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Original article

Synthesis of ruthenium/reduced graphene oxide composites and application for the selective hydrogenation of halonitroaromatics

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ABSTRACT

Reduced graphene oxide (RGO) supported ruthenium (Ru) catalyst was prepared by an impregnation method using $RuCl_3$ as a precursor and RGO as a support. The catalyst Ru/RGO was used for the selective hydrogenation of *p*-chloronitrobenzene (*p*-CNB) to *p*-chloroaniline (*p*-CAN), showing a selectivity of 96% at complete conversion of *p*-CNB at 60 °C and 3.0 MPa H_2. The Ru/RGO catalyst was extremely active for the hydrogenation of a series of nitroarenes, which can be attributed to the small sized and the fine dispersity of the Ru nanoparticles on the RGO sheets characterized by TEM. Moreover, the catalyst also can be recycled five times without the loss of activity.

1. Introduction

Metal catalysts have been extensively investigated because of their wide application in synthetic organic chemistry [1]. For the selective hydrogenation of chloronitrobenzene (*p*-CNB), noble metal catalysts such as Pd [2–5], Pt [6–11], and Ru [12–19] are among the most widely investigated metal catalysts. With respect to catalytic performance, ruthenium seems to be an attractive option with its high selectivity and low cost, but its implementation is offset by low activity. Therefore, many efforts have been exerted to develop effective ruthenium catalysts in order to increase the activity while maintaining the selectivity. Many supports, such as SnO_2 [16], MgF_2 [17–19], and carbon nanotubes [12,13] have been used for dispersing ruthenium nanoparticles. Despite these advances, it should be noted that the catalytic properties of the reported ruthenium catalysts were still unsatisfactory. It still remains a great challenge to develop simple, environmentally friendly, and versatile methods to fabricate ruthenium catalysts that achieve superior performance.

As a one atom-thick sheet of sp^2-bonded carbon atoms, graphene has been considered as a highly promising material with special physical and chemical properties [6]. It is desirable to explore such a material as a support for catalysis. As far as we are aware, no attempt has yet been exerted to improve the catalytic properties of supported ruthenium catalysts for the selective hydrogenation of halonitroaromatics by using reduced graphene oxide (RGO) as a support. In this communication, we reported a facile synthesis of ruthenium-reduced graphene oxide composites (Ru/RGO) and investigated its catalytic properties for selective hydrogenation of *p*-CNB. It was found that the small Ru nanoparticles were uniformly embedded on the surface of RGO sheets with a mean size of about 2.0 nm. The Ru/RGO composites exhibited superior catalytic properties for the hydrogenation of *p*-CNB to the desired product. In addition, the Ru/RGO composites could be reused at least five times without loss of any activity. From a practical point of view, this study may open the way to a new approach for the synthesis of amines.

2. Experimental

2.1. Catalyst preparation

All aromatic compounds (A.R.), solvents (A.R.), and reagents (A.R.) were used as received. GO was synthesized *via* the improved synthesis method reported by Marcano *et al.* [20]. Then, 0.5 g as-prepared GO was added into a flask containing 200 mL deionized water and ultrasonicated for 12 h to get a yellow-brown solution. The solution was heated to 80 °C, and then 5.0 g $NaBH_4$ was added into the flask. After 2 h, the black solid was washed with ethanol and distilled water several times and vacuum dried at 60 °C for 12 h.

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The Ru/RGO composite was synthesized as follows: The as-prepared RGO (0.4 g) was filled with a solution of 5.08 mg/L $RuCl_3$ (10 mL) ultrasonicated for 3 h. Then, an aqueous solution of $NaBH_4$ (0.3 mol/L, 10 mL) was dropped into the solution to reduce Ru^{3+}. The black solid was rinsed with ethanol and distilled water several times and vacuum dried at 60 °C for 12 h. For comparison, the active carbon (AC) supported Ru catalyst (Ru/AC) was prepared with the same procedures except that 0.4 g AC was employed as a catalyst support.

2.2. Characterization of the catalyst

The content of metal was determined by ICP (IRIS Intrepid). Transmission electron microscopy (TEM) measurements were carried out on a JEOL model 2010 instrument operated at an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray diffractometer D/max-2200/PC equipped with Cu Kα radiation (40 kV, 20 mA) over the range of 10–90°. X-ray photoelectron spectroscopy (XPS, Kratos XSAM800) spectra was obtained by using Al Kα radiation (12 kV and 15 mA) as an excitation source ($h\nu = 1486.6$ eV), Au (BE Au4f = 84.0 eV), and Ag (BE Ag3d = 386.3 eV) as reference. All hydrogenation samples were analyzed by gas chromatography (Agilent 7890A) with a FID detector and PEG-20M supelco column (30 m × 0.25 mm, 0.25 μm film).

2.3. Activity test

Typically, to study the catalytic activity, 5.0 mg of catalyst, 1.0 mmol of *p*-CNB, and a mixture of ethanol and water (5 mL, volume ratio of 4:1) were introduced into a 60 mL stainless steel autoclave, and the autoclave was purged with pure hydrogen five times in order to remover air. The reaction was performed with a stirring rate of 1200 rpm at 60 °C and 3.0 MPa hydrogen pressure for 2 h.

