



# Magnetically separable carbon nanocomposite catalysts for efficient nitroarene reduction and Suzuki reactions

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## ABSTRACT

Novel magnetically recyclable carbon nanocomposites were synthesized to support various nanocatalysts using a simple, economical and scalable method. The designed nanocomposites, which are composed of porous carbon and Fe<sub>3</sub>O<sub>4</sub> nanocrystals, can be used as an expandable platform to load versatile nanoparticle catalysts such as Pd and Pt. These nanocomposites with high surface area and permeable porous structure can contain abundant and accessible small-sized catalyst nanoparticles. These characteristics led to efficient catalytic reactions and enhanced catalytic activity, which were verified in selective reduction of nitroarenes and Suzuki cross-coupling reactions. The nanocomposite catalysts provided excellent catalytic activities to yield the desired products in short reaction time and mild reaction conditions. The catalysts could be easily separated from the reaction mixture by a magnet, and recycled five consecutive cycles in reduction of nitrobenzene and Suzuki cross-coupling of bromobenzene without losing significant activities.

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## 1. Introduction

Catalysts play important roles in various fields such as oil refining, fine chemicals and pharmaceutical productions, and energy conversions [1,2]. Catalysts are generally classified into two types: homogeneous and heterogeneous catalysts. Homogeneous catalysts have the advantages of being dissolved in reaction medium, thus providing mild reaction conditions, and higher activities and selectivities compared to their heterogeneous counterparts [3]. For example, homogeneous palladium catalysts have been widely used in various catalytic transformations such as Buchwald–Hartwig amination, hydrogenation, Heck, Sonogashira, and Suzuki reactions [4–9]. These catalysts, however, are of somewhat limited use in the industry due to the difficulties in separating the products contaminated with residual unstable complexes and recycling the expensive catalysts [10,11]. These catalytic reactions need typical work-up steps to isolate the product from the mixture, and the

reusability of the catalyst becomes complicated [12–14]. Consequently, typical industrial heterogeneous catalysts are composed of supported metal nanoparticles (NPs) owing to their advantages of recovering and reusing of the catalysts [15–17]. However traditional micrometer-sized heterogeneous catalysts generally suffer from low catalytic activities due to the slow diffusion of reactants [18,19]. Accordingly, heterogeneous catalytic reactions generally require more severe conditions than those of homogeneous catalysts [20,21]. Recent advancements in the synthesis of uniformly sized NPs offer numerous opportunities to improve the catalytic performance [22–24]. Although nanoparticle-based catalysts (nanocatalysts), which are often considered as a bridge between homogeneous and heterogeneous catalysts, have high catalytic activities because of their high surface-to-volume ratio, they suffer from several drawbacks such as recovery and instability at high reaction temperatures. Furthermore nanocatalysts without any support are usually unstable, and coagulation is inevitable [25,26]. These facts have motivated continuous research efforts for the developments of highly active and sustainable nanocomposite catalysts [27,28].

Of the wide range of catalyst supports, porous carbon materials have been extensively employed in heterogeneous catalysis because of their desirable properties including permeable pores,

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chemical inertness, and good mechanical stability [29–32]. Because the supports strongly affect the activity of catalyst NPs, numerous studies have been performed to modify the properties of carbon supports [33–36]. Nitrogen doping of carbon materials improves chemical/physical properties. In particular, the nitrogenated sites are known to enhance the interaction between nanocatalysts and support [37–40]. Furthermore, it is an important issue to develop economical and scalable approaches for preparing recyclable porous carbon nanocomposites.

Magnetic separation, among the various procedures for removing catalysts, obviates the requirement of catalyst filtration after the completion of reactions and provides an easy technique for recycling nanocatalysts by using a magnet [41–44]. This method minimizes the possibility of nanocatalyst aggregation during recovery and improves the durability of the catalysts [45–48]. The efficiency of the heterogeneous nanocatalysts also depends on the size, shape, composition and their interaction with supports [49–51]. Recently various NPs were immobilized in porous nanocomposite supports for fabrication easily recoverable and highly active catalysts [52–54]. Herein we report an economical scalable procedure to synthesize magnetically retrievable carbon nanocomposite catalysts by combining magnetic NPs, nitrogen-doped porous carbon support and ~ 3 nm-sized catalyst NPs of Pd or Pt. The designed carbon nanocomposite catalysts provide excellent catalytic activities for reduction of nitroarenes and Suzuki cross-coupling reactions.

