

Bayberry Tannin as Stabilizer for the Synthesis of Highly Active and Reusable Heterogeneous Pd Catalysts and Their Application in the Catalytic Hydrogenation of Olefins

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In this study, the homogenous Pd nanoparticles (Pd NPs) were first prepared with bayberry tannin (BT) as the stabilizers. Subsequently, the obtained bayberry tannin-stabilized Pd nanoparticles (BT-Pd) were immobilized onto γ -Al₂O₃ to prepare heterogeneous γ -Al₂O₃-BT-Pd catalysts. Fourier Transformation Infrared Spectrum (FTIR) and X-ray Photoelectron Spectroscopy (XPS) analyses confirmed that the Pd NPs were well stabilized by the phenolic hydroxyl groups of BT. Transmission Electron Microscopy (TEM) observation indicated that the diameter of the Pd NPs can be effectively controlled in the range of 4.2–16.0 nm by varying the amount of BT. It is found that the γ -Al₂O₃-BT-Pd catalysts exhibit highly activity for various olefin hydrogenations. For example, the initial TOF (turnover frequency) of the γ -Al₂O₃-BT-Pd in the allyl alcohol hydrogenation is as high as 12804 mol·mol⁻¹·h⁻¹. Furthermore, the γ -Al₂O₃-BT-Pd can be reused 5 times without significant loss of activity, exhibiting a superior reusability as compared with conventionally prepared γ -Al₂O₃-Pd catalysts.

Key Words : Bayberry tannin, Pd nanoparticles, Heterogeneous catalysts, γ -Al₂O₃, Olefin hydrogenation

Introduction

As metal nanoparticles (NPs) have a large fraction of surface metal atoms due to their high surface-to-volume ratio, they have been applied as highly active catalysts in various organic syntheses, such as hydrogenation and oxidation.¹ Palladium (Pd) NP is one of the most extensively investigated metal NPs catalysts among them because of its remarkable catalytic activity.^{2,3} In general, Pd NPs are dispersed onto solid matrices, such as Al₂O₃ and zeolite, to prepare heterogeneous Pd NPs catalysts since naked Pd NPs are easy to aggregate as Pd black, which leads to a considerable decrease of catalytic activity.⁴

The impregnation method is frequently used for the preparation of heterogeneous Pd NPs catalysts. In a typical synthesis, Pd precursors are first introduced onto solid matrices by impregnation, and then reduced to Pd NPs by use of chemical reducing agents.^{5–8} Although the as-prepared heterogeneous Pd NPs catalysts could be easily recovered by filtration, their reusability need to be greatly improved because of the leakage of metal NPs that are weakly associated with the matrices.⁹ On the other hand, the impregnation method is difficult to control the size and the dispersion of metal NPs, which would significantly influence the catalytic activity in the reactions.¹⁰ As a consequence, it is necessary to find a new strategy for the preparation of size controlled heterogeneous Pd NPs catalysts with high activity and reusability.

Plant tannins, generally extracted from the barks of plants, are natural polyphenols with molecular weight ranging from 500–3000 Da.¹¹ According to their molecule structures, plant

tannins are classified into condensed tannins and hydrolysable tannins. There are a number of ortho-phenolic hydroxyl groups in plant tannins which have highly affinity towards many metal ions,¹² and the phenolic hydroxyl groups can act as stabilizers to prevent the aggregation of Pd NPs. Ideally, the particle size of the Pd NPs should also be tunable by changing the dosage of tannins during the preparation process. More importantly, the phenolic hydroxyl groups of plant tannins are able to form multiple hydrogen bonds with many matrices.¹³ Thus the tannin-stabilized Pd NPs could be further immobilized onto appropriate matrices *via* multiple hydrogen bonding interactions to prepare heterogeneous Pd catalysts. According to the literature,⁹ condensed tannins have high nucleophilic reaction activity, which can be cross-linked using aldehyde agents. To utilize this property, the tannin-stabilized Pd NPs immobilized on the matrices could be further cross-linked to form a network, which can considerably improve the stability of the catalysts during reactions.

