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Pd nanoparticles Supported on Cellulose as a catalyst for vanillin conversion in aqueous media

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ABSTRACT: Palladium nanoparticles were firstly anchored on modified biopolymer as an efficient catalyst for biofuel upgradation. Fluorinated compounds was grafted onto cellulose to obtain amphiphilic supports for on water reactions. Pd catalyst was prepared by straightforward deposition of metal nanoparticles on modified cellulose. The catalyst exhibited excellent catalytic activity and selectivity in hydrodeoxygenation of vanillin (a typical model compound of lignin) to 2-methoxy-4-methylphenol under atmospheric hydrogen pressure in neat water without any other additives under mild conditions.

Development of renewable and sustainable fuel sources to reduce reliance on fossil fuel sources become more and more urgent due to the growing energy demand and global climate change caused by application of fossil-fuel¹⁻³. Biomass has long been regarded as an ideal energy source in the future due to its renewable nature and large reservation on the earth. During the last decades, lots of systems for biomass conversion have been established, biomass could be selectively converted into high-value chemical products and biofuels. High-value chemical products such as phenols can be

directly used in the chemical and pharmaceutical industries, and biofuels seems to be an propitious candidate for fossil-fuel due to their availability, low cost² and lower greenhouse gas emissions than conventional petroleum-based gasoline⁴⁻⁶. However, owing to the large amounts of oxygen components involved in biofuels, calorific value of biofuels is relatively low and biofuel is immiscible with conventional fuels, what's more, biofuels is unstable over time due to the high content of oxygen, which limits its practical application⁷. Therefore, biofuels must be upgraded to lower the oxygen content for future application ⁸. Lignin, which constitutes ~30 wt% of woody biomass, is one of the most abundant bio-sources on earth, derive biofuels form lignin (typical pyrolysis or hydrogenolysis) meets the requirements of green and sustainable society. Nevertheless, upgradation of lignin-derived pyrolysis oil is more challenge due to its highly complex structure ⁹⁻¹³.

To study the upgradation process of lignin-derived pyrolysis oil, vanillin was selected as a model molecule. Vanillin, a common component of lignin derived pyrolysis oil, is expected to hydrogenated into 2-methoxy-4-methyl-phenol (MMP), which is a potential future biofuel in an ideal upgradation process. Recently, special efforts have been focused on water phase-involved hydrodeoxygenation (HDO) reactions to avoid the use of organic solvents. Some novel catalysts have been developed to be effective^{7,14}, El-Shall and co-workers reported Pd nanoparticles immobilized on a mesoporous sulfonic acid-functionalized metal-organic framework SO₃H-MIL-101(Cr) as an efficient bifunctional catalyst for HDO¹⁵. However, these catalysts catalyze the reaction under harsh reaction conditions, such as high temperature (over 90 °C) and high pressure (over 0.5 MPa). Besides, the by-product (4-hydroxymethyl-2-methoxy-phenol, HMP) was always formed as a result of incomplete hydrogenation due to the low catalytic activity of the catalyst. A big challenge exist in water phase-involved organic reactions is the contact between the substrates and the active metal sites, while dispersion of the heterogeneous catalysts in the aqueous medium is the foundation for excellent catalytic performance ^{16,17}. Along this line, we thought that amphiphilic catalysts may guarantee a good dispersion as well as a well contact between the substrates and the active sites in water.

Several approaches for upgradation of bio-fuels to a liquid transportation fuel have been established, among which catalytic HDO is considered to be the most important and feasible strategy. Different noble metal nanoparticles supported on various supports have been demonstrated to be

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effective heterogeneous catalysts in the HDO reactions, such as Ru^{18,19}, Pd^{7,20}, Pt²¹. In those established catalytic systems, activated carbon, metal oxides (e.g. TiO₂, MgO, CeO₂, and g-Al₂O₃), zeolites, SiO₂, and carbon nanotubes are frequently used as catalyst matrixes^{21,22}. However, those supports may suffer from poor dispersion of nanoparticle catalysts, weak catalyst–support interactions, or poor water dispersibility.

