



Supercritical CO₂ mediated synthesis and catalytic activity of graphene/Pd nanocomposites



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ARTICLE INFO

Article history:

Received 30 November 2014

Received in revised form 11 May 2015

Accepted 20 June 2015

Available online 2 July 2015

Keywords:

- A. Metals
- A. Nanostructures
- B. Chemical synthesis
- C. X-ray diffraction
- D. Catalytic properties

ABSTRACT

Graphene sheets were decorated with palladium nanoparticles using a facile and efficient method in supercritical CO₂. The nanoparticles were formed on the graphene sheets by the simple hydrogen reduction of palladium(II) hexafluoroacetylacetonate precursor in supercritical CO₂. The product was characterized by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, transmission electron microscopy, and X-ray photoelectron spectroscopy. Highly dispersed nanoparticles with various sizes and shapes adhered well to the graphene sheets. The composites showed high catalytic activities for the Suzuki reaction under aqueous and aerobic conditions within 5 min. The effects of the different Pd precursor loadings on the catalytic activities of the composites were also examined.

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1. Introduction

Akira Suzuki, known as the designer of the Suzuki reaction, was awarded with the 2010 Nobel Prize for designing the palladium-catalyzed cross-coupling reaction [1]. The Suzuki cross-coupling reaction is one of the most efficient approaches for forming carbon–carbon (C–C) bonds, which are among the most important topics in organic synthesis [2]. This reaction provides a convenient method to construct carbon–carbon bonds in the synthesis of fine chemicals, polymers, herbicides, agrochemicals, and pharmaceutical intermediates [3,4]. The reaction is normally catalyzed by a Pd complex with a range of ligands. In particular, homogenous catalytic processes were used because of their high activity and selectivity, but the difficulty in separating the catalyst from the final product is a significant problem [5]. A heterogeneous catalytic system by the synthesis of Pd nanoparticles with a stabilizer or the immobilization of Pd nanoparticles on an inorganic solid support (such as silica, carbon, zeolite, etc.) is a perfect solution [5,6].

Graphene, a two-dimensional sp²-hybridized carbon material [7], might be one of the best choices as a stabilizer for Pd nanoparticles, because of its excellent properties, such as large specific surface area, unique graphitized plane structure, low production cost, extraordinary mechanical properties and high

chemical stability [8–12]. Thus far, a range of methods has been designed to synthesize graphene/Pd nanocomposite, including solution phase redox reaction [13–20], microwave irradiation [21,22], electrochemical deposition [23–25], laser irradiation [26,27], UV light irradiation [28], incipient wetness impregnation [29,30], chemical vapor deposition [31,32], photocatalytic reduction [33], bubbling H₂ reduction [34], and wet impregnation [35]. However, in these synthetic processes, product separation and residual removal consumes considerable energy and cost. Even toxic solvents and chemicals have been used, causing a great deal of environmental pollution. Therefore, cleaner and simpler methods are needed.

Supercritical fluids (SCFs) are considered as “green” solvents owing to their high adjustable solvent strength, zero surface tension, liquid-like density, gas-like viscosity and diffusivity [36]. Among the SCFs, supercritical CO₂ (scCO₂) is the most commonly used solvent because it is environmental friendly, non-flammable, chemically inert and relatively inexpensive. In addition, the supercritical point of CO₂ (T_c = 31.0 °C, P_c = 7.38 MPa) is quite low compared to other SCFs. Furthermore, CO₂ can be removed easily from products at moderate temperatures and pressures, with no residues remaining in the products. Subramaniam and McHugh [37] reported a uniform dispersion of Pd nanoparticles on graphene surface in a mixture of scCO₂ and methanol using dimethyl amine borane as the reducing agent. In addition, silver nanoparticles were coated efficiently on graphene sheets in scCO₂ [38].

In this study, an environmental friendly and simple process was designed for the synthesis of reduced graphene oxide/Pd (RGO/Pd)

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nanocomposites as a catalyst for the Suzuki reaction. Pd nanoparticles were formed in $scCO_2$ and H_2 was used as reducing agent to keep the system free from organic solvents. X-ray diffraction (XRD), Fourier transform infrared (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) were used to provide structural information and confirm the morphology of the composites. The catalytic activity of the as-prepared composites in the Suzuki reaction was investigated in an aqueous system. In addition, the influence of the weight percentage of Pd to graphene on the Suzuki reaction activity was also examined.

2. Experimental

2.1. Materials

Ultra high purity CO_2 (Deokyang Co., 99.999%), graphite powder (Alfa Aesar), palladium(II) hexafluoroacetylacetonate ($Pd(hfa)_2$, Sigma–Aldrich), idobenzene (Sigma–Aldrich, 98%), sodium dodecyl sulfate (SDS, Sigma–Aldrich, 98.5%), tripotassium phosphate (Sigma–Aldrich, 98%), and phenylboronic acid (Sigma–Aldrich, 95%) were used as received. The other reagents were of analytical grade and used as received. Water was deionized in the laboratory.

2.2. Preparation of reduced graphene oxide (RGO)

Graphene oxide (GO) was prepared from powdered graphite using a modified Hummer and Offeman's method [39]. GO was then reduced to graphene by chemical exfoliation under nitrogen at $1050\text{ }^\circ\text{C}$ for 30 s followed by hydrogen reduction at $400\text{ }^\circ\text{C}$ for 2 h [40].