Based on the above suggestions, we developed a new strategy herein for the preparation of heterogeneous Pd NPs catalysts with high activity and reusability. Bayberry tannin (BT), one of the typical condensed tannins, was employed as stabilizer to synthesize a series of homogenous BT-stabilized Pd NPs (BT-Pd). The obtained homogenous BT-Pd were subsequently immobilized onto γ -Al₂O₃ (a commonly used inorganic solid matrix) by conventional impregnation method, followed by a cross-link reaction using glutaraldehyde as the cross-linking agent. Subsequently, the as-prepared heterogeneous γ -Al₂O₃-immobilized BT-Pd (γ -Al₂O₃-BT-Pd) catalysts were characterized by Fourier Transform Infrared

Spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS), Surface Area and Porosity Analyzer (BET) and Transmission Electron Microscopy (TEM). To evaluate their catalytic activity, the as-prepared heterogeneous Pd NPs catalysts were then used for the catalytic hydrogenation of olefin which included allyl alcohol, 2-methyl-3-buten-2-ol, acrylic acid, methacrylic acid, and cyclohexene. Furthermore, the reusability investigation of the catalyst was also conducted. For comparison, catalytic reactions were conducted using γ -Al₂O₃-Pd, which were prepared by traditional impregnation method without BT participation

Experimental Section

Reagents. Bayberry tannin was obtained from the barks of *myricaesculenta* by extraction with an acetone-water solution (1:1, v/v) and then spray-dried. Palladium chloride (PdCl₂), sodium borohydride (NaBH₄), glutaraldehyde (50%, w/w), γ -Al₂O₃ (surface area: 282.9 m²·g⁻¹; average pore size: 5.9 nm), allyl alcohol, 2-methyl-3-buten-2-ol, acrylic acid, methacrylic acid, cyclohexene and all other chemicals were all analytic reagents and purchased from Aladdin Corporation.

Preparation of BT-Stabilized Pd NPs (BT-Pd). The preparation of BT_x-Pd is quite simple. Firstly, a predetermined quantity of PdCl₂ solution was blended with BT solution at different concentrations. Then 2.0 mL of NaBH₄ solution (3%, w/w) was drop-wise added into the solution to yield BT-Pd. Herein, a series of BT_x-Pd were prepared ($x = 0.5, 1, 2, 3$), where x is the mass ratio of BT/Pd. The concentration of Pd²⁺ is fixed at 200.0 mg/L

Preparation of γ -Al₂O₃ Immobilized BT-Pd (γ -Al₂O₃-BT-Pd). 1.0 g of γ -Al₂O₃ with 100-150 mesh were suspended into the BT_x-Pd colloids prepared above. After constant stirred at 318 K for 12 h, the mixture was transferred into an oven at 353 K for 12 h to completely evaporate water. The resultant was suspended in 7.0 mL of glutaraldehyde solution (14%, w/w), and kept under constant stirring at 313 K for 12 h, which allowed the cross-linking reaction to proceed. Finally, the heterogeneous γ -Al₂O₃-BT_x-Pd were collected by filtration, followed by thoroughly washed with deionized water and dried in an oven at 353 K for 12 h, and it was determined that the content of Pd was 1% in weight.

For comparison, two γ -Al₂O₃-Pd (1% Pd in weight) catalysts were prepared by conventional impregnation methods, which were denoted as γ -Al₂O₃-Pd^a and γ -Al₂O₃-Pd^b, respectively. As for the synthesis of γ -Al₂O₃-Pd^a, 1.0 g γ -Al₂O₃ with 100-150 mesh were suspended in 10 mL Pd²⁺ (1.0 g/L) aqueous solution at 303 K, and kept under constant stirring for 24 h, then transferred into an oven at 353 K to completely evaporate water. The collected solid was dispersed in 50 mL deionized water, and reduced by the addition of NaBH₄ solution (3%, w/w) within 4 h. Finally, the γ -Al₂O₃-Pd^a catalysts were obtained by filtration, followed by fully washed with deionized water and drying. The procedures for the preparation of γ -Al₂O₃-Pd^b were the same as those of γ -Al₂O₃-Pd^a catalyst except that the reduction of Pd²⁺ was

carried out under 2.0 MPa H₂ at 473 K for 2 h.

Characterization. Fourier Transform Infrared Spectroscopy (FT-IR, PerkinElmer, USA) of samples was performed by using compressed films of KBr pellets and sample powders. X-ray Photoelectron Spectroscopy (XPS, Kratos XSAM-800, UK) analysis was conducted by employing Mg-K α X radiation ($h\nu = 1253.6$ eV) and a pass energy of 31.5 eV. The specific surface area and pore structure of catalysts were determined by N₂ adsorption/desorption using Surface Area and Porosity Analyzer (BET, Micromeritics Tristar 3000, USA). The Transmission Electron Microscopy (TEM, JEOL2010, Japan) observation of the catalysts was operated at an acceleration voltage of 200 kV.

