Room temperature selective reduction of nitrobenzene to azoxybenzene over magnetically separable urchin-like Ni/Graphene nanocomposites

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ABSTRACT

Magnetically recyclable Ni/Graphene (Ni/G) nanocomposites were synthesized via an *in situ* reduction growth process for selective reduction of nitroarenes into corresponding azoxybenzene at room temperature and at atmospheric pressure. Here, hydrazine hydrate ($N_2H_4 \cdot H_2O$) is used as the reducing agent which generates harmless by-products such as N_2 and water. The catalyst, when used under controlled reaction conditions, exhibits a 100% conversion and selectivity to the target product without the use of any external additives (turnover number 36.2). Under the optimized conditions, a variety of structurally different nitroarenes were selectively transformed to their corresponding azoxy products in high conversions. Furthermore, a high stability and recyclability of the catalyst were also observed under the investigated conditions (93% conversion, 100% selectivity after the 4th reuse).

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1. Introduction

Selective catalytic reduction of nitrobenzene is an important reaction for the synthesis of intermediates and is a precursor to various industrially valuable products such as aniline, nitroso benzene, azobenzene, and azoxybenzene [1]. Among them, azoxybenzene is one of the most important and essential building blocks of naturally occurring compounds and functional materials due to its conjugated system and polar functionality [2–4]. In addition, azoxybenzene is valuable both as an intermediate and as the high-value compound widely used in industry such as dyes, reducing agents, polymerization inhibitors, and chemical stabilizers. Some azoxybenzene derivatives are used as liquid crystals in electronic displays and therapeutic medicines [5,6]. Moreover, these types of compounds are the precursors for Wallach rearrangements, which offer a simple route for synthesizing hydroxyazobenzene [7,8].

Azoxybenzene is produced as an intermediate in the oxidation of aniline or the reduction of nitroarenes via the condensation of nitrosobenzene and hydroxylamine. These reaction steps are quite complex and lead to different intermediates. Therefore, manipulation of reaction conditions while controlling the selectivity to the azoxy product in the midst of all possible reduction/oxidation products becomes an important research interest [9].

Various methods have been reported for oxidative coupling of aniline using different oxidants such as peracetic acid [10], Pb (OAc)$_4$ [11], and different types of molecular sieves [12,13]. Reducing nitroarenes by alkaline metal borohydrides and metals such as samarium and thallium were also reported in a few studies [14]. However, most of these methods lack environmental benignity and recyclability of the catalyst. Therefore, finding alternative, more benign catalysts that work at atmospheric pressure and comparatively low temperature for producing azoxybenzene with high conversion and selectivity is in high demand.

Herein, we report the preparation of an urchin-like Ni/Graphene nanocomposite for the selective reduction of nitrobenzene to azoxybenzene with a turnover number of 36.2. The nanosize of these materials leads to a high surface area to volume ratio and therefore, to an enhanced contact between reactants and catalyst, which increases the activity dramatically. In this study, hydrazine hydrate ($N_2H_4 \cdot H_2O$) is used which can be considered as a very suitable reagent for the reduction of nitro groups, since only N_2 and water are generated as by-products [15]. Graphene acts as a promising catalyst support with a high surface area on which the metal nanocatalyst can be stabilized. Graphene also prevents metal nanoparticle aggregation and provides a desirable chemical interface between the catalyst and the reaction media thus results in enhanced catalytic performance. Moreover, the catalyst is

magnetic and could be easily retrieved from the reaction mixture and reused by simple magnetic separation after the completion of the reaction.

2. Experimental section

2.1. Synthesis of graphene oxides (GO)

GO was synthesized from natural graphite using a modified Hummers method. Briefly, graphite powder (1.0 g) and $NaNO_3$ (2.0 g) were mixed and added into concentrated H_2SO_4 (48 mL; 98%) in an ice bath. Under vigorous stirring, $KMnO_4$ (4.0 g) was gradually added and the temperature of the mixture was kept below 20 °C. After removing the ice bath, the mixture was stirred at 35 °C in a water bath for 6 h. Then, 200 mL water was slowly added to the mixture in an ice bath. After the dilution, 15 mL of 30% H_2O_2 was added to the mixture and stirred for another 2 h. The mixture was filtered and washed with distilled water and then re-dispersed in water by ultrasonication. Finally the product was separated by centrifugation and vacuum dried at 45 °C for 48 h.

2.2. Synthesis of urchin-like Ni nanomaterial

First, $NiCl_2·6H_2O$ was dispersed in 10 mL of ethanol in order to prepare a 0.25 M solution. Then, 1 mL of KOH solution (0.2 M) and 1 mL of hydrazine hydrate solution (85%) were added under vigorous stirring at 60 °C and the obtained mixture was refluxed at 100 °C for 2 h. The reaction was cooled to room temperature, and the resultant product was washed with distilled water and ethanol for three times and separated by centrifugation. Finally the product was dried in a vacuum oven at 60 °C for 12 h.