2.3. Synthesis of RGO/Pd nanocomposites in $scCO_2$

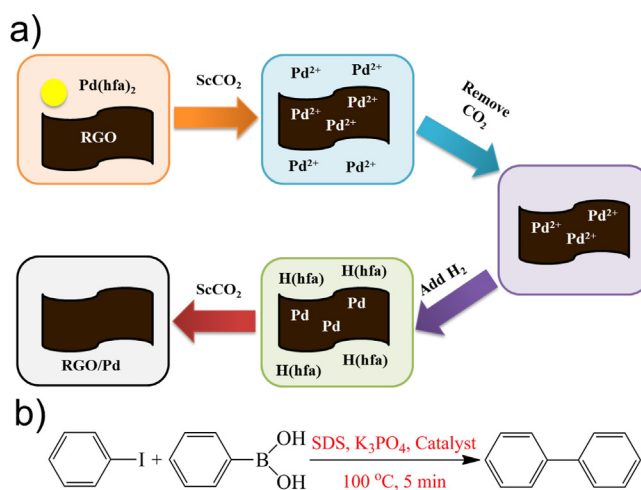
In a typical experiment, 50 mg RGO and approximately 24.46 mg of $Pd(hfa)_2$ were placed in a 10 ml stainless steel high-pressure reactor. The reactor was pressurized with CO_2 to 4000 psi at $45\text{ }^\circ\text{C}$. After 24 h, the CO_2 was released and hydrogen was introduced to the reactor. The reduction of Pd ions was carried out at 1000 psi and $45\text{ }^\circ\text{C}$ for 24 h. The H_2 was then released and the reactor was recharged with $scCO_2$ for a further 24 h under a continuous flow at 4000 psi and $45\text{ }^\circ\text{C}$ to ensure complete extraction of the organic ligands soluble in $scCO_2$ from the RGO, leaving only Pd nanoparticles in the RGO matrix. The products were collected and characterized.

2.4. Suzuki reactions catalyzed by RGO/Pd nanocomposites

The RGO/Pd nanocomposite (13.3 mg) with an 8.8 wt% Pd loading and 1 mmol idobenzene were added to a stirred mixture of sodium dodecyl sulfate (0.5 mmol), K_3PO_4 (2 mmol) and phenylboronic acid (1.2 mmol) in deionized water (5 ml) at $100\text{ }^\circ\text{C}$. After a 5 min reaction, the catalyst was recovered quickly and simply by centrifugation and washed three times with deionized water. The obtained reaction solution was extracted three times with 20 ml ethyl acetate. The combined extract was passed through anhydrous sodium sulfate, and the resulting mixture was analyzed by gas chromatography (GC).

2.5. Characterization

The XRD patterns of the samples were collected on a powder X-ray diffractometer (PANalytical, X'Pert-PRO MPD) using $Cu\text{ K}\alpha$ radiation. FT-IR spectra of the samples were obtained on an Excalibur Series FTS 3000 (Bio-Rad) spectrometer using the KBr



Scheme 1. (a) Schematic diagram of the synthesis process of the RGO/Pd nanocomposite and (b) illustration of the Suzuki reaction.

method. The morphology of the nanocomposites was observed by field emission SEM (FE-SEM, Hitachi, S-4100) and TEM (Philips, CM-200) at an acceleration voltage of 200 kV. Surface elemental compositions of RGO/Pd nanocomposites were obtained by XPS (ULVAC-PHI electron spectrometer, Quantera SXM) using an Al X-ray source. The catalytic activity of the Suzuki reaction was measured by GC (Donam Systems Inc., DS 6200).

3. Results and discussion

3.1. Green synthesis routes for the preparation of RGO/Pd nanocomposites

Scheme 1a shows the preparation process of the RGO/Pd nanocomposite. The precursor $Pd(hfa)_2$ was dissolved in $scCO_2$ at 27.6 MPa and $45\text{ }^\circ\text{C}$ for 24 h. These conditions provided the optimal loading of Pd^{2+} ions onto the RGO surfaces. Because of the presence of few oxygen functional groups on the RGO surface as active sites, Pd^{2+} ions could attach to the RGO surface in $scCO_2$ through an electrostatic effect. The wrinkled surfaces of RGO also promote the generation of Pd nanoparticles on them. Pd^{2+} ions were then reduced by hydrogen:

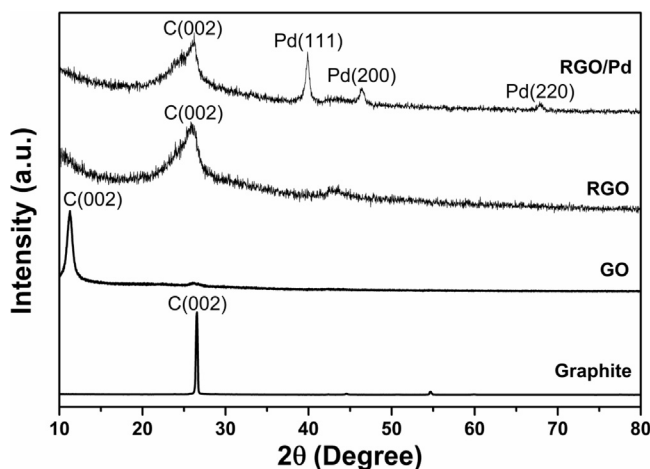
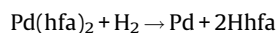


Fig. 1. XRD patterns of graphite, GO, RGO, and the RGO/Pd nanocomposites.

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