Catalytic Hydrogenation. The hydrogenation reaction of allyl alcohol was chosen as the probe reaction to evaluate the catalytic activity of the γ -Al₂O₃-BT_x-Pd. Allyl alcohol (20 mmol), methanol (30.0 mL) and γ -Al₂O₃-BT_x-Pd (containing 9.4 μ mol Pd) were introduced into a 50 mL stainless steel autoclave equipped with a stirring bar. The reaction was carried out at 298K under a constant stirring (1200 rpm) and hydrogen pressure (1.0 MPa). The products of hydrogenation reaction were analyzed using gas chromatograph. The used catalyst was recovered by filtration, thoroughly washed with methanol, and then reused under the same experimental conditions to estimate its reusability. As control, the hydrogenation reaction was also conducted using γ -Al₂O₃-Pd^a and γ -Al₂O₃-Pd^b (1% Pd in weight) under the same experimental conditions. In addition, the activity of γ -Al₂O₃-BT_x-Pd for other olefins was also investigated, including 2-methyl-3-buten-2-ol, acrylic acid, methacrylic acid and cyclohexene. The turnover frequency of the catalyst was calculated according to the following equation:

$$\text{TOF} = \frac{\text{Substrate hydrogenated(mol)}}{[\text{Pd(mol)} \times \text{T(h)}]}$$

Result and Discussion

Preparation and Characterization of the γ -Al₂O₃-BT_x-Pd Catalyst. The molecular structure of BT is shown in Figure 1(a). It can be seen that the BT molecule consists of polymerized avan-3-ols with three phenolic hydroxyl groups located at the B rings, which can chelate with metal ions by the formation of five-membered chelating rings. Hence, when Pd²⁺ was added into BT solution, the Pd²⁺ should be chelated with the phenolic hydroxyl groups of BT. After the addition of NaBH₄, the Pd²⁺ was reduced to elemental Pd, which were aggregated to form Pd clusters and further grown as Pd NPs. Due to the presence of BT in solutions, the excessive growth or aggregation of Pd NPs will be suppressed because the Pd NPs will be stabilized by the phenolic hydroxyl groups of BT *via* electrons donating/accepting interactions, which have been confirmed by the following FTIR and XPS analyses. In this manner, the BT-stabilized Pd NPs (BT-Pd) colloids were prepared. According to the literature,^{14,15} the surface of γ -Al₂O₃ is hydroxylated, and thus, the BT molecules can interact with the -OH

