Preparation of highly active and reusable heterogeneous Al₂O₃–Pd catalysts by the sol–gel method using bayberry tannin as stabilizer

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Abstract A novel heterogeneous Al_2O_3 –Pd catalyst has been prepared by the solgel method; bayberry tannin (BT) was used as stabilizer to prevent the migration and aggregation of Pd species during calcination. According to N₂ adsorption/ desorption determination, Al_2O_3 –Pd has a mesoporous structure and its specific area is as high as 336.5 m²/g. Transmission electron microscopy observation indicated that the size of the Pd particles was greatly reduced by the presence of BT. On the basis of X-ray photoelectron spectra analysis, it was found that the most of Pd nanoparticles were dispersed in the pores, implying that BT can prevent migration of Pd particles from the pores to the outer surface of Al_2O_3 during calcination. For comparison, Al_2O_3 –Pd^{*} was prepared by the sol–gel method but without use of BT. In the hydrogenation of acrylic acid, Al_2O_3 –Pd had high catalytic activity and excellent reusability compared with commercial and traditionally prepared heterogeneous Pd catalysts. The turnover number of Al_2O_3 –Pd is as high as 11,328.0 mol/ mol after recycling seven times, which is much higher than that of a commercial Pd–C catalyst (8048.0 mol/mol).

Keywords Sol–gel method \cdot Al₂O₃–Pd catalyst \cdot Bayberry tannin \cdot Reusability

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Introduction

Palladium (Pd) catalysts are among the most important noble metal catalysts, with remarkable catalytic properties which have been applied in various reactions, for example the Heck reaction, hydrogenation of alkynes and nitro compounds, asymmetric hydrogenation reactions, and oxidation of NO [1–6]. Pd catalysts are generally classified into homogeneous catalysts and heterogeneous catalysts. Homogeneous Pd catalysts often have high activity and selectivity but separation from the reaction system is a problem, and, therefore, their practical application is limited [7]. In contrast, heterogeneous Pd catalysts can be easily recovered by use of a simple operation (filtration, centrifugation, or natural decantation), which is much preferred for practical application and economy [8]. However, the activity of heterogeneous Pd catalysts is often lower than that of homogenous ones and the Pd particles easily migrate to the outer surface of porous supports during calcination. Therefore, preparation of heterogeneous Pd catalysts with high activity and reusability is still a challenge.

Heterogeneous Pd catalysts are conventionally prepared by supporting Pd on porous oxides with a high specific surface area, and impregnation is a frequently used method. In a typical synthetic process, Pd precursors dissolved in solvent are first introduced into solid matrices by impregnation; drying and calcination are then followed by reduction [9, 10]. Unfortunately, because of weak interactions between Pd precursors and matrices, the Pd precursors located in pores of supports might substantially migrate to the outer surface of the support on evaporation of the solvent during drying and calcination, which further leads to serious aggregation and/or partial expulsion of Pd particles after reduction [11]. Such heterogeneous Pd catalysts often have relatively low activity and poor reusability.

The sol-gel method is generally used to prepare porous oxides with a high specific surface area, for example Al_2O_3 , SiO_2 and TiO_2 [12, 13]. On the basis of this method, we assumed that if a water-soluble stabilizer which can chelate with metal ions were added to the sol with the Pd precursors, migration of Pd the species could be substantially suppressed during the drying and calcination process. In this way, the Pd precursors should be well distributed in the porous matrix, and the Pd particles formed from subsequent calcination and reduction would be mainly constrained in the pores of matrix. Accordingly, aggregation and leakage of Pd particles can be alleviated during the catalytic reaction process. Herein, we implemented this new strategy to prepare a novel heterogeneous Al_2O_3 –Pd catalyst, because Al_2O_3 –Pd is commonly used as a heterogeneous Pd catalyst.

Plant tannin is a natural polyphenol extracted from roots, leaves, fruits, and bark of plants [14]. There are numerous phenolic hydroxyl groups in tannin molecules [15] which can chelate with many metal ions [16]. Hence, it is believed that tannin chelated Pd^{2+} can be well dispersed in the alumina sol when using the sol–gel method to prepare the Al_2O_3 support. Moreover, tannin mainly consists of the elements carbon, hydrogen, and oxygen, which can be effectively removed by thermal treatment. In this manner, the pore structure of Al_2O_3 can be well preserved, and the Pd ions can be converted to Pd oxides in the pores of Al_2O_3 , which could be further reduced to elemental Pd by H_2 reduction. On the basis of these ideas we prepared a novel heterogeneous Al_2O_3 -supported Pd nanoparticle (Al_2O_3 -Pd) catalyst. The as-prepared catalyst was then characterized by wide-angle X-ray diffraction (XRD), X-ray photoelectron spectra (XPS), and transmission microscopy (TEM). To investigate the catalytic behavior of this novel catalyst, the catalytic hydrogenation of acrylic acid was used as a probe reaction. The reusability of this catalyst was also investigated. For comparison, catalytic hydrogenation of acrylic acid was also performed, under the same experimental conditions, with Al_2O_3 -Pd^{**} prepared by the sol-gel method without use of BT, γ -Al₂O₃-Pd^{**} prepared by the impregnation method, and commercial Pd–C.

