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Efficient transfer hydrogenation of nitro compounds over a magnetic palladium catalyst

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ABSTRACT

Magnetic hydroxyapatite (HAP) supported Pd nanoparticles (γ-Fe_2O_3@HAP-Pd) were used for the transfer hydrogenation of nitro compounds with $HCOONH_4$ as hydrogen donors. Aniline was produced in an excellent yield (>99%) in water at 25 °C with 6 equiv. $HCOONH_4$. This process is suitable to a wide range of nitro compounds with excellent yields for most cases. Both the HAP support and the Pd nanoparticles showed a synergistic effect on the transfer hydrogenation of nitro compounds. Furthermore, the γ-Fe_2O_3@HAP-Pd catalyst was stable.

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Introduction

Chemical reduction is an important kind of chemical reactions, which can produce lots of readily available chemical feedstocks [1,2]. Among various kinds of chemicals reactions, the reduction of nitro compounds to the corresponding anilines is industrially and academically important. Anilines serve as versatile precursors for the synthesis of organic fine chemicals, dyes, pharmaceuticals, biologically active compounds, agrochemicals, pigments, and polymers [3–5].

In early days, metals such as Zn and Fe were used as reducing agents for the reduction of nitro compounds [6,7]. The methods demonstrated some drawbacks such as the high cost of the reducing agents, and the release of toxic waste to the environment Thus, great effort has been devoted to the development of environmentally friendly methods for the catalytic reduction of nitro compounds, which avoids the use of large excess of expensive and perilous reducing agents. Traditionally, the catalytic hydrogenation of nitro compounds is carried out over metal catalysts, especially noble metal catalysts such as Au, Pd and Ru catalysts [8–13]. According to the reducing agents, there are two types of the catalytic hydrogenation of nitro compounds. One is the use of H_2 for the catalytic hydrogenation of nitro compounds, which is generally carried out at high pressures (10–50 bar) and high temperatures (100–150 °C), thus the process is of "high-energy consumption" [14]. The high hydrogen pressure and high reaction temperature require the use of the specialized equipment, and have the potential safety issues regarding H_2 handling. Moreover, the transport and storage of H_2 gas leads to additional cost to the production of aniline.

Nitro compounds can also be reduced to amines by the extraction of hydrogen from other hydrogen-donor

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molecules, which is called transfer hydrogenation reaction [15–19]. Several kinds of available hydrogen donors including $NaBH_4$, N_2H_4, *iso*-propanol, and formic acid were used for the transfer hydrogenation of nitro chemicals. Among the available hydrogen donors, formic acid and its salts are abundant and cheap hydrogen donors [20,21]. In recent years, many methods have been reported on the transfer hydrogenation of nitro compounds with formic acid as the hydrogen donor over noble metal catalysts [22–25]. For example, TiO_2 supported Au catalyst (Au/TiO_2) could catalyze the hydrogenation of formic acid with 5 equiv. ammonium formate in ethanol [26].

The recycle of supported metal nanoparticles is generally performed by the conventional methods such as filtration or centrifugation, thus it is difficult to collect the catalysts with nono-sized structure. More importantly, the catalyst weight loss can not be avoided during the recycling process. In recent years, magnetic catalysts have emerged as an environmentally friendly and easy-handling catalysts for many kinds of chemicals reactions [27–29], as the magnetic catalysts can be easily separated from the reaction mixture with an external magnet. In our previous work, a magnetic Pd catalyst was prepared, in which the hydroxyapatite encapsulated γ-Fe_2O_3 (γ-Fe_2O_3@HAP) was used as the support to immobilize the Pd nanoparticles to give the magnetic γ-Fe_2O_3@HAP-Pd catalyst, and the as-prepared catalyst showed high catalytic activity toward the oxidation of biomass derived 5-hydroxylmethylfurfural into 2,5-furandicaroxylic acid [30]. Besides its high activity for the oxidation reaction, we wonder whether this catalyst could be used for the transfer hydrogenation of nitro compounds into amines. Herein, the catalytic transfer hydrogenation of nitro compounds was studied over the γ-Fe_2O_3@HAP-Pd catalyst.