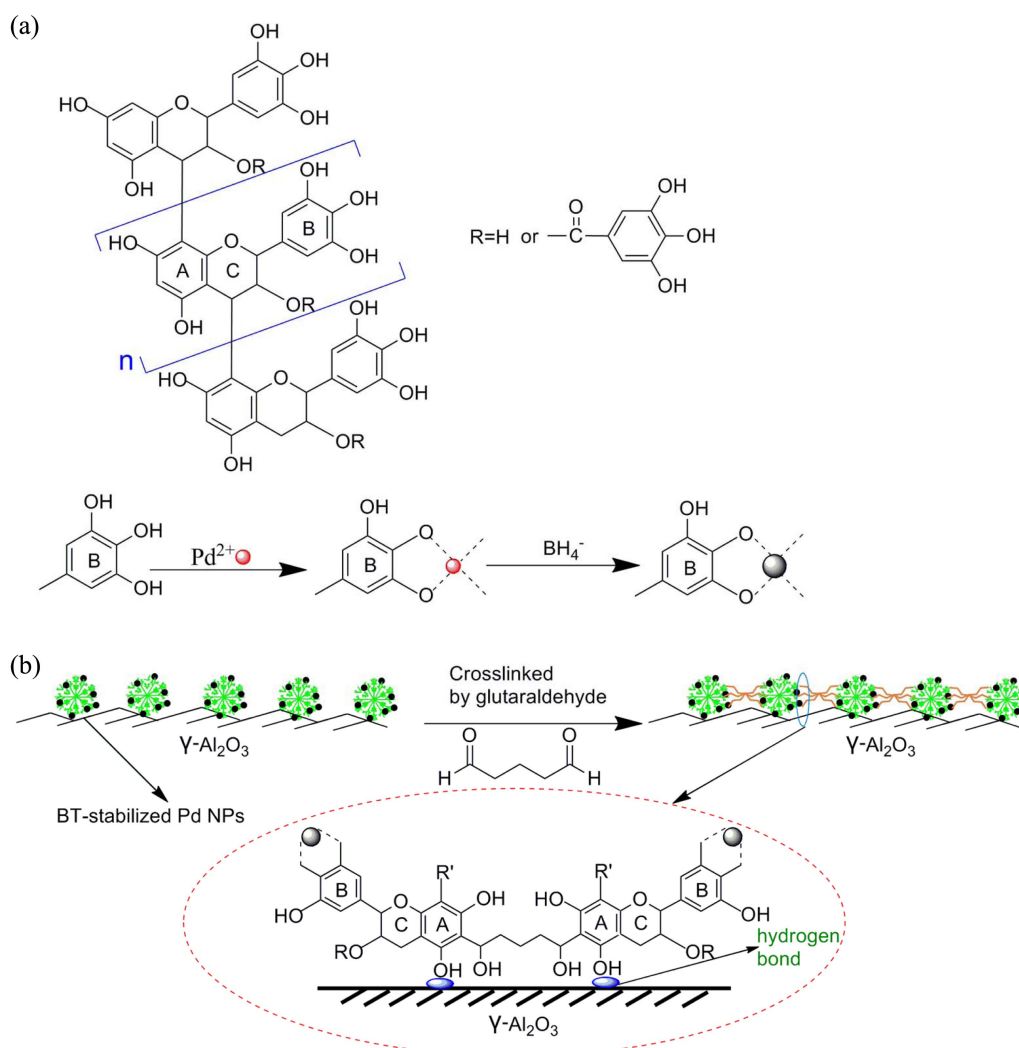


Figure 1. (a) Molecular structure of bayberry tannins, (b) Possible mechanism for the preparation of γ -Al₂O₃-BT_x-Pd.

groups of γ -Al₂O₃ by forming multiple hydrogen bonds, as shown in Figure 1(b). On the other hand, the C6 and C8 positions of A-ring of BT have superior nucleophilic reaction activity.¹⁶ Therefore, glutaraldehyde was used as bi-functional cross-linking agent to form bridges among BT molecules in order to increase the stability of the catalyst. The porous structure of γ -Al₂O₃ is preserved very well according to the analysis of surface area and porosity. It is found that the BET surface area of the γ -Al₂O₃-BT₂-Pd was 250.2 m²·g⁻¹ and its average pore size is 5.8 nm, showing a little decrease compared with raw γ -Al₂O₃ (surface area: 282.9 m²·g⁻¹; average pore size: 5.9 nm). The presence of mesopores in γ -Al₂O₃-BT₂-Pd favors the catalytic activity of catalysts, because the mesoporous structure provides reaction substrates an easy access to the catalytic active sites.¹⁷

Figure 2 is the FT-IR spectra of BT and BT₂-Pd. As shown in Figure 2(a), BT shows a strong peak at 3416 cm⁻¹, which is attributed to the stretching vibration of O-H bond from phenolic hydroxyl groups of BT (C-O-H).¹⁸ Peaks at the range of 1617-1450 cm⁻¹ suggest the presence of aromatic rings of tannins,¹⁹ and the peak at 1536 cm⁻¹ belongs to the special skeletal stretching vibration of the aromatic ring B-

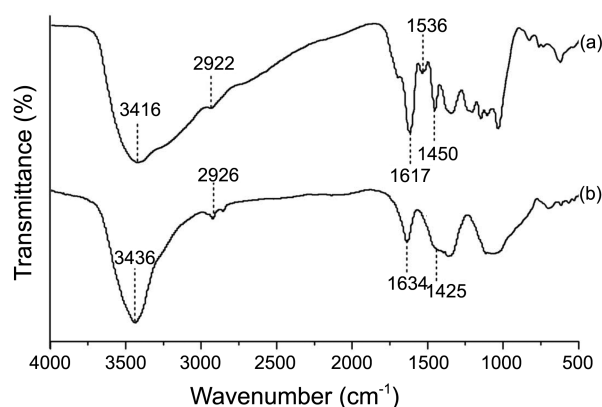


Figure 2. (a) FT-IR spectra of BT, (b) FT-IR spectra of BT₂-Pd.

ring of BT.²⁰ In Figure 2(b), the stretching vibration peak of O-H becomes relatively narrow and shifts from 3416 cm⁻¹ to 3436 cm⁻¹, and the skeletal stretching peak of B ring (located at 1536 cm⁻¹ in Figure 2(a)) almost disappears. Those facts suggest Pd is indeed interacted with the phenolic hydroxyl groups of BT.

