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# Catalytic transfer hydrogenation of nitro compounds into amines over magnetic graphene oxide supported Pd nanoparticles

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## ABSTRACT

The hydrogenation of nitro compounds into amines is of great importance both from academic and industrial points. In this study, graphene oxide was simultaneously decorated by Fe<sub>3</sub>O<sub>4</sub> and Pd nanoparticles to generate magnetic C–Fe<sub>3</sub>O<sub>4</sub>–Pd catalyst, which showed high catalytic activity towards the transfer hydrogenation of nitro compounds by the use of NaBH<sub>4</sub> as the hydrogen donor at room temperature. Aniline was produced in a high yield of 99% after 30 min at 25 °C. A wide variety of substituted nitroarenes with other reducible groups were also successfully converted into the corresponding amines with high yields. Kinetic studies revealed the active energy of the transfer hydrogenation of nitrobenzene was 31.1 kJ mol<sup>-1</sup>. One of the main reasons of the high catalytic activity of the C–Fe<sub>3</sub>O<sub>4</sub>–Pd catalyst was due to the fact that the catalyst showed high ability to absorb the substrate on its surface. The transfer hydrogenation of nitrobenzene was confirmed to proceed via azobenzene as the intermediate. More importantly, the catalyst was very stable without the loss of its catalytic activity.

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## Introduction

Catalytic reduction of nitro compounds is an important chemical reaction both from industrial and academic viewpoints [1]. Amines serve as versatile intermediates in the synthesis of pharmaceuticals, polymers, pesticides, explosives, fibers, dyes and cosmetics [2–4]. The traditional method of the reduction of nitro compounds required the use of stoichiometric amount of metal under acidic conditions, thus generated a large amount of waste [5,6]. In contrast to the traditional method, the catalytic hydrogenation of nitro

compounds has received a great interest due to its high efficiency, high selectivity and more environmental-friendly. According to the hydrogen source, there are two types of the hydrogenation of nitrobenzene. One method is performed by the direct use of H<sub>2</sub> as the hydrogen source [7–10]. The catalytic hydrogenation of nitro compounds by H<sub>2</sub> is generally carried out at high pressure (up to 3 MPa) and high temperature (up to 300 °C) [11]. Thus, this method is an energy-consumption step. In addition, the use of explosive H<sub>2</sub> at high reaction temperature requires the use of specialized equipment, and has the potential safety issues. In addition, the storage and transportation of H<sub>2</sub> also increases

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the production cost. Thus, the search of new facile, cost-effective, and environmentally friendly procedures for the reduction of nitro compounds has attracted substantial interest. Besides  $H_2$ , the reduction of nitro compounds can also be performed by the extraction of hydrogen from other hydrogen donors, which is called “catalytic transfer hydrogenation” [12,13]. The catalytic transfer hydrogenation of nitro compounds can be performed under mild conditions (e.g. room temperature, atmospheric pressure) [14–19]. Catalytic transfer hydrogenation of nitro compounds was generally performed over metal catalysts, especially noble metal catalysts such as Pd, Au, Ru catalysts, and the hydrogen donors including hydrazine, silanes and sodium borohydride. The use of  $NaBH_4$  for the transfer hydrogenation of nitro compounds has verified to be mild and safe with no detrimental byproducts.

