0
Cyclohexane	28.5	17.1	100	0	0

[a] Reaction conditions: 2.0 MPa H_2 pressure; 60 °C; 0.032 g Pd-BT-CF (6×10^{-3} mmol Pd); 1 mmol quinoline.

reused. As shown in Fig. 8, the activity of the Pd-BT-CF catalyst is not significant reduced after 6 times reused, exhibiting a potential to be used in practical application. On the contrary, the commercial Pd–C catalyst shows a quite poor reusability due to that the Pd–C catalyst is completely inactive for quinoline hydrogenation after used for 3 times. To investigate the reasons for the reusability of the Pd-BT-CF catalyst, we detected the leached Pd in reaction solvent by ICP-AES when using Pd-BT-CF as the catalyst. It was found that only trace amount of Pd was leached into the solvent, which was responsible for the relatively good reusability of the as-prepared Pd-BT-CF catalyst. Furthermore, the catalyst was analyzed by TEM after its 6 time recycles, and no obvious aggregation of Pd was observed. Hence, the satisfied reusability of the Pd-BT-CF catalyst should be attributed to the high stability and dispersion of the Pd nanoparticles, and we believe that these properties of the Pd-BT-C catalyst are derived from the stabilizing effect of BT-CF support.

4. Conclusions

A heterogeneous Pd catalyst was prepared by using plant tannin grafted collagen fiber as the support. Subsequently, the catalytic hydrogenation of quinoline was systematically investigated, including the effect of reaction time, temperature, H_2 pressure, and solvent. Our experimental results suggested that due to the stabilization effect of tannin to Pd nanoparticles and the fibrous morphology of the collagen fiber, the prepared Pd-BT-CF catalyst was highly active for the catalytic hydrogenation of quinoline, and can be recycled at least 6 times without significant loss of the activity.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.03.023.

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