



Preparation of platinum nanoparticles supported on bayberry tannin grafted silica bead and its catalytic properties in hydrogenation

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ABSTRACT

Bayberry tannin (BT), a natural plant polyphenol, was used as a stabilizer to prepare supported platinum catalysts. Bayberry tannin was first grafted onto aminated SiO₂ beads and subsequently coordinate with Pt(IV) species. Then a series of heterogeneous Pt–bayberry tannin–SiO₂ (Pt–BT–SiO₂) catalysts was obtained after reduction with NaBH₄. The catalysts were characterized by UV–DR, XRD and TEM, and the coordination state of Pt(IV) with BT grafted on SiO₂ beads was investigated by XPS. It was found that the Pt–BT–SiO₂ catalysts were highly active and stable in aqueous hydrogenation of acrylic acid, α -methacrylic acid, allyl alcohol and 2-methyl-3-buten-2-ol. Moreover, the Pt–BT–SiO₂ catalysts could be conveniently recovered from the reaction systems simply by filtration, and be reused at least five times without loss of activity.

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1. Introduction

Homogeneous noble metal catalysts usually have the advantages of high activity and selectivity in a broad range of synthetic reactions [1], while their practical application remains limited in scope because of the difficulties associated with the removal of catalysts from reaction systems and the recycle of catalysts. Therefore, there is a growing preference for developing heterogeneous noble metal catalysts that can be simply recovered and subsequently reused.

The most widely adopted approach to prepare heterogeneous metal catalysts is to load nano-scaled metals (or metal oxides) onto insoluble supporting matrix [2,3]. Inorganic supports, such as silica, are commonly used for this purpose because of their high physical strength and chemical inertness [4]. However, most of the supported metal catalysts often suffer from reduced catalytic activity and/or selectivity due to the leakage of supported metal species, which are weakly associated with the support [5].

To overcome this disadvantage, inorganic supports are often grafted with organic polymers, which can coordinate with metal species by their ligands, so that the metal leakage from support is suppressed and the catalytic activity of supported catalysts is retained [6,7]. Moreover, the activity and selectivity of the

supported metal catalysts can be facilely controlled via organic polymers with varying structures and ligands [8]. It has been reported that heterogeneous palladium catalysts with high size-based selectivity was prepared by supporting Pd(0) nanoparticles on dendrimer-grafted silica [9].

Tannins, which are widely distributed in plants, are the soluble polyphenols with molecular weight between 500 and 3000 Da. According to the chemical structures of tannins, they are classified into hydrolyzable tannins and condensed tannins. The general characteristics of tannins are that they are able to chelate with many kinds of metal ions through their dense ortho-phenolic hydroxyls, and capable of scavenging free radicals so as to prevent metal species from oxidation [10–12]. These properties of tannins imply that they could be used as an ideal stabilizer of metal species. Bayberry tannin, the polymers of flavan-3-ols and flavan-3-ols gallate (see Fig. 1), is a typical condensed tannin, and can be chemically grafted on –NH₂ containing supports through a Mannich reaction [13]. Our previous study indicated that bayberry tannin can form covalent bonds with –NH₂ groups of collagen fiber through cross-linking of aldehyde [14]. In this study, a series of novel Pt–bayberry tannin–SiO₂ (Pt–BT–SiO₂) heterogeneous catalysts were prepared by supporting platinum nanoparticles on bayberry tannin grafted SiO₂ beads, and characterized by UV–DR, XRD, SEM and TEM. The mechanism of coordinative interaction between platinum and bayberry tannin was investigated by X-ray photoelectron spectroscopy (XPS). Furthermore, the activity, stability and reusability of the catalysts in aqueous hydrogenation were evaluated by using acrylic

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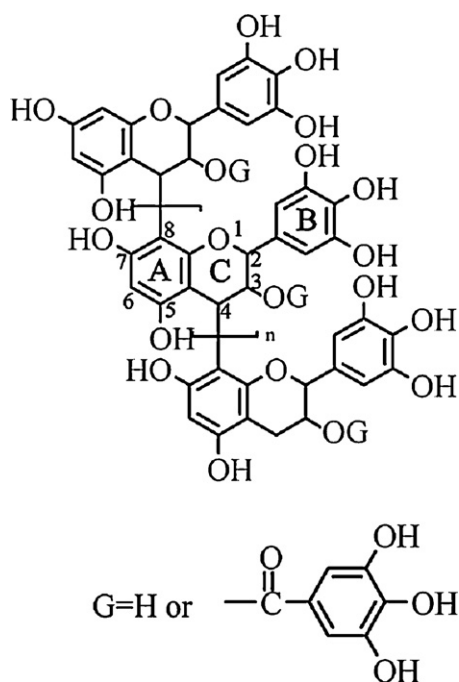


Fig. 1. Scheme of molecular structure of bayberry tannin.

acid, α -methacrylic acid, allyl alcohol and 2-methyl-3-buten-2-ol as model substrates.

