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Short Communication

Highly active and selective catalytic transfer hydrogenolysis of α -methylbenzyl alcohol catalyzed by supported Pd catalyst

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ABSTRACT

A novel supported Pd catalyst was synthesized by using plant tannin grafted collagen fiber as the supporting matrix. The as-prepared Pd catalyst was subsequently used for the catalytic transfer hydrogenolysis of α -methylbenzyl alcohol. Due to the fibrous morphology of collagen fiber and the well dispersed Pd nanoparticles anchored by tannins, the as-prepared Pd catalyst showed superior activity for the catalytic transfer hydrogenolysis of α -methylbenzyl alcohol when compared with the Pd catalyst supported on inorganic oxides. Moreover, the as-prepared Pd catalyst can be reused at least 6 times without significant loss of activity and selectivity, suggesting a satisfied reusability.

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1. Introduction

Catalytic transfer hydrogenolysis (CTH) is an important synthetic technique, which has been widely used in biomass conversion [1–3], pharmaceutical production [4,5] and organic synthesis [6–8]. By using organic compound as hydrogen donor, CTH can be conveniently carried out under mild conditions, which exhibits distinct advantages over the conventional hydrogenolysis methods that need to be performed with molecular hydrogen at high pressure. In addition, CTH is available for various functional groups including alcohol, halo, nitro and benzyl [9–13], thus providing an environmental benign synthetic route for a large number of organic compounds.

In general, noble metals, such as palladium [6,7], platinum [14] and nickel [15], have been employed as the catalysts in CTH, and those metals were often immobilized onto insoluble matrices to improve their reusability. Inorganic oxides with high specific surface area are commonly used as the supporting matrices, including active carbon, γ -alumina and silica etc. [16]. Unfortunately, those immobilized metal species often suffered from a reduced catalytic activity due to their poor distribution with aggregation. Furthermore, the metal species may also be leached into the solvent during reaction owing to the weak association with supporting matrices, which inevitably leads to a decreased activity when the catalyst was recycled. Ideally, the metal species should be stably immobilized onto the supporting matrix via suitable interaction, and the metal species are also need to be highly dispersed on the surface of supporting matrix. As a consequence, the design of supporting matrix becomes the crucial factor for preparing noble metal catalyst with high activity and stability for CTH reaction.

Our previous research showed that collagen fiber was able to react with plant tannins to prepare adsorbents, which were highly effective for the adsorptive recovery of Pd^{2+} and Pt^{2+} from aquoues solutions [17]. Moreover, Pd^{2+} and Pt^{2+} absorbed by the adsorbent can be desorped using diluted acid solution, indicating that the interaction of Pd^{2+}/Pt^{2+} with tannin is mild. In addition, the fibrous morphology of collagen fiber can considerably decrease the mass transfer resistance. resulting fast adsorption rate. Based on unique characteristics of the fibrous adsorbent, we proposed herein a feasible strategy for synthesis of highly active and recoverable heterogenous Pd catalyst for CTH reaction, that is the use of plant tannins grafted collagen fiber as the supporting matrix to prepare heterogenous supported Pd nanoparticles catalyst. In this supporting matrix, the phenolic hydroxyls of plant tannins act as the anchors of Pd nanoparticles, thus ensuring a high dispersion and stability of Pd nanoparticles. Additionally, the low mass transfer resistance nature of the fibrous supporting matrix should be also beneficial for the CTH reaction performance, resulting in a higher catalytic activity. At present investigation, α -Methylbenzyl alcohol (MBA) was employed as model compound to study the activity and selectivity of the as-preapred Pd catalyst in CTH reaction of alcohol (C-OH bond). As shown in Scheme 1, the target product in CTH of MBA was ethylbenzene (EB) while acetophenone (AP) may also be formed as the by-product. We therefore systematically investigated the effects of various experimental conditions on the

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Scheme 1. The disproportionation-type reaction of MBA during the CTH process.

activity and selectivity of the as-prepared Pd catalyst in CTH of MBA, such as water content in reaction medium, type of hydrogen donor and reaction temperature. For comparison, Pd/C, Pd/SiO₂, and Pd/Al₂O₃ catalysts were also used in CTH of MBA under the same conditions.

2. Experimental

2.1. Materials

PdCl₂, formic acid, NaBH₄, and other chemicals were all analytical reagents and purchased from Sigma-Aldrich Corporation, which were used as received without further purification. Pd/C (2.0%) and MBA (97%) was purchased from Alfa Aesar. Collagen fiber (CF) was purchased from Institute of Chemical Industry of Forest Product (China). Black wattle tannin (BT), a typical condensed tannin, was

provided by the plant of forest product in Guangxi province (China). Pd/SiO₂, and Pd/Al₂O₃ were prepared by conventional impregnation methods (see supporting information).