Recently, hybrid materials have been developed as catalyst supports with enhanced catalytic performances.²³ Cellulose, an earth-abundant environmentally benign biomass-derived material²⁴ has been widely used as support for its biodegradability²⁵⁻²⁸. Here we focus on the use of cellulose, which has 3 distinct advantages as a catalyst support: i) it is insoluble in common solvents, ii) it bears many hydroxyl groups that are expected to stabilize metal NPs effectively, and iii) it has great water wettability in aqueous phase. Using cellulose as catalyst support has attracted much attention due to these outstanding properities. Various metal nanoparticles supported on cellulose have been reported to catalyze different reactions²⁹⁻³⁴, for example, cellulose-supported chiral Rh nanoparticle (NP) catalysts have been developed by Kobayashi and co-workers for asymmetric 1,4-addition of arylboronic acids to enones and enoates. Interestingly, cellulose nanocrystals also have been demonstrated to have chiral properties and could work as chiral introducer in heterogeneous reactions³⁵. Various surface modifications have been made to cellulose to improve its ability of stabilizing NPs³⁶ or enhance catalyst activity by grafting functional groups³⁷. In our previous works, we report a perfluorobutyl modified cellulose supported Pd catalyst for hydrogenation of nitroarenes in water at room temperature, in which fluorinated compounds were demonstrated to be able to stabilize metal nanoparticles³⁸. What's more, researchers also found that modified the catalyst support with fluorinated ligand can enhance its lipophilicity³⁹, which may improve the local concertation of the substrate around the catalyst, thus greatly boost the reaction process. Other hydrophobic compounds combined with catalyst support have been proved to be able to enhance catalytic organic reaction in water by creating a hydrophobic environment around the active sites^{40,41}.

Herein, an amphiphilic catalyst was fabricated by introducing a trifluoromethyl group in cellulose support (CF₃-Cell), Pd nanoparticles (NPs) were directly deposited on the modified cellulose. The Pd/CF₃-Cell catalyst exhibited excellent catalytic activity and selectivity in hydrodeoxygenation of vanillin to MMP, the reaction proceed smoothly under atmospheric hydrogen pressure in neat water without any additives at low reaction temperature (50°C). Excellent

performance of the catalyst may be due to the good dispersion of the catalyst in the reaction medium (water), what's more, introducing trifluoromethyl group on cellulose improve the lipophilicity of the support, which accelerate the absorption of the substrates on the catalyst, thereby accelerating the reaction process. To the best of our knowledge, this is the first catalytic system based on the biomass-derived material for the upgradation of bio- fuels.

1 Cell modification



Scheme 1. Modification of cellulose

Scheme 1 briefly illustrates the preparation of the CF_3 -Cell. The CF_3 -Cell composite was prepared by using a modified procedure reported by MacLachlan et al⁴². Cellulose and trimethoxy(3,3,3-trifluoropropyl)-silane were dispersed in toluene and stirred under reflux temperature.

2 Catalyst characterization



Fig. 1. IR spectrum of Cellulose and CF₃-Cell

Cellulose and CF₃-Cell were characterized by IR spectrum (Fig.1). The strong peak around 3300 cm⁻¹ which is due to the stretching vibration of the O-H bonds has an obvious decrease in the peak intensity after cellulose was modified, which showed that the modification process has acted. A part of the O-H bonds on the surface of cellulose has been changed into parts with trifluoromethyl group. The O-H bending vibration frequencies at 1640 cm⁻¹ demonstrated that the sample combined micro amount of water, which nearly disappeared after fully dried. Compared to cellulose, new absorbance

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bands at 600 cm⁻¹ corresponding to the symmetric stretching vibrations and the bending mode of Si–O were detected.

The amount of the palladium supported on CF₃-Cell was 2.833 mg/g determined by ICP, which was a little lower than the theoretical value (2.99 mg/g).

Morphology of Pd/ CF₃-Cell was directly observed by Scanning electron microscopy (SEM) (Fig.S1). As shown in Fig.S1, the catalyst support is rod shaped with rough surface. The elemental mapping was showed on Fig.S2, indicating that element F is successfully grafted on cellulose and Pd is dispersed uniformly throughout the obtained CF₃-Cell Deposition of Pd NPs on CF₃-Cell is examined by TEM (Fig.2a). The TEM image of the catalyst authenticated the formation of palladium nanoparticles, which was amorphous spherical morphology with an average diameter of $2\sim3$ nm as showed in Fig.2b. However, few particles in the size range of 5–7 nm was also found.



Fig. 2. (a) TEM image of Pd/ CF₃-Cell. (b) Size distribution of Pd NPs of Pd/ CF₃-Cell

Fig. S4 depicts the XPS spectrum in the Pd 3d region for Pd/CF₃-Cell, the intense doublet centering at 335.7 and 340.8 eV belongs to metallic Pd. And there is no other doublets ascribed to the +2 oxidation state of Pd, illustrating no metal salts exists on nanoparticle surface.