Experimental section

Materials and methods

All of the chemicals were purchased from Aladdin Chemicals Co. Ltd. (Shanghai, China). All of the solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All of the chemical and solvents were used directly without purification.

Catalysts preparation

The γ-Fe_2O_3@HAP-Pd catalyst with a Pd weight percentage of 2.5% was prepared and characterized as described in our previous work [30]. Briefly, Fe_3O_4 nanoparticles were encapsulated by layer of hydroxyapatite (HAP) with a formula of $Ca_{10}(PO_4)_6(OH)_2$, which was formed from Ca^{2+} and PO_4^{3-} at pH = 11, and then calcined at 300 °C to give the γ-Fe_2O_3@HAP support. The exchange of Ca^{2+} in γ-Fe_2O_3@HAP with Pd^{2+} generated γ-Fe_2O_3@HAP-Pd^{2+}, which was a brown powder. Then, Pd^{2+} was reduced by $NaBH_4$ in ethanol to generate the γ-Fe_2O_3@HAP-Pd catalyst.

Determination of Pd loading

The Pd content in the catalyst was determined by inductively coupled atomic emission spectrometer (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation). The acid digestion was composed of concentrated HNO_3 (7.5 mL), and 2.5 mL concentrated HCl (2.5 mL). 0.5 g sample was digested in the above acid digestion on the flat electric furnace. After digestion, the sample was made to 25 mL with deionized water and centrifuged at 3000 rpm. The supernatant liquid was taken for ICP-AES analysis. The ICP-AES operation conditions were as follows: Incident power: 1.1 KW, carrier gas flow rate: 0.8 L min^{-1}, auxiliary gas flow rate: 0.4 L min^{-1}, coolant gas flow rate: 16 L min^{-1}, observation height: 10 mm.

Procedure of the hydrogenation of nitro compounds

Typically, nitrobenzene (1 mmol), ammonium formate (6 mmol) and H_2O (6 mL) were charged in a 10 mL round-bottomed flask. Then the γ-Fe_2O_3@HAP-Pd catalyst (30 mg) with the molar ratio of the substrate/Pd = 141 was added, and time zero was recorded. The reaction was carried out in the air at room temperature. After reaction, the organic chemicals in the reaction mixture were extracted by ethyl acetate, and analyzed by gas chromatography.

Analytic method

Analysis of the products was conducted on a 7890F gas chromatography (Techcomp Scientific Instrument Co., Ltd., China) with a crosslinked capillary HP-5 column (30 m × 0.32 mm × 0.4 mm) equipped with a flame ionization detector. Operating conditions were as follows: The flow rate of the N_2 carrier gas was 40 mL min^{-1}, the injection port temperature was 250 °C, the oven temperature was 190 °C, and the detector temperature was 280 °C. The peaks were identified by comparison of the retention time of the unknown compounds with those of standard compounds and quantified based on the internal standard method. Benzylamine was used as the internal standard.

Catalyst recycling experiments

After reaction, the γ-Fe_2O_3@HAP-Pd catalyst was collected from the reaction mixture by an external magnet. The spent catalyst was washed with water and ethanol. Finally, the spent catalyst was dried in a vacuum oven at 50 °C overnight, and reused in the next run.

Results and discussion

Transfer hydrogenation of nitro compounds over different catalysts

Initially, the transfer hydrogenation of nitrobenzene was performed in water at room temperature over various catalysts with HCOOH as the hydrogen donor. As a control experiment, no conversion was observed without catalyst (Table 1, Entry 1). The Fe_2O_3@HAP-Pd catalyst could promote the transfer hydrogenation of nitrobenzene, affording 77% conversion of nitrobenzene and aniline selectivity >99% after 3 h (Table 1, Entry 2). In addition, control experiments were also carried out over the Fe_2O_3@HAP-Pd^{2+} and Fe_2O_3@HAP

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