2. Experimental

2.1. Reagents and methods

Cyclohexane, 1-hexanol, tetraethyl orthosilicate (TEOS), 3-aminopropyltriethoxysilane (APES), glutaraldehyde, allyl alcohol, platinum chloride (PtCl_4) and other chemicals were all analytic reagents and purchased from Aladdin Corporation. Bayberry tannin was obtained from the barks of *myrica esculenta* by extraction with an acetone–water solution (1:1, v/v) and then spray-dried.

The concentration of bayberry tannin in solutions was analyzed by ultraviolet–visible spectrum (UV–vis, TU-1901). The Pt(IV) concentration in solutions was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, PerkinElmer Optima 2100 DV). Wide-angle X-ray diffraction (XRD) patterns of the catalysts were recorded by an X'Pert PRO MPD diffractometer (PW3040/60) with $\text{Cu-K}\alpha$ radiation. Transmission microscopy (TEM) images of the catalysts were obtained in a FEI-Tecna G2 microscope. X-ray photoelectron spectra (XPS) of the catalysts were recorded by a Shimadzu ESCA-850 spectrometer, and the binding energy was calibrated by placing the principal C 1s peak at 284.7 eV. Ultraviolet–visible diffusion reflection spectra (UV–DR) of the samples were measured by a Cary 500 spectrophotometer. The composition of catalytic reaction systems was analyzed by gas chromatography (Shimadzu, CG-2010).

2.2. Preparation of aminated silica beads

1 mL of 1-hexanol, 1 mL of Triton X-100 and 4 mL of cyclohexane were added to 500 mL deionized water with vigorous stirring to obtain emulsion. Then, 9 mL of TEOS (silica source) and 3 mL of APES (aminating agent) were added to the emulsion, followed by vigorous stirring at 303 K for 2 h. A proper amount of ammonia was dropwise added into the mixture to promote the hydrolysis of the silica precursor, and then the mixture was further stirred

at 303 K for another 2 h. Afterwards, 2 mL of acetone, used as the emulsion breaker, was added to the emulsion. When the breaking of the emulsion was completed, the aminated silica beads (SiO_2 beads) were collected by filtration, washed thoroughly with deionized water and dried in vacuum at 353 K for 24 h.

2.3. Preparation of bayberry tannin grafted SiO_2 beads

In 50 mL deionized water was dissolved 0.05, 0.1, 0.2, 0.5 and 1.0 g of bayberry tannin, and then mixed with 1.0 g of aminated SiO_2 beads prepared above, followed by constant stirring at room temperature for 2 h. 2 mL of glutaraldehyde (50%, w/w) was dropwise added to the mixture under constant stirring in order to graft bayberry tannin onto the SiO_2 beads. After reaction for 12 h at 313 K, bayberry tannin grafted SiO_2 beads ($\text{BT}_x\text{-SiO}_2$, x : grafting degree of bayberry tannin on SiO_2) were collected by filtration, fully washed with deionized water and dried in vacuum at 303 K for 24 h. The grafting degree of bayberry tannin on $\text{BT}_x\text{-SiO}_2$ was defined as:

$$\frac{\text{amount of bayberry tannin grafted onto SiO}_2(\text{g})}{\text{amount of SiO}_2(\text{g})}$$

Therefore, the grafting degree of bayberry tannin on the $\text{BT}_x\text{-SiO}_2$ prepared was approximately 0.04, 0.09, 0.18, 0.30, and 0.42.

2.4. Preparation of Pt– $\text{BT}_x\text{-SiO}_2$ and Pt– SiO_2

1.0 g of $\text{BT}_x\text{-SiO}_2$ ($x = 0.04, 0.09, 0.18, 0.30, \text{ and } 0.42$) was added to 20 mL of PtCl_4 solution at pH 3.0, where the concentration of Pt(IV) was 400.0 mg/L. The reaction was conducted at 303 K with constant stirring for 24 h. Pt(IV)– $\text{BT}_x\text{-SiO}_2$ was obtained after filtration and washed with deionized water. The Pt(IV)– $\text{BT}_x\text{-SiO}_2$ was subsequently added to 50 mL of deionized water, and Pt(IV) was reduced by dropwise adding a proper amount of NaBH_4 solution. Finally, the Pt– $\text{BT}_x\text{-SiO}_2$ was collected after fully washed with deionized water and dried in vacuum at 303 K for 24 h.