2 Catalytic hydrodeoxygenation of vanillin

Considering that water is a desirable solvent for chemical reactions due to its environmentally friendly nature, low cost and easy handling, we first conducted the reaction in water and found that excellent results for the selective hydrodeoxygenation could be achieved over the cellulose-supported Pd catalyst including a 100% conversion of vanillin with a 100% selectivity for the 2-methoxy-4-methylphenol product within 2h (Table 1, entry 1). The rapid reaction might because of the hydrophobicity of trifluoromethyl compounds. In the initial stage of the reaction, reactants can be easily adsorbed by trifluoromethyl compounds, which improves the local concertation of the substrate around the catalyst and then accelerates the reaction. While in the presence of 10 wt% Pd/C catalyst, a rather low catalytic activity and selectivity were obtained when the reaction was carried out under the same conditions (Table 1, entry 10). The results clearly show that the Pd/CF₃-

Cell catalyst shows significantly higher activity and 2-methoxy-4-methylphenol selectivity as compared to the Pd/C catalyst. Over the pure support CF₃-Cell, however, no reaction took place, implying that Pd nanoparticles are inevitable for vanillin hydrodeoxygenation (Table 1, entry 11). And the conversion and selectivity did not decrease obviously until the amount of catalyst was decrease to 0.7 mol%, which means only 1 mol% catalyst can catalyze the reaction completely within 2h (Table 1, entries 1-4). Temperature is also crucial for this reaction. Unreduced vanillin and byproduct was found when temperature was lower than 50°C.

 Pd/CH_3 - Cell and Pd/C_4F_9 - Cell were also examined in the reaction (Table 1, entries 12-13). Lower activity and selectivity were obtained. This might because CH_3 - Cell has less hydrophobicity and can not adsorb organic reactants efficiently while C_4F_9 - Cell has more hydrophobicity and the catalyst dispersed poorly in water.

Table 1 Optimization of Hydrodeoxygenation of vanillin Conditions ^a.



Entry	Cat.(%)	T(℃)	Con. ^b (%)	Sel. ^b (%)	
				В	С
1	Pd/CF ₃ -Cell(2.0)	100	100	0	100
2	Pd/CF3- Cell (1.0)	100	100	0	100
3	Pd/CF3- Cell (0.7)	100	94	64	36
4	Pd/CF3- Cell (0.5)	100	93	96	4
5	Pd/CF3- Cell (1.0)	80	100	0	100
6	Pd/CF3- Cell (1.0)	60	100	0	100
7	Pd/CF3- Cell (1.0)	50	100	0	100
8	Pd/CF ₃ - Cell (1.0)	40	94	59	41
9	Pd/Cell(1.0)	50	92	69	31
10	Pd/C(1.0)	50	45	78	22
11	CF ₃ - Cell (1.0)	50	0	0	0
12	Pd/CH3- Cell (1.0)	50	75	83	17
13	Pd/C4F9- Cell (1.0)	50	41	78	22

^a Reaction conditions: vanillin (0.05mmol), catalyst, water

(3 mL), H₂ (0.1 MPa)

^b Conversion and selectivity were analyzed by GC.



Fig. 3 Trend of reactants and product proportion as a function of reaction time

Fig. 3 shows the evolution of the product concentrations as a function of reaction time. There is a rapid increase in the content of vanillin accompanied with the decrease of content of vanillin in first 60 min. In the next 60 min, hydrogenolysis of vanillin alcohol proceeded very rapidly and almost all of the vanillin alcohol had been converted to 2-methoxy-4-methylphenol via hydrogenolysis. This trend illustrates that vanillin is mainly hydrogenated to vanillin alcohol in the first step and then vanillin alcohol hydrogenated to 2-methoxy-4-methylphenol. The primary reaction mechanism was proposed as follows: at the initial stage of the reaction, H₂ is activated by Pd NPs supported on the catalysts and vanillin is rapidly adsorbed by the lipophilic trifluoromethyl compounds on the catalyst. And then vanillin was mainly hydrogenated to the vanillin alcohol

3 Catalysts reusability

The catalyst can be easily separated from the reaction solution by simple centrifugation and the reusability of the catalyst was tested. The recovered catalyst was washed with ethyl acetate $(3\times5 \text{ ml})$ and deionized water $(3\times5 \text{ ml})$. Then the recovered catalyst was used directly in next run without further drying. The catalyst is highly stable and can be reused for four cycles with only a little loss of its activity and selectivity as demonstrated (Table S1).