Experimental

Materials and instrument

Bayberry tannin (BT) was extracted from the bark of *Myrica esculenta* with acetone–water solution (1:1, v/v) and then spray-dried. The tannin content of BT is 67.3%, and its average molecular weight is 5,000 Da. Aluminum isoproposide (AIP), PdCl₂, and other chemicals were all analytical-grade reagents and used as received.

Preparation and characterization of catalysts

AIP (10.27 g) was added to a mixture of 50 mL hexamethylene and 5 mL deionized water. The resulting mixture was supersonically dispersed for 15 min at room temperature, and then kept under vigorous stirring for 12 h at 335 K. This process resulted in the formation of well dispersed sol. Subsequently, 50 mL 20 g/L BT solution was mixed with 2.5 mL 10 g/L Pd²⁺ solution, and this mixture was then added drop-wise to the above sol. After stirring for another 12 h, hydrolysis of AIP was complete and the sol had changed into a gel. The resulting gel was collected by centrifugation, dried, calcined (550 °C for 3 h), and reduced (at 200 °C and 2 MPa H₂ pressure for 2 h). The as-prepared catalyst was denoted "Al₂O₃-Pd" and the Pd content was 0.98% (w/w). For comparison, $Al_2O_3-Pd^*$ was prepared by the same procedures in the absence of BT. In addition, γ -Al₂O₃-Pd^{**} prepared by the impregnation method and commercial Pd-C (Pd 10%) were used for comparison. For preparation of γ -Al₂O₃-Pd^{**}, 1.0 g commercial γ -Al₂O₃ was suspended in 10 mL 1 g/L Pd²⁺ solution and then dried at 80 °C. The collected solid product was calcined at 550 °C for 3.0 h, followed by reduction with 2.0 MPa H₂ at 200 °C for 2.0 h. The Pd content of γ -Al₂O₃-Pd^{**} was determined to 0.96% (*w/w*).

The crystalline structures of Al_2O_3 –Pd, Al_2O_3 –Pd^{*}, and γ -Al₂O₃–Pd^{**}were characterized by XRD (X'Pert Pro, Philips, The Netherlands). X-ray photoelectron spectroscopy (XPS, Kratos XSAM-800, UK) analysis was conducted with Mg Ka radiation (hv = 1253.6 eV) and the pass energy was 31.5 eV. All of the binding energy peaks of XPS spectra were calibrated by placing the principal C 1 s binding energy peak at 284.7 eV. The specific surface area and pore structure of the catalysts were analyzed by N₂ adsorption/desorption by use of a surface area and

Hydrogenation of acrylic acid

Catalytic hydrogenation of acrylic acid was used to assess the activity and reusability of Al_2O_3 –Pd, Al_2O_3 –Pd^{**}, γ - Al_2O_3 –Pd^{**}, and Pd–C. All the reactions were carried out in a stainless steel Parr autoclave equipped with a stirring bar. In a typical catalytic reaction, 25.0 mL methanol was added into the reactor, and then specific amounts of catalyst (containing 5 µmol Pd) and acrylic acid (10.0 mmol) were added. Subsequently, the reactor was heated to 30 °C and kept at 1.0 MPa H₂ under constant stirring. When the reaction was complete, the products were analyzed by gas chromatography (GC) and the catalysts were collected by centrifugation, followed by thorough washing with methanol. The turnover frequency (TOF) and turnover number (TON) of the catalysts were calculated by use of the equations:

$$TOF = Substrate hydrogenated(mol)/[Pd(mol) \times t(h)]$$
(1)

$$TON = Substrate hydrogenated(mol)/Pd(mol)$$
(2)