2.2. Preparation and characterization of Pd nanoparticles supported on black wattle tannin grafted collagen fiber (Pd–BT–CF)

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%), used as bifunctional cross-linking agent, was added into the above mixture at pH 6.5, and 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 black wattle tannin grafted collagen fiber (BT–CF) supporting matrix was obtained. Based on ultraviolet measurement, the grafting degree of BT on BT–CF was determined to be 60% by weight.

Subsequently, 1.0 g of BT–CF was suspended in 100.0 mL of PdCl₂ solution, of which the concentration of Pd²⁺ was 2.0×10^{-3} mol/L. After the solution pH was adjusted to 4.5, the mixture was stirred at 303 K for 8.0 h, allowing the chelating adsorption of Pd²⁺ on BT–CF. Then, the mixture was filtrated and fully washed with deionized water. The collected intermediate product was reduced by 20.0 mL of 0.1 M NaBH₄ 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.



Fig. 1. The molecular structure of BT, and the proposed preparation mechanism of the Pd-BT-CF catalyst.

The obtained Pd–BT–CF was then characterized by Scanning Electron Microscopy (SEM, JEOL LTD JSM-5900LV), X-ray Photoelectron Spectroscopy (XPS, Kratos XSAM-800, UK) and Transmission Electron Microscopy (TEM, Tecnai G² F20 S-TWIN, U.S.).

2.3. CTH of MBA

The CTH reaction of MBA was carried out in a 50.0 mL roundbottomed flask equipped with water-cooled condenser and magnetic stirrer. The flask was added with 10.0 mL of ethanol, an appropriate amount of water, 1.5 mmol of MBA, a certain amount of hydrogen donor and 50.0 mg of palladium catalyst (containing 10.0 µmol Pd). During the reaction, the flask was placed in the oil bath and maintained at the given temperature under atmosphere pressure. The reaction mixture was analyzed at regular intervals using a gas chromatograph equipped with a flame ionization detector and a capillary column (ECTM-WAX, 30.0 m×0.25 mm×0.25 mm). For comparison, the CTH of MBA was also performed using commercial Pd/C (2.0%) catalyst under the same conditions. The turnover frequency (TOF) of the catalysts was calculated

as: Substrate reacted(mol)

Pd(mol) \times t(h)

3. Results and discussion

3.1. Preparation and characterization of the Pd-BT-CF catalyst

The molecular structure of BT is shown in Fig. 1a. it can be seen that there are large numbers of phenolic hydroxyls located at the B rings of BT, which are able to chelate with many metal ions with empty d orbits, like Pd²⁺[18]. On the other hand, the A rings of BT have high nucleophilic reaction activity, and thus, BT can be covalently bound with the amino groups of CF using glutaraldehydes as the crosslinking agents (Fig. 1b). Additionally, the hydrogen bonds formed between BT and the amino groups of CF can also improve the stability of BT-CF. Subsequently, the obtained BT-CF was used for the adsorption of Pd^{2+} , and further reduced to Pd nanoparticles by NaBH₄, and finally, the Pd–BT–CF catalyst was obtained (Fig. 1c–d). Due to the electron donating/accepting interactions of phenolic hydroxyls of BT with Pd nanoparticles, the Pd nanoparticles should be stably anchored by the BT grafted onto CF, which can prevent the aggregation of Pd nanoparticles and improve its stability during catalytic reaction process.

To confirm the proposed preparation mechanism, XPS analyses of BT–CF, Pd²⁺–BT–CF and Pd–BT–CF were carried out. In Fig. 2a, the O 1s spectrum of BT-CF shows two peaks at 533.0 eV and 531.6 eV, respectively. The peak at 533.0 eV is assigned to the oxygen in -C-O-H bond (mainly attributed to phenolic hydroxyls of BT) while the peak 2 at 531.6 eV is related to the oxygen in -C O bond [19,20]. After the adsorption of Pd^{2+} on BT-CF, the O 1s spectrum of Pd²⁺–BT–CF exhibits a new peak at 534.1 eV (Fig. 2b), which should belong to the electron donating-accepting interaction of Pd²⁺ with BT when considering the strong chelating ability of BT towards transition metal ions. After the reduction of Pd^{2+} , another new peak with high binding energy of 537.3 eV is observed at the O 1s spectrum of Pd-BT-CF (Fig. 2c). This new peak is likely to be associated with the stabilization interaction of hydroxyl oxygens of BT to the formed Pd nanoparticles. Consequently, it can be concluded that the BT-CF support is able to stabilize the Pd nanoparticles by its phenolic hydroxyls. In addition, the Pd 3d XPS analysis of Pd-BT-CF revealed that about 63.9% of Pd²⁺ has been reduced to elemental Pd (data is not shown here).

