



Short communication

Chemoselective hydrogenation of nitroarenes catalyzed by cellulose-supported Pd NPs



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ABSTRACT

Cellulose-supported palladium nanoparticles (NPs) were prepared by straightforward deposition of metal NPs on modified cellulose. The catalyst exhibited excellent catalytic activity and selectivity in room-temperature hydrogenation of various nitroarenes to arylamines under atmospheric hydrogen pressure in neat water without any additives. High chemoselectivity was also achieved in the hydrogenation of substituted nitroarenes with multiple reducible groups. The catalyst can be recycled by simple centrifugation and reused for at least 4 times without significant decline of yields.

1. Introduction

Arylamine is one of the most important intermediates in the manufacture of pharmaceutical preparation, dyes, polymers, and biologically active substances [1–3]. Arylamines can be synthesized by several methods, such as reduction of aryl azides [4], amination of aryl halides [5], catalytic reduction of nitroarenes [6] and so on. Among them, the metal-catalyzed reduction of nitroarenes is one of the most cost-efficient methodologies as well as a fundamental transformation in organic chemistry [7–9]. Numerous metals have been reported for catalyzing the reduction of nitroarenes, including noble metals (Pd [10], Rh [11], Ir [12]) and earth-abundant metals (Fe, Co [8,13], Ni [13–14]). Compared with unrecoverable homogeneous metal catalysts, heterogeneous catalysts are more favorable in industry for economic and environmental consideration.

Heterogeneous catalysis is at the heart of the modern energy and chemical industries [15–17]. Heterogeneous catalysts, especially supported metal catalysts play decisive roles in both industry and academic. A plenty of materials have been applied as supports of different catalysts, such as SiO₂ [18–20], TiO₂ [21], carbon materials [22–23] and so on. The use of biopolymers as support materials for metal catalysts has been widely developed since the 1990s [24–25]. Cyclodextrin, chitosan, cellulose and some other biomass materials have been used for their biodegradability. Here we focus on the use of cellulose, for this material is a kind of earth-abundant and environmental-friendly biopolymer and bears many hydroxyl groups which make it can be easily modified and stabilize metal NPs effectively. Furthermore, cellulose is insoluble and stable in water and common organic solvents, so it can be separated by simple centrifugation as catalyst support. Indeed,

the application of cellulose in catalytic systems has already been realized. A cellulose supported Pd complex catalyst catalyzed Tsuji–Trost reaction was reported in 2001 [26]. Various mono-dispersed metal NPs immobilized on cellulose fibers via NaBH₄-mediated reduction of cellulose fibers immersed in a metal salt was reported by Kunitake and co-workers [27]. After these reports, the capability of cellulose as catalyst support attracted much attention from many researchers. Various metal nanoparticles supported on cellulose have been reported to catalyze different reactions, for example Pd NPs [28], Au NPs [29] and Cu NPs [30]. What's more, cellulose supported metal NPs can even combine with chiral ligands to catalyze synthesis of chiral products [31]. However, surface of cellulose without any modification is smooth, catalyst can only reuse for no more than 3 times because of metal leaching and aggregation. Various surface modifications have been made to cellulose to improve its ability of stabilizing NPs. Previously, both Vallribera's group and our group showed that metal nanoparticles could be stabilized by fluorinated compounds and immobilized on fluorosilica gel by fluorosilica–fluorine interactions, and the catalyst could also be applied in a series of coupling reactions [32–33]. Along this line, fluorinated cellulose can be synthesized to stabilize and immobilize NPs directly.

Recently, great progresses had been made in the hydrogenation of nitroarenes catalyzed by heterogeneous catalysts. Zhang and co-workers reported a Pd@zeolite catalyst for nitroarene hydrogenation with high chemoselectivity, arising from sterically controlled adsorption in the zeolite micro-pores [34]. Nevertheless, high hydrogen pressure is needed. Indeed, robust reducing reagent, high hydrogen pressure or high temperature are often required in previous works. The critical issue in the synthesis of amines is to choose an efficient and environmental-friendly heterogeneous catalyst with high activity, selectivity and

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reusability that can catalyze the reaction under mild conditions.

Herein we report a perfluorobutyl modified cellulose supported Pd catalyst for hydrogenation of nitroarenes in water at room temperature. Instead of robust or toxic reducing reagent (NaBH_4 or $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$), molecular hydrogen was chosen as hydrogen donor. This protocol allows an efficient transformation of nitroarenes under mild conditions.

2. Experimental section

2.1. Cellulose modification

All chemicals were purchased from commercial sources and used without further treatment. In a typical procedure, α -cellulose (500 mg) was dispersed in dry DMF (10 ml). Then the mixture was sonicated for 30 mins to obtain equally distributed cellulose suspension. The suspension was cooled to 0°C and NaH (900 mg) was added in two portions. After stirring for 15 min, perfluorobutyl iodide (500 mg) was slowly added and the reaction mixture was warmed to room temperature. After stirring overnight, the reaction mixture was filtrated. The solid was washed with ethyl acetate (3×15 ml), deionized water (3×15 ml) and ethanol (3×15 ml) before dried at 60°C for 5 h. The final product was obtained as yellowish solid.

2.2. Catalyst preparation

Pd catalyst was prepared by chemical reduction with NaBH_4 as reductant. 1 mg PdCl_2 was dissolved in 0.5 ml water and 1 mg NaCl was added to accelerate dissolution. To $\text{C}_4\text{F}_9\text{-Cell}$ (200 mg) in ethanol (6 ml) in a round-bottom flask (50 ml), the PdCl_2 solution was added and the mixture was stirred at room temperature for 5 h. Then a fresh prepared ethanol solution of NaBH_4 (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 5 h, the mixture was filtrated and the solid was dried in vacuum oven at 25°C for 12 h and stored in a desiccator.