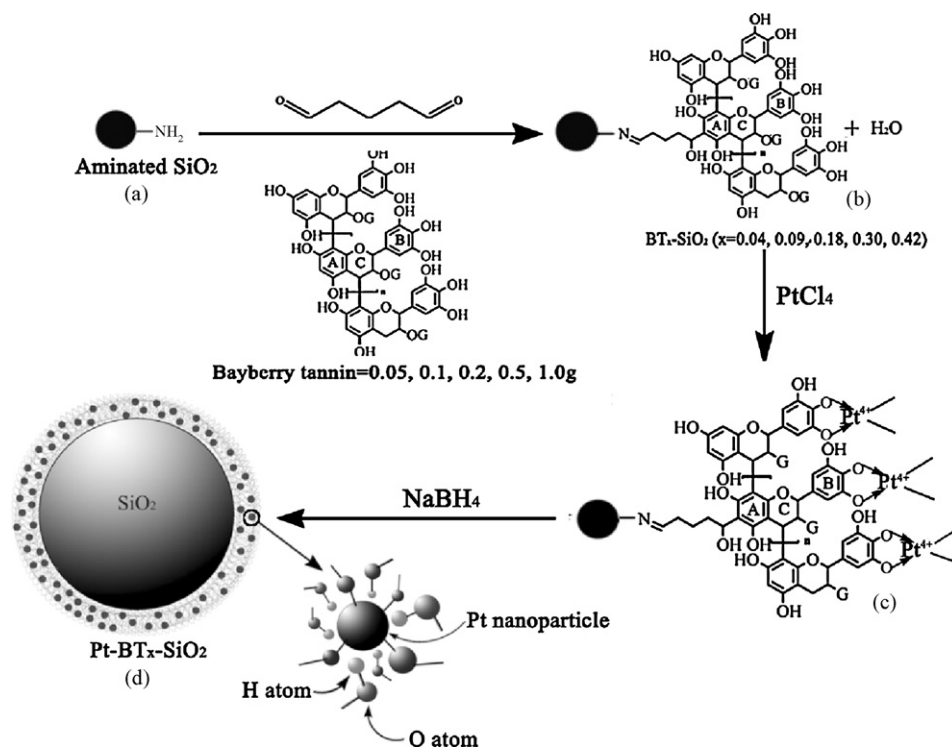
As for preparation of Pt– SiO_2 catalyst, SiO_2 beads were suspended in PtCl_4 solution, and gently stirred at room temperature for 2 days. Then the product was transferred into an oven at 353 K to completely evaporate water. The collected solid was fully washed with deionized water and then reduced by NaBH_4 solution under vigorous stirring. Finally, the Pt– SiO_2 catalyst was obtained by filtration, fully washed with deionized water and dried in vacuum at 313 K for 24 h. The loading degree of Pt on Pt– SiO_2 was found to be 0.47% (w/w).

2.5. Catalytic hydrogenation reactions

Acrylic acid (10.0 mmol), Pt– $\text{BT}_x\text{-SiO}_2$ catalyst (containing 10.0 μmol Pt) and methanol (30.0 mL) were introduced into a 50 mL stainless steel autoclave equipped with a stirring bar. The catalytic reaction was carried out at 298 K under a constant stirring (1200 rpm) and hydrogen pressure (1.0 MPa). The products of hydrogenation reaction were analyzed using gas chromatography. The used catalyst was recovered by filtration, thoroughly washed with methanol, and then reused. The turnover frequency (TOF) of the catalysts was calculated according to the following equation:

$$\frac{\text{substrate hydrogenated (mol)}}{\text{Pt (mol)} \times t (\text{min})}$$

As control, the hydrogenation was also carried out by using 0.47% Pt– SiO_2 as catalysts. Additionally, hydrogenations of α -methacrylic acid, allyl alcohol and 2-methyl-3-buten-2-ol catalyzed by Pt– $\text{BT}_x\text{-SiO}_2$ catalysts were also carried out to evaluate the applicability of Pt– $\text{BT}_x\text{-SiO}_2$ in aqueous hydrogenation. The



Scheme 1. Proposed mechanism for the preparation of Pt-BT_x-SiO₂.

experimental conditions for these reactions were the same as those for acrylic acid hydrogenation.

3. Results and discussion

3.1. Bayberry tannin grafted SiO₂ beads

Fig. 1 illustrates the molecular structure of bayberry tannin. It can be seen that bayberry tannin has well-defined molecular structure and mainly consists of polymerized flavan-3-ols. There are a large number of adjacent phenolic hydroxyls located at the B-ring of bayberry tannin, which have strong affinity towards many kinds

of metal ions. The C-ring of bayberry tannin partly attached to galloyl groups that can enhance chelating ability of bayberry tannin towards metal ions [15]. On the other hand, the C₆ and C₈ positions of A-ring of bayberry tannin possess excellent nucleophilic reaction activity, and therefore, bayberry tannin can form covalent bonds with the amino groups grafted on SiO₂ beads through cross-linking of glutaraldehyde [16]. As illustrated in Scheme 1a and b, the grafting of bayberry tannin on SiO₂ beads is easy to handle, and the reaction takes place in water solution without use of organic solvent.