## 2. Experimental

### 2.1. Characterization

The loading amount of palladium and platinum in the magnetically recyclable nanocomposite catalysts was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES). The intermediates and final nanocomposite catalyst materials were characterized by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), High resolution powder X-ray diffraction (HRXRD), X-ray fluorescence (XRF) spectrometry, attenuated total reflection infrared spectroscopy (ATR-IR) and CHN elemental analysis. TEM images were obtained using a JEOL JEM-2010 microscope. High resolution TEM (HRTEM) images were obtained using a JEOL JEM-3010 microscope equipped with energy-dispersive X-ray spectroscopy (EDX) detector at an acceleration voltage of 200 kV. Scanning transmission electron microscopy (STEM) and High resolution STEM (HRSTEM) images were acquired using a JEOL JEM-2100F. The mi-micromeritics 3 Flex-surface characterization analyzer was used to measure the physisorption isotherms and surface area of the magnetically recyclable nanocomposite catalysts. ICP-AES was used for the elemental analysis using a Shimadzu ICPS-7500 Japan instrument. XPS was performed to collect core level spectra of Pd (3d) and Pt (4f) scans using Al K $\alpha$  source (Sigma probe, VG Scientifics). HRXRD was obtained by a Bruker D8 Advance instrument. XRF spectrometry was recorded by a Bruker AXS S4 pioneer. The IR spectra were recorded with an ATR-IR Perkin Elmer spectrometer frontier. The products of the catalytic reactions were analyzed by gas chromatography mass spectrometers (GC-MS) using an Agilent Technologies 5975C VL MSD with triple-axis detector and a Hewlett Packard 5973 mass selective detector GC-MS.

### 2.2. Synthesis of iron oxide NPs

Iron oxide NPs were synthesized using the previously reported methods [55,56]. In a typical synthesis of iron-oleate complex, 10.8 g of iron chloride (FeCl $_3$ ·6H $_2$ O, 40 mmol) and 36.5 g of sodium

oleate (120 mmol) were dissolved in a mixture solvent composed of 80 ml ethanol, 60 ml distilled water and 140 ml hexane. The resulting solution was heated to 70 °C and kept at that temperature for 4 h. Then, the upper organic layer containing the iron-oleate complex was washed three times with distilled water in a separatory funnel. After washing, hexane was evaporated off resulting in iron-oleate complex in a waxy solid form. The synthesized iron-oleate complex (36 g, 40 mmol) and 5.7 g of oleic acid (20 mmol) were dissolved in 200 g of 1-octadecene at room temperature. The reaction mixture was heated to 300 °C with a constant heating rate of 3.3 °C min $^{-1}$  and then kept at that temperature for 1 h. The resulting solution containing the nanocrystals was then cooled to room temperature and 500 ml of ethanol was added to the solution to precipitate the nanocrystals. The nanocrystals were separated by centrifugation and dispersed in chloroform.

### 2.3. Synthesis of magnetically recyclable polymer and carbon nanocomposite catalysts

In a typical synthesis, 0.5 g of Fe $_3$ O $_4$  NPs was dispersed in 400 ml of chloroform and stirred at room temperature for 15 min. To this solution 15 ml pyrrole was directly added. While stirring vigorously 400 mg of palladium(II) acetate dissolved in 30 ml of CHCl $_3$  was added dropwise and the mixture was stirred for 8 h at room temperature to yield the magnetically recyclable polymer nanocomposite catalyst. The product was isolated by centrifugation and washed several times with chloroform. Finally the product was carbonized at 400 °C for 4 h under hydrogen gas flow to produce the magnetically recyclable carbon nanocomposite catalyst.

### 2.4. Heterogeneous Suzuki cross-coupling reactions catalyzed by nanocomposite Pd catalyst

Nanocomposite Pd catalyst (1 mol%) was added to a round-bottom flask (25 ml) and dispersed in dimethylformamide (DMF)/H $_2$ O (2:1) mixture. Then, aryl halide (0.5 mmol), aryl boronic acid (0.6 mmol), K $_2$ CO $_3$  (1.5 mmol), and a small stirring bar were added to the round-bottom flask. The flask containing reaction mixture was placed in an oil bath (100 °C) and stirred under air atmosphere. After completion of reaction, the mixture was cooled to room temperature and the nanocomposite Pd catalyst was separated using a magnet. The separated catalysts were washed several times with DMF. Finally the products were analyzed by a GC-MS.

### 2.5. Heterogeneous reduction of nitroarenes catalyzed by nanocomposite Pt catalyst

The reduction of nitroarenes was carried out in a 25 round-bottom flask. In a typical procedure, 1 mol% of nanocomposite Pt catalyst was dispersed in EtOH. Then, nitrobenzene (0.5 mmol), hydrazine (2 equiv.), and a small stirring bar were added to the flask. The flask containing reaction mixture was placed in an oil bath (80 °C) and stirred under air atmosphere. After completion of reaction, the mixture was cooled to room temperature and the nanocomposite Pt catalyst was separated using a magnet. The separated catalysts were washed several times with EtOH. The products were analyzed by a GC-MS.

## 3. Results and discussion

The overall synthetic procedure to prepare magnetically recyclable carbon nanocomposite catalysts is illustrated in Fig. 1. Polymer nanocomposite was first prepared via a redox reaction between pyrrole and Pd(OAc) $_2$  in the presence of iron oxide NPs. Pyrrole monomers can be chemically polymerized using palladium(II) acetate as an oxidizing agent. Subsequently the magnetic

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