2.3. Catalytic reduction of nitroarenes

Hydrogen was chosen as hydrogen donor for the hydrogenation of nitroarenes. The hydrogenation reactions were carried out in a Schlenk tube. Typically, the reactant and catalysts were dispersed into the solvent, then the Schlenk tube was purged with H_2 four times to replace air. Then the mixture was stirred at room temperature for a desired period. After reaction, the reaction 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 (3×15 ml), deionized water (3×15 ml) and then used in the next cycle.

3. Results and discussion

3.1. Characterization of catalyst

Cellulose and $\text{C}_4\text{F}_9\text{-Cell}$ were characterized by IR spectrum (Fig. 1). The strong peak around 3300 cm^{-1} is due to the stretching vibration of the O–H bonds. It is an obvious decrease in the peak intensity at 3300 cm^{-1} after cellulose was modified, showed that some of the O–H bonds in cellulose reacted. And there is also an increase of peak intensity at 1600 cm^{-1} which may be attributed to the stretching vibration of the C–F bonds. The peak around 1050 cm^{-1} due to the stretching vibration of the C–O–C bonds increased slightly, indicating perfluorous compounds was attached to cellulose by ether linkage.

Scanning electron microscopy (SEM) image of $\text{Pd}/\text{C}_4\text{F}_9\text{-Cell}$ demonstrated the morphology of cellulose after modified (Fig. S1). the

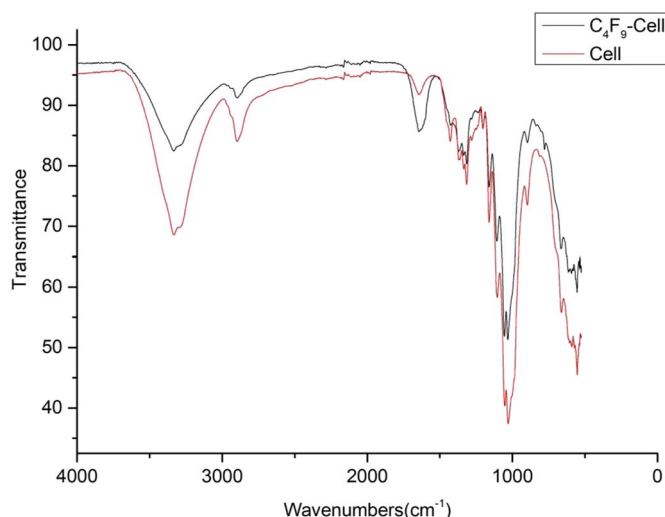


Fig. 1. IR spectrum of cellulose (Cell) and $\text{C}_4\text{F}_9\text{-Cell}$.

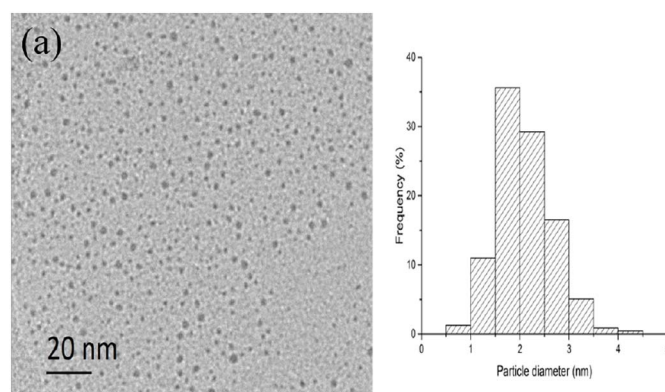


Fig. 2. (a) TEM image of $\text{Pd}/\text{C}_4\text{F}_9\text{-Cellulose}$. (b) Size distribution of Pd NPs of $\text{Pd}/\text{C}_4\text{F}_9\text{-Cellulose}$.

catalyst is rod shaped with rough surface. The deposition of Pd NPs on $\text{C}_4\text{F}_9\text{-Cell}$ is examined by TEM (Fig. 2a). The TEM micrograph indicates that the prepared Pd NPs are well-proportioned anomalous spherical with an average diameter of 2–3 nm. Pd NPs on unmodified cellulose was also characterized by TEM image (Fig. S2), it is obviously that Pd NPs aggregated on cellulose surface.

Fig. 3 depicts the XPS spectrum in the Pd 3d region for $\text{Pd}/\text{C}_4\text{F}_9\text{-Cell}$,

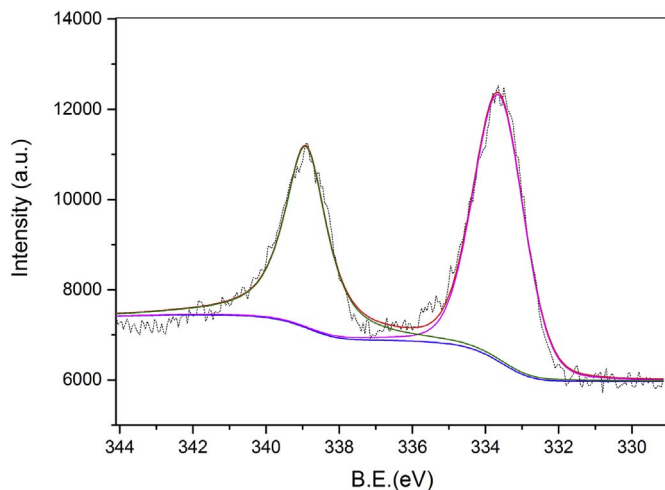


Fig. 3. XPS spectrum of Pd 3d region of $\text{Pd}/\text{Cell-C}_4\text{F}_9$.

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