To further investigate the interaction mechanism of Pd

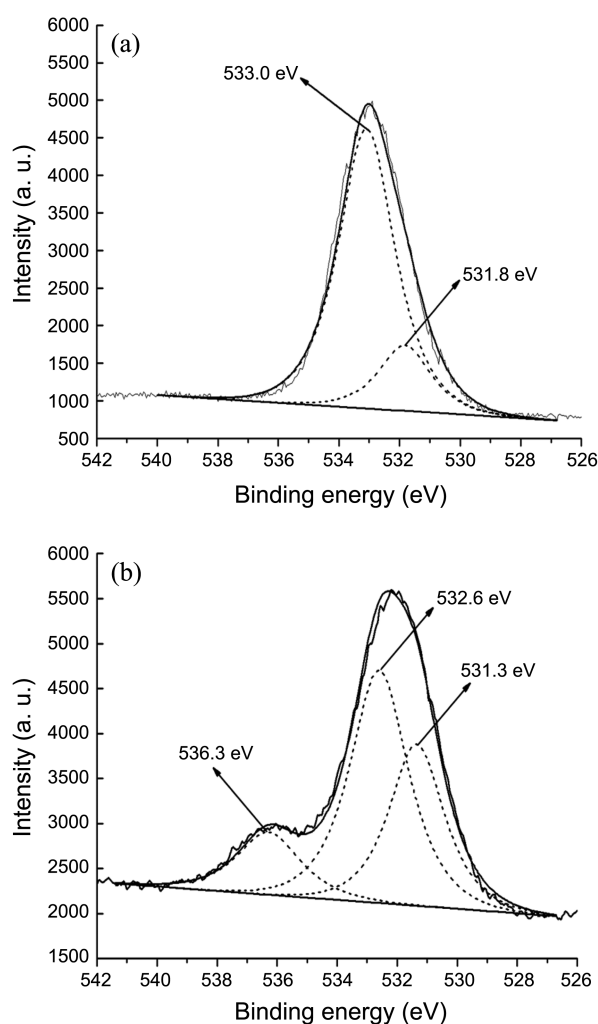


Figure 3. (a) O1s XPS spectra of BT, (b) O1s XPS spectra of BT₂-Pd colloid.

NPs with BT, XPS analyses were performed. As shown in Figure 3(a), the O1s XPS spectra of BT exhibits two peaks at 531.8 eV and 533.0 eV, respectively. The major peak at 533.0 eV is attributed to the C-O bonds in the phenolic hydroxyl groups of BT. While the relative smaller peak at 531.8 eV is assigned to the -C=O bonds.^{21,22} As for BT₂-Pd colloid, the peak intensity corresponding to the C-O bonds (532.6 eV) in the phenolic hydroxyl groups of BT shows a remarkable decrease, while the peak intensity of -C=O bonds (531.3 eV) shows an obvious increase and a new peak is observed at 536.3 eV. These changes suggest that a part of phenolic hydroxyl groups of BT have interacted with Pd NPs by donating their electrons to the Pd NPs, which is consistent with the determination of FTIR analyses.

Figure 4 is the Pd 3d XPS spectra of γ -Al₂O₃-BT₂-Pd, which exhibits two pairs of doublets from the spin-orbital splitting of the 3d 7/2 and 3d 5/2. The doublets observed at 336.9 eV and 340.4 eV show the existence of Pd(0), and another doublets located at 335.2 eV and 342.1 eV belong to Pd²⁺.²³ Based on integral calculation, about 54% Pd²⁺ has been reduced to its elemental form.

Figure 5 shows the TEM images of the γ -Al₂O₃-BT_x-Pd

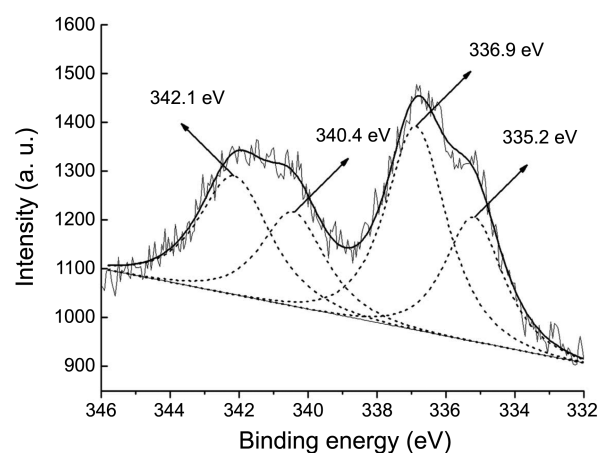


Figure 4. Pd (3d) core level XPS spectra of γ -Al₂O₃-BT₂-Pd.