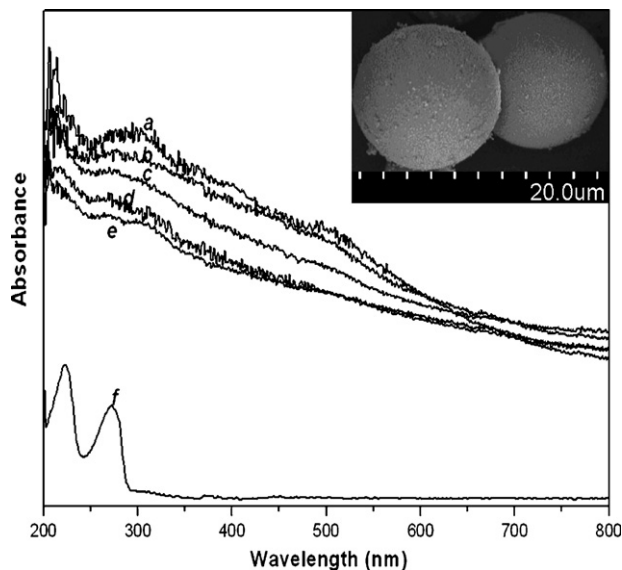


Fig. 2. Ultraviolet–visible diffusion reflection spectrum (UV–DR) of BT_{0.42}-SiO₂ (a), BT_{0.30}-SiO₂ (b), BT_{0.18}-SiO₂ (c), BT_{0.09}-SiO₂ (d), BT_{0.04}-SiO₂ (e) and SiO₂ (f).

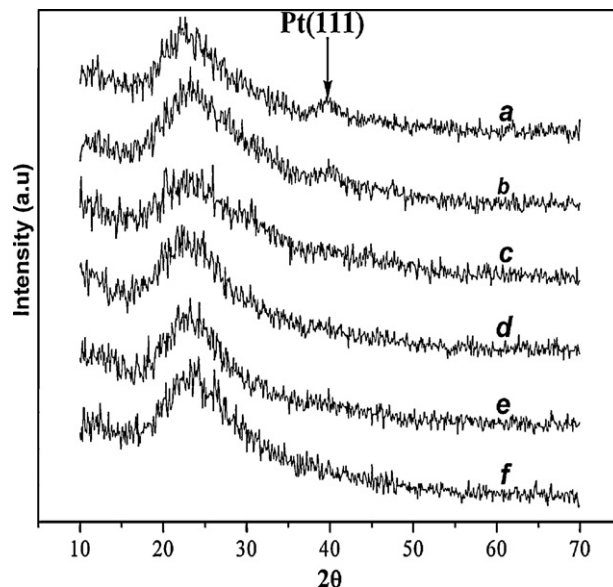


Fig. 3. Wide-angle X-ray diffraction (XRD) patterns of Pt-SiO₂ (a), Pt-BT_{0.04}-SiO₂ (b), Pt-BT_{0.09}-SiO₂ (c), Pt-BT_{0.18}-SiO₂ (d), Pt-BT_{0.30}-SiO₂ (e) and Pt-BT_{0.42}-SiO₂ (f).

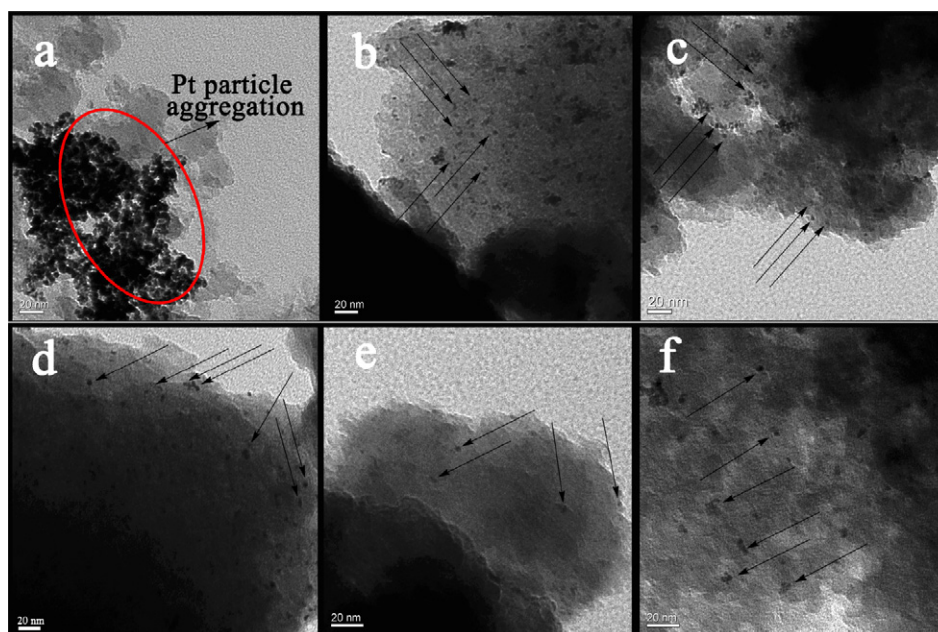


Fig. 4. Transmission microscopy (TEM) images of Pt-SiO₂ (a), Pt-BT_{0.04}-SiO₂ (b), Pt-BT_{0.09}-SiO₂ (c), Pt-BT_{0.18}-SiO₂ (d), Pt-BT_{0.30}-SiO₂ (e), and Pt-BT_{0.18}-SiO₂ reused five times (f).