Results and discussion

Characterization of catalysts

Figure 1 shows the XRD patterns of Al₂O₃-Pd, Al₂O₃-Pd^{*}, and γ -Al₂O₃-Pd^{**}. It can be observed that these three Pd catalysts have similar XRD spectra which contain the characteristic peaks of y-Al₂O₃ at 36.7°, 48.7°, and 67.1° [17]. y-Al₂O₃ is often used as supporting matrix to prepare heterogeneous metal catalysts, because of its high specific surface area and well defined porosity [18]. N_2 adsorption/ desorption was used for analysis of the structural features of the as-prepared Al₂O₃-Pd, Al₂O₃-Pd^{*}, and γ -Al₂O₃-Pd^{**}. The N₂ adsorption/desorption isotherm curves of Al₂O₃-Pd, Al₂O₃-Pd^{*}, and γ -Al₂O₃-Pd^{**} are shown in Fig. 2a-c; all have type IV or V hysteresis loops, suggesting the mesoporous structures of the catalysts [19]. However, the specific surface area of Al_2O_3 -Pd is as high as 336.5 m²/g, which is much higher than that of Al_2O_3 -Pd^{*} (225.4 m²/g). In addition, the average pore diameter of Al₂O₃–Pd (5.83 nm) is also larger than that of Al₂O₃–Pd^{*} (3.66 nm), as shown in Fig. 2d-e. The different structural properties of those two catalysts is probably because of the use of BT during the sol-gel preparation of the catalysts. Actually, tannins can interact with each other by hydrophilic and/or hydrophobic interactions, and thus, supramolecules may be formed by assembly of the tannins. It can be reasoned that these supramolecules could act as templates during the solgel process, and are subsequently removed by calcination, creating more developed pores. From the perspective of mass transfer, the Al2O3-Pd should have much better catalytic activity, owing to its higher specific surface area and larger pores.



Fig. 1 X-ray diffraction patterns of Al₂O₃-Pd, Al₂O₃-Pd^{*}, and γ -Al₂O₃-Pd^{**}

The physical properties of Al_2O_3 -Pd, Al_2O_3 -Pd^{**}, γ -Al_2O_3-Pd^{**}, and Pd-C are summarized in Table 1.

To confirm that use of BT in the preparation of Al_2O_3 –Pd can suppress the migration of Pd particles to the outer surface of Al_2O_3 , ICP–AES and XPS analysis was performed. The Al_2O_3 –Pd was first digested by nitric acid, and the concentration of Pd in the digested solution was then determined by ICP–AES. On the basis of ICP–AES analysis, the average Pd content of the Al_2O_3 –Pd was calculated to be 0.98% (*w/w*). On the basis of XPS after reduction, the Pd content at the outer surface of Al_2O_3 –Pd was just 0.64%. According to the literature, XPS analysis results mainly reflect the surface composition of samples. Thus, it is believed that the Pd particle of Al_2O_3 are mainly dispersed in the inner pores of the Al_2O_3 because of the chelation and stabilization effect of BT toward Pd²⁺, which substantially prevents the migration of Pd²⁺ with the solvent which evaporates during calcination process.

Figure 3 is the Pd 3d XPS spectrum of Al_2O_3 –Pd. It contains two pairs of doublets, one located at 335.000 and 339.770 eV, which are assigned to elemental Pd(0), and another pair located at 336.370 and 341.620 eV, which belong to Pd²⁺. Actually, approximately 40% of Pd²⁺ has been reduced to the elemental form.

Figure 4 show the TEM images of Al_2O_3-Pd , $Al_2O_3-Pd^*$, γ - $Al_2O_3-Pd^{**}$, and Pd–C. It is obvious that distribution of Pd nanoparticles in the Al_2O_3-Pd is much better than for other three Pd catalysts. Moreover, the average particle size of Pd in the Al_2O_3-Pd is 3–5 nm, which is much smaller than that of $Al_2O_3-Pd^*$ (10–23 nm), γ - $Al_2O_3-Pd^{**}$ (21–42 nm), and Pd–C (19–35 nm) (Fig. 5). When considering the porous structure of Al_2O_3-Pd and $Al_2O_3-Pd^*$, the Pd nanoparticles in Al_2O_3-Pd should be mainly located in the pores of the Al_2O_3 , whereas a substantial number of Pd particles are located on the outer surface of Al_2O_3 for $Al_2O_3-Pd^*$. In addition, migration and aggregation of Pd species indeed occurred during the preparation of $Al_2O_3-Pd^*$ when BT was not introduced.



Fig. 2 a N₂ adsorption-desorption isotherms of Al₂O₃-Pd. b N₂ adsorption-desorption isotherms of Al₂O₃-Pd^{*}. c N₂ adsorption-desorption isotherms of γ -Al₂O₃-Pd^{**}. d pore size distributions of Al₂O₃-Pd^{**}.