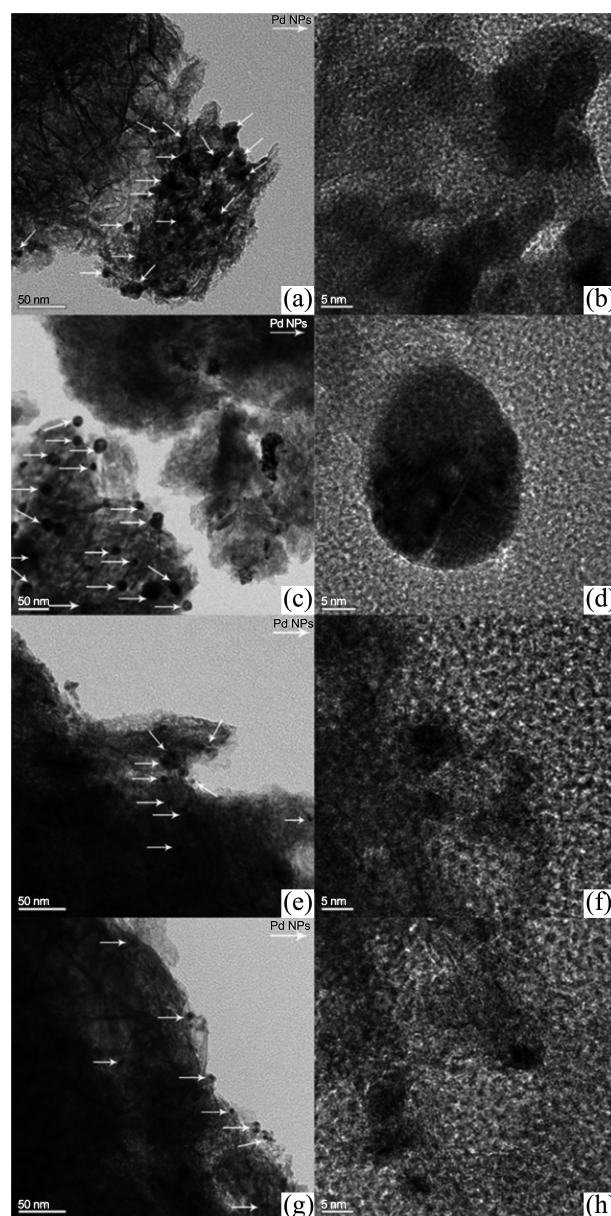


Figure 5. (a-b) TEM images of γ -Al₂O₃-BT_{0.5}-Pd, (c-d) TEM images of γ -Al₂O₃-BT₁-Pd, (e-f) TEM images of γ -Al₂O₃-BT₂-Pd, (g-h) TEM images of γ -Al₂O₃-BT₃-Pd.

prepared with $\text{BT}_x\text{-Pd}$ colloids with different mass ratio of BT/Pd . As for $\gamma\text{-Al}_2\text{O}_3\text{-BT}_{0.5}\text{-Pd}$, the particle size of the Pd NPs is in a wide range from 3.3 to 26.2 nm, and the aggregation of Pd NPs is very obvious (Figure 5(a)-(b)). These results suggest that the size controlling effect of BT toward Pd NPs is not sufficient when low amount of BT are used. With higher mass ratio of BT/Pd , Pd NPs with smaller particle size are found to be predominated. As shown in Figure 5(c)-(h), the average particle sizes of the Pd NPs in the $\gamma\text{-Al}_2\text{O}_3\text{-BT}_1\text{-Pd}$, $\gamma\text{-Al}_2\text{O}_3\text{-BT}_2\text{-Pd}$ and $\gamma\text{-Al}_2\text{O}_3\text{-BT}_3\text{-Pd}$ are 16.0 nm, 5.1 nm and 4.2 nm, respectively. Moreover, the size distribution of the Pd NPs also becomes more uniform along with the increase of BT content. Possibly, during the preparation of $\text{BT}_x\text{-Pd}$ colloids, high dosage of BT in solutions can provide enough steric hindrance to prevent the excessive growth and/or aggregation of Pd nuclei when the Pd^{2+} is reduced by NaBH_4 . Considering the uniform dispersion and small particle size of Pd NPs, high catalytic activity of the $\gamma\text{-Al}_2\text{O}_3\text{-BT}_x\text{-Pd}$ catalysts can be expected in the following hydrogenation reactions.

Catalytic Hydrogenation of Olefins. Pd catalysts are commonly used for the catalytic hydrogenation of olefin. Hence, allyl alcohol was used as a probe substrate to investigate the catalytic activity of the $\gamma\text{-Al}_2\text{O}_3\text{-BT}_x\text{-Pd}$ catalysts. The target product of the catalytic reaction is n-propanol while the isomerization of allyl alcohol may occur over Pd catalysts.