Fig. 2 shows the UV-DR spectra of BT_x-SiO₂ ($x = 0.04, 0.09, 0.18, 0.30, \text{ and } 0.42$) and SiO₂ beads. It can be seen that SiO₂ beads have only a weak absorbance in the wavelength region of 200–300 nm, corresponding to the white color of SiO₂ beads. However, all the BT_x-SiO₂ exhibit a relatively strong absorbance in 200–800 nm, corresponding to the dark brown color of BT_x-SiO₂. Additionally, the absorption intensity of BT_x-SiO₂ increases with the increase in the degree of grafting of bayberry tannin. All these facts confirm that bayberry tannin was successfully grafted onto SiO₂ beads. In addition, the XPS C 1s spectrum of BT-SiO₂ exhibited three peaks in relation to C-C, C-O and C=O [Supporting information 1 (SI 1)], which also confirm the successful grafting of BT on SiO₂.

3.2. Preparation of Pt-BT_x-SiO₂

Scheme 1 shows a proposed mechanism for the preparation of Pt-BT_x-SiO₂. Pt(IV) is adsorbed on the surface of BT_x-SiO₂ via the formation of a five-membered ring complex with adjacent phenolic hydroxyls of bayberry tannin. Then, Pt(IV)-BT_x-SiO₂ is converted to Pt-BT_x-SiO₂ [Pt = Pt(0) or Pt(II)] with the reduction of NaBH₄, and the formed Pt nanoparticles are still anchored by the phenolic hydroxyls of bayberry tannin. This proposed mechanism has been proved by XPS analyses in Section 3.3. Herein, a series of Pt-BT_x-SiO₂ ($x = 0.04, 0.09, 0.18, 0.30, \text{ and } 0.42$) catalysts were prepared (SI 2), and the Pt loadings of all the catalysts were calculated according to the concentration difference of Pt(IV) in solution before and after the loading reaction of Pt(IV).

XRD patterns of Pt-BT_x-SiO₂ catalysts are illustrated in Fig. 3. It can be seen that all the Pt-BT_x-SiO₂ catalysts present a peak of SiO₂ at 24.4°, which indicates that the structure of amorphous SiO₂ beads is well preserved after the grafting of bayberry tannin. In addition, the peak at 40.5° can be attributed to the (1 1 1) reflection of Pt(0) crystals [17], which suggests that Pt(0) particles are formed in the catalysts. Moreover, this peak gradually disappears with increasing amount of grafted bayberry tannin, implying that the Pt(0) particles are more uniformly dispersed in Pt-BT_x-SiO₂ catalyst at a high content of bayberry tannin.

TEM images of Pt-SiO₂, Pt-BT_x-SiO₂ ($x = 0.04, 0.09, 0.18, \text{ and } 0.30$) and the reused Pt-BT_{0.18}-SiO₂ are presented in Fig. 4. As

shown in Fig. 4a, aggregation of Pt nanoparticles on pure SiO₂ bead is obviously observed because there is no ligand to stabilize Pt nanoparticles that have extremely high surface energy and tend to aggregate together. Compared with Pt-SiO₂, the aggregation of Pt nanoparticles on Pt-BT_x-SiO₂ catalysts is prevented due to the stabilizing effect of phenolic hydroxyls of bayberry tannin, and the dispersion of Pt nanoparticles is more remarkable at a higher content of bayberry tannin (Fig. 4c–e). The average particle sizes of Pt-BT-SiO₂ with different tannin contents are 5.83 (Pt-BT_{0.04}-SiO₂), 4.67 (Pt-BT_{0.09}-SiO₂), 4.17 (Pt-BT_{0.18}-SiO₂) and 2.68 nm (Pt-BT_{0.3}-SiO₂) (SI 3). The stabilization of bayberry tannin towards Pt nanoparticles is so effective that even a small amount of bayberry tannin can prevent Pt nanoparticles from aggregation (Fig. 4b). Considering the well dispersion of Pt nanoparticles, a high catalytic activity of Pt-BT_x-SiO₂ can be expected in the following hydrogenation reactions.