3. Results and discussion

3.1. Catalyst characterization

The content of Ru in catalyst Ru/RGO was 3.0 wt.%, as estimated by ICP. Fig. 1 shows the typical TEM images of the product of Ru/RGO. The results demonstrate that the graphene flakes are likely to be in the form of single- or few-layer sheets, which indicates that the graphite was exfoliated to graphene flakes upon oxidation and ultrasonication [20]. Moreover, the images also show that the Ru nanoparticles are well dispersed on the surface of the RGO with a narrow particle size distribution of 1.0–2.0 nm. The average Ru particle size was estimated to 1.5 nm. The small size and even distribution of Ru nanoparticles on the surfaces of the RGO are attributed to the surface functional groups of the RGO sheets that can act as a capping material, inhibiting the aggregation of Ru clusters during reduction.

The crystal structure of Ru-RGO was also characterized by XRD in the range from 10° to 90°. For comparison, the XRD patterns of GO and RGO were also investigated and the results are shown in Fig. 2. The major diffraction lines in the powder pattern of GO comes at $2\theta = 10.0°$ (Fig. 2a), suggesting that graphite has been successfully oxidized. When the GO was reduced by $NaBH_4$, it can be seen that the diffraction peaks at 10.0° disappeared and two new peaks appeared at 25.4 and 43.1° (see inset of Fig. 2) corresponding to (0 0 2) and (1 0 0) reflection of RGO [6], respectively, indicating that GO was successfully reduced using $NaBH_4$ as a reducing agent. Moreover, no obvious changes were observed after depositing Ru nanoparticles on the surface of the RGO, and the corresponding diffraction peaks of Ru were not

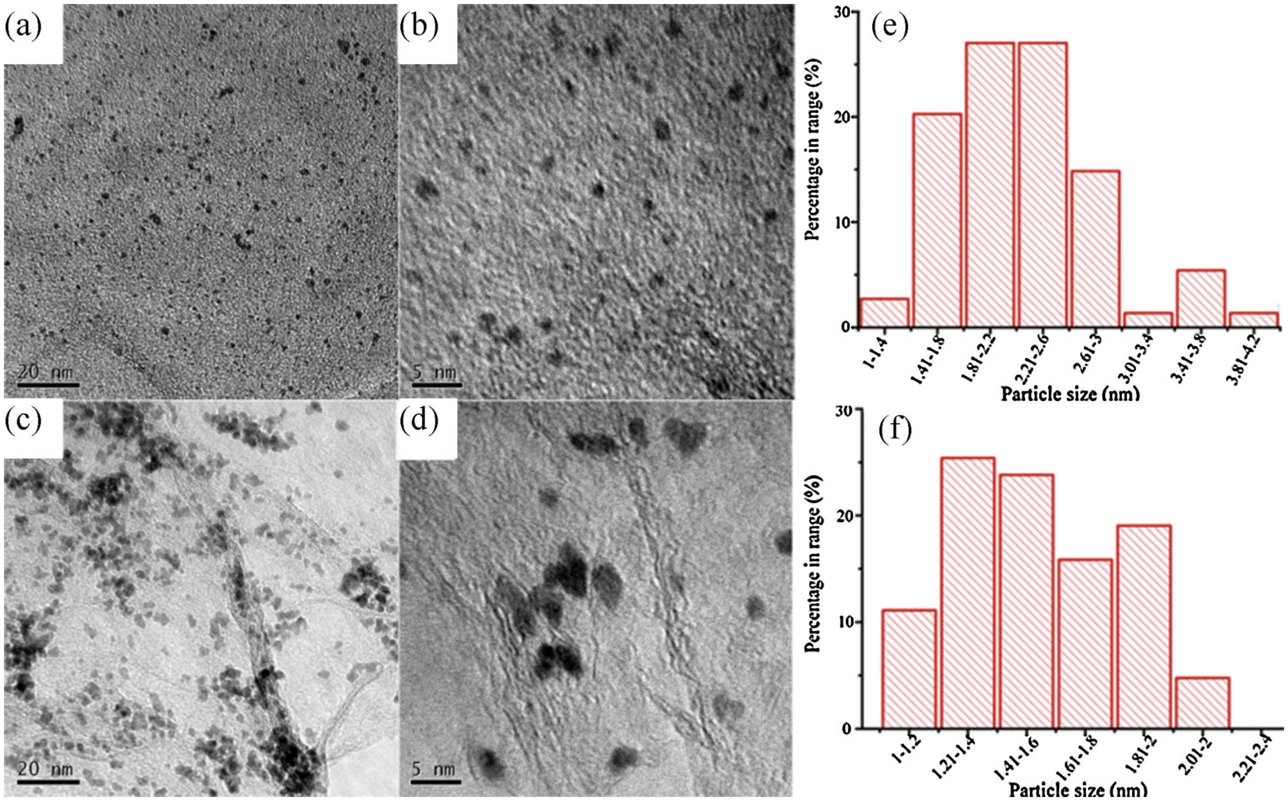

Fig. 1. TEM images of the fresh Ru/RGO catalyst (a, b) and used five times (c, d); Ru particle size distribution of fresh Ru/RGO (e) and used five times (f).