Table 1 summarizes the corresponding experimental results. The initial TOF of the $\gamma\text{-Al}_2\text{O}_3\text{-BT}_{0.5}\text{-Pd}$ is $11023 \text{ mol}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$. Along with the increase of mass ratio of BT/Pd , the initial TOF of the catalyst is gradually increased and reaches the maximum value of $12804 \text{ mol}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$ when $\gamma\text{-Al}_2\text{O}_3\text{-BT}_2\text{-Pd}$ is employed. The increased catalytic activity should be attributed to the improved dispersion of the Pd NPs and the gradually decreased particle size of the Pd NPs (confirmed by the TEM analyses above), because a smaller metal particle size means that a larger fraction of metal atoms are exposed for catalysis and thus shows better activity. However, the hydrogenation rate decreased as the particle size of Pd NPs decreased from 5.1 nm in $\gamma\text{-Al}_2\text{O}_3\text{-BT}_2\text{-Pd}$ to 4.2 nm in $\gamma\text{-Al}_2\text{O}_3\text{-BT}_3\text{-Pd}$. One reasonable explanation for this result is that a over high content of bayberry tannin may introduce a high density of phenolic

hydroxyl groups around Pd NPs, which could sterically restrict the substrates to access the active sites of catalysts and eventually lead to a lower catalytic activity.²² According to CG-MS analysis, acetone is the main by-product, when the $\gamma\text{-Al}_2\text{O}_3\text{-BT}_x\text{-Pd}$ catalysts are used for the catalytic hydrogenation of allyl alcohol. For the $\gamma\text{-Al}_2\text{O}_3\text{-BT}_x\text{-Pd}$ with different content of BT, the selectivity to n-propanol shows a little change ranging from 80.2%-83.0%.

As for Pd NPs catalysts based on functionalized supports or stabilizers, the polar microenvironment around Pd species can be constructed by the around functional groups, and thus profoundly influence the catalytic ability.²⁴ Accordingly, we believe that the large numbers of phenolic hydroxyl groups of BT would also construct the polar microenvironment around Pd species, and then affects the catalytic activity and selectivity of catalysts. To confirm this hypothesis, hydrogenation reactions catalyzed by conventionally prepared $\gamma\text{-Al}_2\text{O}_3\text{-Pd}$ catalysts were performed as the comparative experiment. The experimental result indicates that the $\gamma\text{-Al}_2\text{O}_3\text{-BT}_x\text{-Pd}$ exhibits much higher activity and selectivity than those of $\gamma\text{-Al}_2\text{O}_3\text{-Pd}^a$ and $\gamma\text{-Al}_2\text{O}_3\text{-Pd}^b$, of which the initial TOF are $11649 \text{ mol}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$ and $10548 \text{ mol}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$, and the selectivity are only 77.5% and 76.3%, respectively (see in Table 1). These facts suggest that those as-prepared $\gamma\text{-Al}_2\text{O}_3\text{-BT}_x\text{-Pd}$ catalysts are more active for catalytic hydrogenation of allyl alcohol, and their catalytic activity is affected by the content of BT. Considering that the $\gamma\text{-Al}_2\text{O}_3\text{-BT}_2\text{-Pd}$ exhibits excellent activity, following catalytic reactions were therefore carried out using $\gamma\text{-Al}_2\text{O}_3\text{-BT}_2\text{-Pd}$.

The reusability of a catalyst is very important in view point of practical applications, and thus, the reusability of the $\gamma\text{-Al}_2\text{O}_3\text{-BT}_2\text{-Pd}$ in the catalytic hydrogenation of allyl alcohol was also conducted. As shown in Figure 6, the $\gamma\text{-Al}_2\text{O}_3\text{-BT}_2\text{-Pd}$ can be reused 5 times without significant loss of the catalytic activity. In the 5-run, the TOF of the $\gamma\text{-Al}_2\text{O}_3\text{-BT}_2\text{-Pd}$ can till reaches $6002 \text{ mol}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$, suggesting a satisfied reusability. On the contrary, the activity of $\gamma\text{-Al}_2\text{O}_3\text{-Pd}^a$ and $\gamma\text{-Al}_2\text{O}_3\text{-Pd}^b$ are decreased drastically during the cycles. In the 5-run, the TOF of $\gamma\text{-Al}_2\text{O}_3\text{-Pd}^a$ and $\gamma\text{-Al}_2\text{O}_3\text{-Pd}^b$

Table 1. Catalytic activity of $\gamma\text{-Al}_2\text{O}_3\text{-BT}_x\text{-Pd}$ and controlled samples for the hydrogenation of allyl alcohol^c