3.3. Preparation mechanism of Pt-BT_x-SiO₂

The XPS survey scan spectrum of Pt-BT-SiO₂ is shown in Fig. 5. The main components of Pt-BT-SiO₂, such as O, Si and C, exhibit strong absorption intensity, while Pt shows relatively weak absorption intensity because of its low content (0.47%) in the catalysts. To investigate the preparation mechanism of Pt-BT-SiO₂, XPS fine scan of the catalysts was carried out. As shown in Fig. 6a, BT_{0.18}-SiO₂ presents a single peak at 532.75 eV, showing the existence of phenolic hydroxyls (C-O-H) of bayberry tannin [18]. Note that this interpretation assumes that due to the presence of BT, oxygen and surface hydroxyls of SiO₂ do not make a significant contribution to the O1 s signal. After the adsorption of BT_{0.18}-SiO₂ to Pt(IV), the O1 s peak of the phenolic hydroxyls shifts to 533.10 eV (Fig. 6b), which indicates a partial decrease in the electronic density around the O atoms due to the coordination of Pt atoms with the phenolic hydroxyls of bayberry tannin [C-O-Pt(IV)]. The small peak at 532.76 eV in Fig. 6b is correlated to the free phenolic hydroxyls (free C-O-H). It is well known that Pt often exists as oxide when exposed to air [19,20]. Thus the small peak at 531.87 eV in Fig. 6b is attributed to Pt oxide, which may form during the adsorption process [21]. Fig. 6c shows a small peak at 531.67 eV and a major

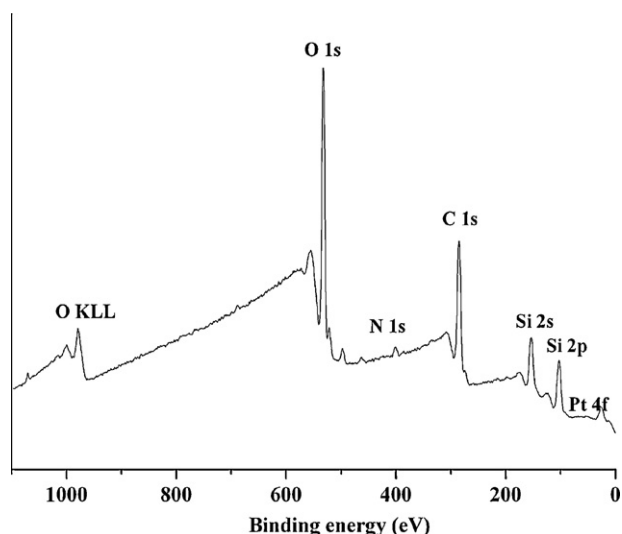


Fig. 5. Survey scan of Pt-BT_{0.18}-SiO₂ in the range of 0–1100 eV.

peak at 532.80 eV. The peak at 531.67 eV is assigned to Pt oxide of Pt-BT-SiO₂, and its intensity obviously increased in comparison with the peak of Pt oxide in Pt(IV)-BT-SiO₂ (531.87 eV, Fig. 6b). This observation suggested that a part of Pt(IV) was formed to the corre-

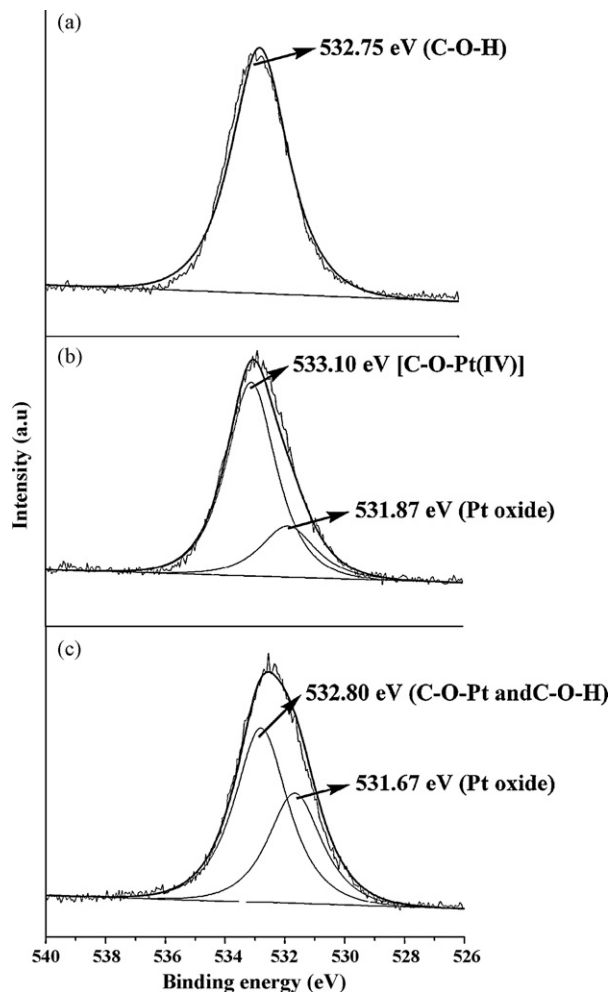


Fig. 6. O 1s XPS spectrum of BT_{0.18}-SiO₂ (a), Pt(IV)-BT_{0.18}-SiO₂ (b) and Pt-BT_{0.18}-SiO₂ (c).