The amount of the palladium supported on cellulose after 5 runs was 2.37 mg/g determined by ICP, indicating metal slight leaching during the reaction procedure, which might be the main reason for the decrease of catalytic activity. As for every catalytic process, the Pd leaching in product solution after centrifugation was measured by ICP and listed in Table S2. The recovered catalyst was examined by TEM analysis and a slight increase of palladium particle size was observed (Fig. S5a and Fig. S5b), which was believed to be another reason for the de-activation of the catalyst.

Meanwhile, XPS spectrum of Pd 3d region of Pd/ CF_3 -Cell after 5 runs showed Pd nanoparticles maintained Pd⁰ state (Fig. S6). This is might because the reaction proceeded under H₂ atmosphere.

In conclusion, we have developed a heterogeneous tandem catalyst for the hydrodeoxygenation of vanillin, a common component in lignin-derived bio-oil, under mild reaction conditions. The developed Pd/CF₃-Cell catalyst exhibited high catalytic activity and selectivity in tandem hydrogenation–deoxygenation reactions and could be reused for four times with only slight loss in activity and selectivity. The high catalytic performance of Pd/ CF₃-Cell is attributed to the unique characteristics of the CF₃-Cell support, which leads not only good dispersion of the catalyst in water but also increase the local concertation of the substrate around the catalyst. This Pd/ CF₃-Cell catalyst holds promising potential for the biofuel upgrade process in aqueous phase.

EXPERIMENTAL SECTION

1 Chemicals

All reagents with AR purity (analytical reagent grade) were purchased and used as received without further purification.

2 Cellulose modification

In a typical procedure, α -cellulose (1 g) was dispersed in toluene (20ml). Then trimethoxy(3,3,3-trifluoropropyl)-silane (0.5 g) was added. The mixture was stirred at 110°C with a condenser for 24h. The final solid was separated by filtration and washed with deionized water (3×15 ml) and ethanol (3×15 ml) before dried at 60°C for 5 hours.

3 Catalyst preparation

Pd catalyst was prepared by chemical reduction with NaBH₄ as reductant. 1 mg PdCl₂ was dissolved in 0.5 ml water and 1 mg NaCl was added to accelerate dissolution. To CF₃-Cell (200 mg) in ethanol (6 ml) in a round-bottom flask (50 mL), the PdCl₂ solution was added and the mixture was stirred at room temperature for 5 h. Then a fresh prepared ethanol solution of NaBH₄ (0.8 mg, in 0.5 mL ethanol) was added into the reactor quickly under vigorous stirring at room temperature under argon atmosphere. The color of the mixture would turn to black immediately which indicates that metal salts have been reduced to metal particles. After stirring for another 1 h, the mixture was filtrated and the solid was dried in vacuum oven at 25°C for 12 h and stored in a desiccator.

4 Catalyst characterization

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Infrared (IR) spectra were collected on a Nicolet NEXUS670 Fourier transform IR spectrophotometer at room temperature.

The Pd content in the Pd/CF₃-Cell catalyst was measured by using an IRIS Intrepid II XSP inductively coupled plasma-atomic emission spectrometer (ICP-AES).

Scanning electron microscopy (SEM) was performed using a Hitachi S-4800 apparatus on a sample powder previously dried and sputter-coated with a thin layer of gold.

Transmission electron microscopy (TEM) was carried out on a JEOL JEM-1200 operating at 300 kV. The sample was diluted in ethanol and sonicated for 10 min to get an suspension. The ethanol slurry was then added dropwise onto a Cu grid covered with a thin film of carbon.

The surface electronic states were investigated by X-ray photoelectron spectroscopy (XPS, Thermo VG ESCALAB25 using AlKa radiation). The XPS data were internally calibrated, fixing the binding energy of C 1s at 284.6 eV.

5 Catalytic HDO of vanillin

Hydrogen was chosen as the hydrogen donor for the hydrodeoxygenation of vanillin. The catalytic hydrodeoxygenation of vanillin was carried out in a schlenk tube. Typically, the reactant and catalysts were dispersed into water, then the schlenk tube was purged with H_2 four times to replace air. Then the mixture was stirred at desired temperature. After reaction, the mixture was extracted by ethyl acetate. The product and unreacted reactant were analyzed by GC-MS. The catalysts were separated by centrifugation and washed with ethyl acetate (3×5 ml), deionized water (3×5 ml) and then directly used in the next cycle.

ASSOCIATED CONTENT

Supporting Information Available: HPLC spectra and MS spectra of synthesized compounds. This material is available free of charge *via* the Internet at <u>http://pubs.acs.org</u>.

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Notes

The authors declare no competing financial interest.

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