Catalysts	Initial TOF ($\text{mol}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$) ^d	Selectivity (%)
$\gamma\text{-Al}_2\text{O}_3\text{-BT}_{0.5}\text{-Pd}$	11023	80.2
$\gamma\text{-Al}_2\text{O}_3\text{-BT}_1\text{-Pd}$	11526	82.1
$\gamma\text{-Al}_2\text{O}_3\text{-BT}_2\text{-Pd}$	12804	83.0
$\gamma\text{-Al}_2\text{O}_3\text{-BT}_3\text{-Pd}$	11803	81.2
$\gamma\text{-Al}_2\text{O}_3\text{-Pd}^a$	11649	77.5
$\gamma\text{-Al}_2\text{O}_3\text{-Pd}^b$	10548	76.3

^cCatalysts/Substrate, 9.4 $\mu\text{mol}/20 \text{ mmol}$; Temperature, 298 K; Solution (methanol), 30.0 mL; H_2 Pressure, 1 MPa. ^dTOF in the first 5 minutes

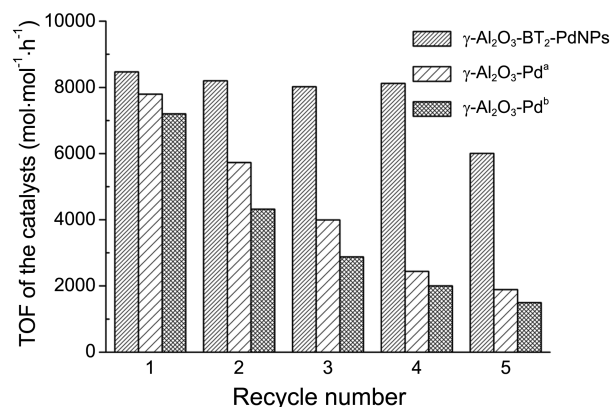


Figure 6. Recycles of $\gamma\text{-Al}_2\text{O}_3\text{-BT}_2\text{-Pd}$ and controlled samples for the hydrogenation of allyl alcohol. (Catalysts/Substrate, 9.4 $\mu\text{mol}/20 \text{ mmol}$; Temperature, 298 K; Solution (methanol), 30.0 mL; H_2 Pressure, 1.0 MPa.)

Table 2. Hydrogenation of various substrates catalyzed by γ -Al₂O₃-BT₂-Pd^a

Entry	Substrates	Products	TOF (mol·mol ⁻¹ ·h ⁻¹)
1			8471
2			7579
3			7327
4			3848
5			2341

^aCatalysts/Substrate, 9.4 μ mol/20 mmol; Temperature, 298 K; Solution (methanol), 30.0 mL; H₂ Pressure, 1 MPa

Pd^b are only 1893 mol·mol⁻¹·h⁻¹ and 1500 mol·mol⁻¹·h⁻¹. These recycling experimental results confirm that the bayberry tannin indeed plays a crucial role in the immobilization of Pd NPs onto γ -Al₂O₃.

To further evaluate the activity of γ -Al₂O₃-BT_x-Pd in the catalytic hydrogenation of other olefins, 2-methyl-3-buten-2-ol, acrylic acid, methacrylic acid, and cyclohexene were also employed as the substrates. Table 2 summarizes the corresponding results. It can be seen that the γ -Al₂O₃-BT₂-Pd is highly active for all the substrates. For example, the TOF of methacrylic acid is as high as 3848 mol·mol⁻¹·h⁻¹. On the other hand, the γ -Al₂O₃-BT₂-Pd exhibits size-based selectivity to the substrates. As for methyl-3-buten-2-ol, its TOF is 7579 mol·mol⁻¹·h⁻¹, which is lower than that of allyl alcohol (8471 mol·mol⁻¹·h⁻¹). Similar phenomenon is also observed between acrylic acid and methacrylic acid. It is understandable that the γ -Al₂O₃-BT₂-Pd exhibits relatively lower TOF for the substrate with substituent and/or rings. In general, the γ -Al₂O₃-BT₂-Pd can be used as a highly active catalyst in the catalytic hydrogenation of olefins.

Conclusion

In this study, heterogeneous Pd catalysts with highly activity and reusability can be prepared by immobilizing bayberry tannin-stabilized Pd nanoparticles (BT-Pd) onto γ -Al₂O₃ thorough the hydrogen bonding interaction. Due to the stabilization and size controlling effect of BT, the Pd nanoparticles with controlled size can be well dispersed onto γ -Al₂O₃, and this stabilization of BT is further increased after glutaraldehyde cross-linked. The as-prepared γ -Al₂O₃-BT₂-Pd can be used for highly active hydrogenation of olefins, and reused 5 times without significant loss of the

catalytic activity, which exhibits a superior reusability as compared with conventionally prepared heterogeneous Pd catalysts.

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