The SEM image of the Pd–BT–CF catalyst is shown in Fig. 3a. It is clearly observed that the fibrous morphology of collagen fiber was well preserved after the grafting of BT and the anchoring of Pd nanoparticles. According to the literature [21], fibrous materials usually offer better mass transfer characteristics, and thus higher



Fig. 2. The O 1s XPS spectra of BT-CF (a), Pd²⁺-BT-CF (b) and Pd-BT-CF (c).

catalytic activity of the Pd–BT–CF catalyst for CTH of MBA can be expected. Further TEM analysis revealed that the Pd nanoparticles with an average diameter of 4.0–6.0 nm were well dispersed in the Pd–BT–CF catalyst (Fig. 3b), which confirmed the anchoring effect of BT towards the Pd nanoparticles. Based on the above XPS analysis of Pd 3d spectrum of Pd–BT–CF, the observed Pd nanoparticles in Fig. 3b should be Pd(0) nanoparticles and/or Pd(0)-Pd(II) hybrid nanoparticles.

3.2. CTH of MBA

3.2.1. Effect of water content

In general, the mixture of water and ethanol is often used as the solvent in CTH because the use of water is able to promote the



Fig. 3. SEM and TEM images of the Pd-BT-CF catalyst.

ionizability of hydrogen donor [22], which therefore results in the formation of more active hydrogen species. As a consequence, we first investigated the effect of water content on the CTH of MBA. As shown in Fig. 4, the increase of water content always promotes the conversion of MBA, which reaches the maximum when the volume ratio of water to ethanol was 2:10. Considering the fact that HCOOH is soluble in pure ethanol, the promoted conversion of MBA should be due to the promoted dissolution of HCOOH by water but not the increased solubility of HCOOH in water/ethanol mixture. On the other hand, the selectivity to EB first increases with the increase of water content (from 0 to 20%), and then gradually decreases along with the further increase of water content from 20% to 100%. These facts suggested that the use of water can promote the conversion of MBA, but excessive use of water leads to the decrease in selectivity to EB. Therefore, the content of water was fixed at 20% (v/v) in the following experiments.

3.2.2. Effect of hydrogen donor

From the perspective of green chemistry, HCOOH and formate salts are more environmental benign hydrogen donors than other organic compounds such as 2-propanol and hydrazine [23]. Hence, HCOOH and formate salts were used as the hydrogen donors to perform the



Fig. 4. Effect of water content on the CTH of MBA.

CTH of MBA. Table 1 summarized the activity and selectivity of the Pd-BT-CF catalyst in CTH of MBA using different hydrogen donors. By using HCOOH as the hydrogen donor, the Pd-BT-CF catalyst exhibits the highest activity and selectivity while much lower conversion and selectivity to EB were observed when formate salts were employed. Feng et al. suggested that the dissociative chemisorption of HCOO⁻on Pd metals and the protonation of MBA by H⁺ are the key factors in CTH of MBA [16]. Hence, HCOOH can provide both HCOO⁻ and H⁺ and ensures the highest activity and selectivity in CTH of MBA. This suggestion is consistent with our experiments. It should also be noted that due to the well dispersion of Pd nanoparticles as well as the fibrous morphology of the catalyst, the TOF value of the Pd-BT-CF catalyst $(316.6 \text{ mol mol}^{-1} \text{ h}^{-1})$ was much higher than those of conventional supported catalyst using inorganic oxides as the supporting matrices (Entry 1-4). For example, the average TOF of the Pd-BT-CF catalyst was almost 5-folds higher than that of the commercial Pd/C catalyst (60.0 mol mol⁻¹ h⁻¹) when HCOOH was used as the hydrogen donor. Compared with the commercial Pd/C catalyst, the superior activity of the as-prepared Pd catalyst directly supports our claimed strategy that the fibrous morphology of collagen fiber and the well dispersed Pd nanoparticles anchored by tannins can improve the activity of the supported Pd catalyst for the catalytic transfer hydrogenolysis of α -methylbenzyl alcohol.



Fig. 5. Effect of reaction temperature on CTH of MBA.



Fig. 6. Recycling of the Pd-BT-CF catalyst in the CTH of MBA.