sponding oxides during the reduction of Pt(IV)-BT-SiO₂. The major peak at 532.80 eV should be attributed to free phenolic hydroxyls (C-O-H) as well as the phenolic oxygens bounded to Pt species (C-O-Pt). A reasonable explanation for this attribution is that a part of the phenolic oxygens chelated with Pt(IV) (O 1s peak at 533.10 eV, Fig. 6b) were reconverted into free phenolic hydroxyls by recombining protons from NaBH₄ which leads to a down-shifting of the binding energy, while a part of them still bound to Pt nanoparticles because of the high activity of surface Pt atoms. The N 1s spectrum of BT_{0.18}-SiO₂ has two peaks at 402.2 and 399.9 eV (SI 4), which should be attributed to -N-C and -NH₂ groups, respectively. After adsorption of Pt(IV) ions, the binding energy and the areas of these two peaks are almost unchanged (SI 5), which confirms that Pt(IV) is mainly chelated with phenolic hydroxyls of bayberry tannin but not with the amino groups of aminated SiO₂. A reasonable explanation for these facts is that, compared with single amino groups of aminated SiO₂, the adjacent phenolic hydroxyls of bayberry tannin have much stronger chelating ability towards Pt(IV). In SI 6, the Pt 4f spectrum of Pt-BT_{0.18}-SiO₂ shows two pairs of doublets from the spin-orbital splitting of the 4f_{7/2} and 4f_{5/2}. The doublets observed at 71.89 and 74.99 eV are attributed to Pt(0) while those at 73.0 and 76.59 eV are assigned to Pt(II). These facts indicate that all the Pt(IV) species are reduced to Pt(II) and about half of the Pt(II) species are further reduced to Pt(0), which suggests that the Pt nanoparticles observed in the TEM images of Pt-BT_x-SiO₂ catalysts (Fig. 4b–f) should be Pt(0) nanoparticles and/or Pt(0)-Pt(II) hybrid nanoparticles. Similar observation has been reported by other researchers [22].

3.4. Hydrogenation reaction

3.4.1. The effect of degree of grafting of bayberry tannin on hydrogenation reaction

The dependence of hydrogenation rate on the degree of grafting of bayberry tannin is shown in Table 1. When the grafting degree was 0.04, the content of bayberry tannin is not high enough for Pt nanoparticles to be well dispersed. As a result, the hydrogenation rate of acrylic acid on Pt-BT_{0.04}-SiO₂ is only 13.15 mol/mol min. With the increase in the grafting degree of bayberry tannin, the hydrogenation rate of Pt-BT_x-SiO₂ catalysts increases and reaches to maximum (16.22 mol/mol min) at the grafting degree of 0.18. A further increase in the grafting degree leads to a decrease in TOF. A reasonable explanation for this phenomenon is that the excessive content of bayberry tannin grafted on the surface of SiO₂ beads restricts the access of reactant to the surface of Pt nanoparticles. Since Pt-BT_{0.18}-SiO₂ has the highest activity, it was used in the following experiments.

3.4.2. Aqueous hydrogenation of α -methacrylic acid, allyl alcohol, and 2-methyl-3-buten-2-ol

In addition to acrylic acid, other substrates including α -methacrylic acid (1), allyl alcohol (2), and 2-methyl-3-buten-2-ol

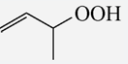
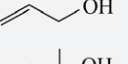
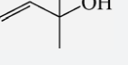
Table 1

TOFs (mol/mol min) of hydrogenation of acrylic acid catalyzed by different catalysts.^a

Catalyst	Activity of the catalysts	
	TOFs (mol/mol min)	Conversion yield (%)
Pt-BT _{0.04} -SiO ₂	13.15	99.8 (180 min)
Pt-BT _{0.09} -SiO ₂	14.99	99.8 (88 min)
Pt-BT _{0.18} -SiO ₂	16.22	99.8 (80 min)
Pt-BT _{0.30} -SiO ₂	12.14	99.8 (100 min)
Pt-BT _{0.42} -SiO ₂	4.52	99.8 (238 min)

^a Catalyst/substrate, 10 μ mol Pt/10 mmol; pressure, 1 MPa; reaction time, 30 min; temperature, 298 K.

Table 2TOF and conversion of hydrogenation of unsaturated substrates catalyzed by Pt–BT_{0.18}–SiO₂.

Substrate	TOF (mol/mol min) ^a	Conversion (%)
	7.05 ^b /7.13 ^c	99.8 ^b /99.8 ^c
	12.86/12.56	99.8/99.8
	6.57/6.86	99.8/99.8

^a Reaction time, 30 min.^b Hydrogenation by using fresh catalyst.^c Hydrogenation by using catalyst stored in air for two months.