Pd catalyst	Support	Average Pd content (%)	Specific area (m ² /g)	Pore size (nm)
Al ₂ O ₃ –Pd	Al ₂ O ₃	0.98	336.5	5.83
Al ₂ O ₃ -Pd*	Al ₂ O ₃	0.98	225.4	3.66
γ -Al ₂ O ₃ -Pd ^{**}	γ -Al ₂ O ₃	0.96	315.8	5.60
Pd-C	Activated carbon	10.0	998.3	1.72

Table 1 Physical properties of Al₂O₃-Pd, Al₂O₃-Pd^{*}, γ-Al₂O₃-Pd^{**}, and Pd-C

Fig. 3 Pd 3d XPS spectrum of the Al_2O_3 -Pd



Hydrogenation of acrylic acid

Hydrogenation of acrylic acid was used to evaluate the catalytic performance of Al_2O_3-Pd , $Al_2O_3-Pd^*$, γ - $Al_2O_3-Pd^{**}$, and Pd–C. Figure 6 shows the catalytic activity and reusability of these four Pd catalysts. Compared with $Al_2O_3-Pd^*$, the Al_2O_3-Pd has much greater activity. The TOF of the Al_2O_3-Pd is 7792.0 mol/mol/h whereas it is only 3044.0 mol/mol/h for $Al_2O_3-Pd^*$. As shown in Table 1, the specific surface area of Al_2O_3-Pd is approximately 1.5 times that of $Al_2O_3-Pd^*$. Moreover, the Pd particles in Al_2O_3-Pd have a small particle size of 3-5 nm and are well dispersed in the pores of Al_2O_3 , whereas the Pd particles in $Al_2O_3-Pd^*$ are of larger size (11–21 nm) and have suffered serious aggregation, as shown in Fig. 5. According to the literature, the size of metal nanoparticles greatly affects their catalytic activity [20–22]. In general, metal particles with smaller size have a larger fraction of surface metal atoms, and will have greater activity than the corresponding counterparts with larger Pd particle size. Thus, it is understandable that the $Al_2O_3-Pd^*$ with larger Pd particle size has much lower catalytic activity than Al_2O_3-Pd .

The reusability of Al_2O_3 -Pd was excellent; it was reused seven times without significant loss of activity. In the 7th run, the TOF of the Al_2O_3 -Pd was 7384.0 mol/mol/h, which was approximately 94.7% of that in the 1st run. In contrast, the reusability of Al_2O_3 -Pd^{*} is quite poor. It was found that its TOF in the 3rd run was drastically decreased to 921.6 mol/mol/h. The excellent reusability of the Al_2O_3 -Pd could be because leakage and aggregation of Pd particles were greatly inhibited.



Fig. 4 TEM images and particle size distribution of Pd catalysts

All these results imply that BT indeed plays a crucial role in preventing Pd migration during the preparation of the catalyst, which further ensures the high activity and reusability of the catalyst.

 γ -Al₂O₃-Pd^{**} has the lowest activity and its reusability is also quite poor. Compared with Al₂O₃-Pd, γ -Al₂O₃-Pd^{**} had similar physical properties (Table 1). However, the TEM images indicated the diversity of Pd particle size and distribution. The large size and uneven distribution of Pd particles could be the main reason for the low catalytic activity and reusability of γ -Al₂O₃-Pd^{**}. The commercial Pd-C catalyst has the highest initial catalytic activity of these four Pd catalysts, but its reusability is also quite poor. The average Pd content of Pd-C was much higher and the TEM images revealed serious migration of Pd particles. The high Pd content and serious migration lead to partial expulsion of Pd particles during the reaction process and caused the sharp decrease of catalytic activity. To evaluate the efficiency of these four catalysts, their corresponding TON was calculated, and is in the sequence: Al₂O₃-Pd (11328.0 mol/mol) > Pd-C



Fig. 5 Particle size distribution of Pd catalysts



Fig. 6 The activity and reusability of Al₂O₃-Pd, Al₂O₃-Pd*, γ-Al₂O₃-Pd**, and Pd-C

 $(8048.0 \text{ mol/mol}) > Al_2O_3-Pd^*$ $(3074.8 \text{ mol/mol}) > \gamma-Al_2O_3-Pd^{**}$ (2155.5 mol/mol). Therefore, Al_2O_3-Pd prepared by our novel method has the highest efficiency.

Conclusions

In this study, we demonstrated that BT can significantly suppress Pd migration and aggregation during the preparation of the catalyst because of its chelation and stabilization effects. The Pd particles were reduced in size and well dispersed in the as-prepared heterogeneous Al_2O_3 -Pd compared with the catalyst produced without use of BT. Therefore, Al_2O_3 -Pd had high activity and excellent reusability in the catalytic hydrogenation of acrylic acid.

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