2.3. Synthesis of urchin-like Ni/Graphene nanocomposite

About 15 mL of 1 mg/mL GO suspension was prepared by ultra-sonication, the resultant solution was added to the 0.25 M $NiCl_2$-·6H_2O$ solution and the same procedure was followed to synthesize the Ni/Graphene nanocomposite.

2.4. Catalyst characterization

Powder X-ray diffraction (XRD) analyses were performed on a Rigaku Ultima IV diffractometer with Cu Kα (λ = 0.15406 nm) radiation with a beam voltage of 40 kV and a beam current of 44 mA. Continuous scans were taken in a 2θ range of 5–80° with a scanning rate of 2.0°/min, and the phases were identified using the International Center for Diffraction Data (ICDD) database.

Surface morphologies of the synthesized materials were studied using a field emission scanning electron microscope (FE-SEM) on a Zeiss DSM 982 Gemini instrument with a Schottky emitter at an accelerating voltage of 2.0 kV with a beam current of 1.0 mA. The samples were ultrasonically suspended in absolute ethanol and dispersed on Au-coated silicon chips and then dried overnight under vacuum. The EDX analysis was done using an Oxford X-max80 EDX analyzer operating at an electron accelerating voltage of 10 kV.

Transmission electron microscopy (TEM) was used to examine the surface morphologies and the crystalline structures of the materials using a JEOL 2010 instrument with an accelerating voltage of 200 kV. The samples were prepared by dispersing the material in ethanol. Then a drop of the dispersion was placed on a carbon coated copper grid and allowed to dry before analysis.

The nitrogen sorption experiments were performed using Quantachrome Autosorb iQ$_2$ instrument using N$_2$ gas as the adsorbate at 77 K by a multipoint method. The Brunauer–Emmett–Teller (BET) method was used to determine the specific surface area and the Barrett–Joyner–Halenda (BJH) desorption method was used to calculate the pore size distribution and pore volume. Prior to the analysis, all the samples were degassed at 150 °C for 12 h in order to remove any adsorbed species.

Raman measurements were taken at room temperature on a Renishaw 2000 Ramascope attached to a charge-coupled device (CCD) camera, with an Ar$^+$ ion laser (514.4 nm) as the excitation source. Before each measurement was taken, the spectrometer was calibrated with a silicon wafer. Curve fitting for the determination of spectral parameters was performed with the software program GRAMS/32.

Thermogravimetric mass spectrometry (TG-MS) was studied using a Netzsch Libra TG209 F1 thermogravimetric analyzer coupled to a Netzsch Aëolos QMS 403C quadrupole mass spectrometer. Approximately 15 mg of sample was loaded into an alumina crucible. Air was flowed through the sample chamber at 50 SCCM while the temperature was ramped from room temperature to 850 °C at a rate of 10 °C per minute while TG and MS signals were recorded.

2.5. Catalytic activity measurements

Liquid phase reduction of nitrobenzene was carried out at room temperature (25 °C) in a double neck round bottom flask in an oil bath using 0.025 g catalyst, 5 mL ethanol, 22.5 mmol hydrazine and 15 mmol nitrobenzene. Small aliquots were collected from the reaction mixture at regular intervals for analysis. For the reusability test, the spent catalyst was recovered from the reaction mixture by magnetic separation and washed thoroughly with acetone and dried at 120 °C for 12 h. The gas chromatography–mass spectroscopy (GC–MS) method was used for the quantitative analysis and identification of the reaction product. Analyses were performed using a HP 5971 mass selective detector coupled to a HP 5890 Series II gas chromatograph equipped with a thermal conductivity detector (TCD) through an HP-1 (nonpolar cross-linked methyl siloxane) column with dimensions of 12.5 m × 0.2 mm × 0.33 μm.

3. Results

3.1. Structure and characterization

XRD patterns of as synthesized Ni nanomaterial and Ni/G nanocomposite are displayed in Fig. 1. Both samples exhibit three well-resolved peaks at 2θ = 44.5°, 51.8°, and 76.4°, which coincide
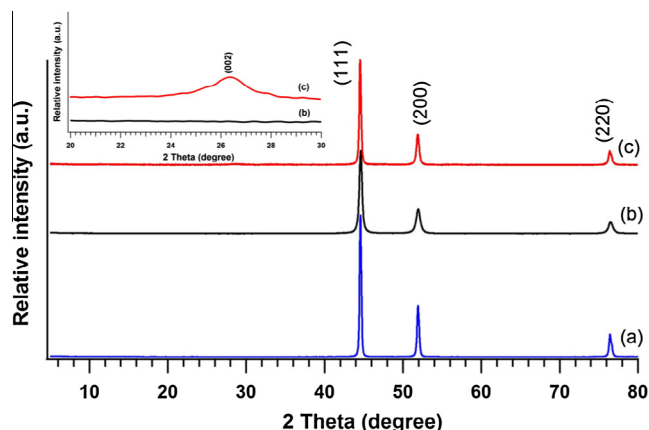

Fig. 1. X-ray diffraction patterns of (a) commercial Ni powder, (b) Ni nanomaterial and (c) Ni/G nanocomposite.