3.2.3. Effect of molar ratio of HCOOH to MBA

As mentioned above, the HCOOH provides both HCOO⁻ and H⁺ in CTH of MBA, thus the molar ratio of HCOOH to MBA should influence the conversion of MBA as well as the selectivity to EB. We therefore investigated the effect of molar ratio of HCOOH to MBA in CTH of MBA. The corresponding results are summarized in Table 2. As expected, the conversion of MBA and the selectivity to EB are both considerably increased with the increase of molar ratio of HCOOH to MBA, which roughly reaches the maximum when the molar ratio is 2.0. When the molar ratio is 4.0, the conversion, TOF and selectivity of EB were 100%, 319.1 and 99.5%, respectively.

3.2.4. Effect of reaction temperature

The effect of reaction temperature on the catalytic activity of the Pd-BT-CF catalyst was also investigated, and the corresponding results are shown in Fig. 5. It can be seen that the increase of reaction temperature accelerates the reaction rate in CTH of MBA. When the temperature is increased from 20 °C to 60 °C, the conversion of MBA is significantly increased from 21.1% to 99.2%. As for the selectivity to EB, it is also steadily increased along with the increase of temperature in the temperature range of 20-60 °C. Therefore, the reaction temperature should not be lower than 60 °C in order to obtain high conversion and selectivity.

Table 1

Effect of hydrogen donors on the CTH of MBA*.

Entry	Hydrogen donor	Conversion (%)	Average TOF $(mol mol^{-1} h^{-1})$	Selectivity (%)	
				EB	AP
1 ^a	НСООН	99.2	316.6	99.0	1
2 ^b	HCOOH	18.8	60.0	98.7	1.3
3 ^c	HCOOH	3.4	10.9	65.4	34.6
4 ^d	HCOOH	16.4	52.3	76.7	23.3
5 ^a	HCOOLi	9.8	31.3	39.9	60.1
6 ^a	HCOONa	8.1	25.9	57.6	42.4
5 ^a	HCOOK	17.3	55.2	81.2	18.8
6 ^a	HCOONH ₄	21.5	68.6	32.3	67.7

Reaction conditions: 1.5 mmol MBA, 3.0 mmol hydrogen donor, 10.0 mL ethanol, 2.0 mL H₂O, 60 °C and 30 min.

50.0 mg Pd-BT-CF (10 µmol) was used as the catalyst.

50.0 mg Pd/C (10 μ mol) was used as the catalyst.

50.0 mg Pd/SiO₂ (10 μ mol) was used as the catalyst. d

50.0 mg Pd/Al₂O₃ (10 μ mol) was used as the catalyst.

Table 2	
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Effect of molar ratio of HCOOH to MBA on the CTH of MBA*.

Entry	Molar ratio of HCOOH/MBA	Conversion (%)	Average TOF (mol mol ⁻¹ h ⁻¹)	Selectivity (%)	
				EB	AP
1	1.0	91.2	291.2	87.5	12.5
2	1.5	96.7	308.6	95.8	4.2
3	2.0	99.2	316.6	99.0	1.0
4	3.0	99.7	318.2	99.2	0.8
5	4.0	100	319.1	99.5	0.5

Reaction conditions: 1.5 mmol MBA, 50.0 mg Pd-BT-CF catalyst, 10.0 mL ethanol, 2.0 mL H₂O, 60 °C and 30 min.

3.2.5. Reusability of the Pd-BT-CF catalyst

As shown in Fig. 6, the catalytic activity of the Pd–BT–CF catalyst was almost unchanged after six times repeated application (the TOF value was a little changed from 318.2 to 310.9 mol mol⁻¹ h⁻¹), exhibiting satisfied reusability of the Pd-BT-CF catalyst. On the contrary, the reusability of commercial Pd/C catalyst should be improved, of which the TOF in sixth time was only about 59.5% of the fresh catalyst (from 60.0 to $35.7 \text{ mol mol}^{-1} \text{ h}^{-1}$). We believed that the anchoring effect of plant tannins to the Pd nanoparticles should be the main reason for the high stability of this novel catalyst.

4. Conclusions

Highly active and selective heterogeneous Pd catalyst was prepared by using collagen fiber grafted plant tannin as the supporting matrix. Due to the presence of plant tannin on collagen fiber, the supported Pd nanoparticles were stably anchored and well dispersed. Moreover, the fibrous morphology of collagen fiber ensured a high catalytic activity due to its nature of low mass transfer resistance. The as-preapred can be used for the catalytic transfer hydrogenolysis of α -methylbenzyl alcohol, which exhibited the distinct advantages of high activity, selectivity and reusability.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2011.04.009.

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