(3) were selected to evaluate the universality of application of Pt–BT_x–SiO₂ catalysts in aqueous hydrogenation. Table 2 lists TOFs and conversion of the reactions catalyzed by Pt–BT_{0.18}–SiO₂. It was found that Pt–BT_{0.18}–SiO₂ exhibits satisfactory catalytic activity for all the substrates. The TOF of hydrogenation of α -methacrylic acid is 7.05 mol/mol min, which is lower than that of acrylic acid (16.22 mol/mol min). This should be due to the fact that the methyl group of α -methacrylic acid hinders its access to the active sites. Similarly, it is understandable that the TOF of hydrogenation of 2-methyl-3-buten-2-ol (6.57 mol/mol min) is lower than that of allyl alcohol (12.86 mol/mol min). It should be noted that the catalytic activity of Pt–BT_{0.18}–SiO₂ is much higher than those of other heterogeneous Pt catalysts [23]. Therefore, Pt–BT_x–SiO₂ catalysts may be widely usable for catalytic hydrogenation of unsaturated double bonds of organic substrates.

3.4.3. Reusability of Pt–BT_{0.18}–SiO₂

The reusability of a catalyst is of great importance in consideration of industrial application, and therefore, is one of the prior factors being considered in catalyst design [24]. Table 3 lists the initial hydrogenation rate of allyl alcohol catalyzed by Pt–BT_{0.18}–SiO₂ and Pt–SiO₂ in the recycling test. The activity of Pt–BT_{0.18}–SiO₂ is almost unaffected when it is used five times, which indicates the key role of bayberry tannin on stabilizing Pt nanoparticles in the catalyst. Interestingly, the catalytic activity of Pt–BT_{0.18}–SiO₂ slightly increased during recycling. In addition to the significantly increased Pt(0) content in the reused Pt–BT_{0.18}–SiO₂ (SI 6), the stable catalytic activity of this catalyst should be mainly attributed to the fact that the structure and dispersion of Pt nanoparticles in the catalyst are well preserved during recycling (Fig. 4f). In contrast, the activity of Pt–SiO₂ is drastically decreased during recycling uses due to the relatively weak interaction between Pt and SiO₂ (SI 7). These facts suggest that the grafting of bayberry tannin on SiO₂ surface is essentially important for stabilization of Pt nanoparticles.

Table 3TOFs and conversion of hydrogenation of allyl alcohol catalyzed by recycled catalysts.^a

Recycle	Pt–BT _{0.18} –SiO ₂	Pt–SiO ₂
1	12.8 ^b /99.8 ^c	17.5/99.8
2	12.4/99.8	11.7/70.7
3	12.4/99.8	7.3/45.6
4	13.2/99.8	3.6/32.2
5	13.4/99.8	2.5/20.5

^a Catalyst/substrate, 10 μ mol Pt/10 mmol; pressure, 1 MPa; temperature, 298 K.^b TOF (mol/mol min) in 30 min.^c Conversion (%) in 120 min.

3.4.4. Stability of Pt–BT–SiO₂ catalysts

Generally, the aggregation and oxidation of Pt nanoparticles will take place during the storage of supported Pt nanoparticle catalysts, which often lead to deactivation of the catalysts [25]. However, the tests using Pt–BT_{0.18}–SiO₂ showed that Pt–BT–SiO₂ catalysts are stable enough to retain the activity even stored under ambient conditions for two months, as shown in Table 1. In fact, tannins are widely used as antioxidants in food industry because they are capable of scavenging free radicals and terminating oxidation processes [26]. Thus, bayberry tannins grafted on Pt–BT–SiO₂ catalysts not only promote the dispersion of Pt nanoparticles but also serve as antioxidant to prevent Pt(0) species from oxidation during storage or reaction process.

It should be pointed out that the bayberry tannin is unlikely hydrogenated during the hydrogenation process. As shown in Fig. 1, unsaturated bonds of BT are mainly phenyl and C=O. In general, the hydrogenation of phenyl and C=O is much more difficult than that of C=C, and their hydrogenations are often carried out under relatively higher pressure and temperature. In this study, the hydrogenation of C=C-containing substrates was conducted under mild conditions. In addition, the TOFs of Pt–BT–SiO₂ were not reduced in each recycling. Therefore, it is reasonable to suggest that BT was not hydrogenated during the hydrogenation process.

4. Conclusion

We have demonstrated that Pt nanoparticles can be well dispersed on bayberry tannin grafted SiO₂ beads. The Pt–BT_x–SiO₂ catalysts prepared by this method exhibited high catalytic activity in hydrogenation reactions as well as excellent stability of storage and recycling. Pt–BT_x–SiO₂ can be easily recovered and reused without loss of activity. In addition, it can be expected that this strategy could be applied to the synthesis of other highly dispersed metal nanoparticle catalysts.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2009.12.013.

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