Recently, supported metal nanoparticles catalysts have received great attention, because the transition from bulk to nanosize regime leads to massive changes in the physical and chemical properties of the nanoparticles, resulting in high catalytic activity [20,21]. The catalytic performance of the metal catalysts is generally affected by the support and the metal nanoparticles, thus the support is also crucial to the activity and stability of the heterogeneous catalysts. In recent years, carbon materials have been found to be an excellent support for metal nanoparticles [22]. Among them, graphene with one atom-thick two-dimensional graphitic carbon structure has attracted increasing interest as the support of the metal nanoparticles due to its high surface area and excellent electronic, thermal, and mechanical properties [23]. Graphene oxide (GO), a derivative of graphene has particularly been considered as an ideal support material for anchoring noble metal catalysts for many kinds of chemical reactions [24]. Compared with graphene, the surface of the graphene oxide is enriched with oxygen-containing functional groups such as hydroxyl groups and carboxylic groups. The oxygen functional groups have a strong ability to anchor the metal nanoparticles, thus benefiting the metal catalyst–carbon support interactions, which substantially enhanced catalyst activity and stability. Graphene oxide supported platinum group metals demonstrate great importance in catalysis, forming the backbones of various important industries. For example, graphene oxide supported Pd nanoparticles have been widely used for a wide range of organic reactions, including hydrogenation, oxidation, C–C coupling and so on [25,26]. While the graphene oxide supported Pd nanoparticles showed high catalytic activity, the recycle of the graphene oxide supported Pd nanoparticles was difficult due to its nanosize. Recently, magnetic catalysts have emerged a great interest in green and sustainable chemistry [27,28]. Compared with the common heterogeneous catalysts with nano-size structure, the recycle of the magnetic catalysts do not require the tedious procedure such as the filtration and centrifugation. The magnetic catalysts can be easily recovered from the reaction mixture by an external magnet.

In our previous work, we have prepared magnetic graphene oxide supported Pd (C– $Fe_3O_4$ –Pd) nanoparticles, which showed high catalytic activity towards the oxidation reaction [29]. The C– $Fe_3O_4$ –Pd catalyst was prepared by the

simultaneous deposition of Pd and  $Fe_3O_4$  nanoparticles on the surface of the graphene oxide. In continuous research of this catalyst, we wonder whether this catalyst can be used for the catalytic transfer hydrogenation of nitro compounds. Herein, the catalytic transfer hydrogenation of nitro compounds was studied over C– $Fe_3O_4$ –Pd.

## Experimental section

### Materials and reagents

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

### Catalyst preparation

The C– $Fe_3O_4$ –Pd catalyst was prepared and characterized as described in our previous work [29]. Briefly, the commercially available graphite was firstly oxidized by  $KMnO_4$  according to Hummer's method. The surface of the as-prepared graphene oxide was enriched with the oxygen-containing groups, which were used to anchor  $Pd^{2+}$  and  $Fe^{3+}$  ions. Then, the thermal treatment of  $Pd^{2+}$  and  $Fe^{3+}$  ions modified graphene oxide in ethylene glycol generated graphene oxide supported  $Fe_3O_4$  and Pd nanoparticles, which was abbreviated as C– $Fe_3O_4$ –Pd catalyst in this study. As described in our previous work [29], the weight percentage of Pd in the C– $Fe_3O_4$ –Pd catalyst was 1.95 wt.% by ICP-AES analysis.

### Catalytic transfer hydrogenation of nitro compounds

In a typical run, 1 mmol of nitrobenzene and 3 mol of  $NaBH_4$  were added into 6 mL of ethanol, and the mixture was magnetically stirred to give a clear solution. Then the C– $Fe_3O_4$ –Pd catalyst (20 mg) was added with the molar ratio of nitrobenzene/Pd being 271. Time zero was recorded after the addition of the catalyst. After reaction, the C– $Fe_3O_4$ –Pd catalyst was separated from the reaction mixture with an external magnet. Then, the products in the reaction solution were analyzed by GC. The structure of the product was confirmed by GC–MS. The spent catalyst was repeatedly washed with water and ethanol to remove the organic and inorganic part and dried for further use.

### Analytic methods

Analysis of the products was performed by a gas chromatography (GC) on a 7890 F instrument (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  $40\text{ mL min}^{-1}$ , the injection port temperature was  $250\text{ }^\circ\text{C}$ , the oven temperature was  $190\text{ }^\circ\text{C}$ , and the detector temperature was  $280\text{ }^\circ\text{C}$ . The peaks were identified by comparison of the retention time of the unknown compounds with those of standard compounds and

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