Catalysis Communications 69 (2015) 97–103

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Palladium nanoparticles supported on reduced graphene oxide as an efficient catalyst for the reduction of benzyl alcohol compounds

Maryam Mirza-Aghayan [a,*], Mahdieh Molaee Tavana [a], Rabah Boukherroub [b]

[a] Chemistry and Chemical Engineering Research Center of Iran (CCERCI), P.O. Box 14335-186, Tehran, Iran
[b] Institut d'Electronique, de Microélectronique et de Nanotechnologie (IEMN, UMR 8520), Cité Scientifique, Avenue Poincaré - CS 60069, 59652 Villeneuve d'Ascq, France

ARTICLE INFO

Article history:
Received 9 February 2015
Received in revised form 9 May 2015
Accepted 28 May 2015
Available online 1 June 2015

Keywords:
Palladium nanoparticles
Reduced graphene oxide
Sonochemical
Benzyl alcohols
Hydrogenolysis
Triethylsilane

ABSTRACT

Palladium nanoparticles were prepared on reduced graphene oxide (Pd NPs/rGO) by using a sonochemical procedure. Pd NPs with a mean diameter of 37 ± 22 nm were deposited on reduced graphene oxide sheets by the reaction between $PdCl_4^{2-}$ and graphene oxide (GO) under sonochemical conditions. The catalyst was characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), infrared spectroscopy (FT-IR), transmission electron microscopy (TEM) and inductively coupled plasma optical emission spectroscopy (ICP-OES). The Pd NPs/rGO nanocomposite was successfully applied as a reusable catalyst for the reduction of benzyl alcohol derivatives into the corresponding methylene compounds in the presence of triethylsilane. The reductive dehydroxylation of benzyl alcohols takes place under mild conditions affording high yields of the corresponding methylene compounds in short reaction times.

1. Introduction

The transformation of a hydroxyl functional group into the corresponding alkyl group is a delicate process. Alcohol deoxygenation constitutes a powerful synthetic tool especially used in complex natural product synthesis. The Barton–McCombie methodology is the most commonly used, mainly for secondary alcohols, due to its versatility and compatibility with different functional groups [1,2]. The main disadvantage of this reaction is the use of tributylstannane which is toxic, expensive and difficult to remove from the reaction mixture. Since hydroxyl group is a poor leaving group, its transformation into a good leaving group is generally employed [3]. Several reagents and catalysts have been reported for the reduction of benzyl alcohols [4–6]. For example, Pd/C and H_2 in compressed CO_2/water [4], iridium catalyst with hydrazine at 160 °C [5], palladium chloride ($PdCl_2$) and polymethylhydrosiloxane (PMHS) as hydride source [6] have been investigated for this chemical transformation. However, it should be noted that high pressure autoclave or high temperatures and long reaction times were required for this process. Different benzylic alcohols were successfully reduced into the corresponding deoxygenated compounds by using 2.0 equiv. of Ti(III) and 1.5 equiv. of reducing agent such as Mn dust in tetrahydrofuran as solvent [7]. Recently, direct electrolysis of primary alcohols in excess of methyl toluate was reported for the synthesis of the corresponding deoxygenated products in high yield [8].

Organosilanes are used to reduce alcohols to alkanes in the presence of strong Lewis and Brønsted acids [9]. Egi et al. have reported on the direct catalytic deoxygenation of propargyl alcohols with the combination of $H_3[PW_{12}O_{40}]\cdot nH_2O$ (1 mol%) and Et_3SiH in $Cl(CH_2)_2Cl$ or CF_3CH_2OH as solvent [10]. Chan et al. demonstrated the efficiency of $FeCl_3$ as catalyst for the selective dehydroxylation of secondary benzylic alcohols using PMHS as hydride source [11].

We have investigated the efficiency of $Et_3SiH/PdCl_2$ system for several transformations [12–14] such as reduction of benzyl alcohols to the corresponding methylene compounds under homogeneous conditions [15].

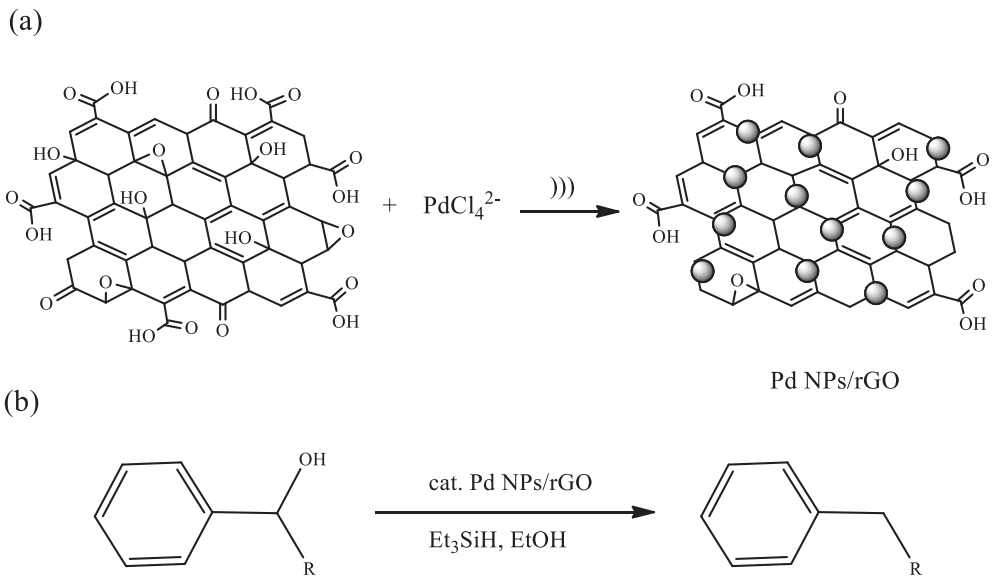
Graphene oxide and graphite oxide have been successfully applied as effective heterogeneous catalysts for several organic transformations [16–21].

Noble metal nanoparticles have widely been used as catalysts to promote various chemical reactions [22,23]. Graphite oxide, graphene oxide (GO), reduced graphene oxide (rGO), and graphene in combination with metal nanoparticles have been utilized as catalyst supports [24,25].

In continuation of our efforts on the use of $PdCl_2/Et_3SiH$ system [12–15] and graphite oxide [18–21], we propose in the present study a simple procedure for the preparation of palladium nanoparticles supported reduced graphene oxide (Pd NPs/rGO) under ultrasound conditions (Scheme 1a). The nanocomposite material was characterized using XRD, TGA, SEM, FT-IR, TEM and ICP-OES. The catalytic activity of the Pd NPs/rGO was further investigated for the reduction of benzyl alcohol derivatives into the corresponding methylene compounds in the presence of triethylsilane (Scheme 1b).

* Corresponding author.
E-mail address: m.mirzaaghayan@ccerci.ac.ir (M. Mirza-Aghayan).

http://dx.doi.org/10.1016/j.catcom.2015.05.023
1566-7367/



Scheme 1. (a) Synthesis of Pd NPs/rGO using ultrasonication; (b) reduction of benzyl alcohol compounds using Et_3SiH and Pd NPs/rGO nanocomposite catalyst.

2. Experimental

2.1. General information

Elmasonic P ultrasonic cleaning unit (bath ultrasonic) and ultrasonic homogenizer Bandelin Sonoplus HD 3100 (probe ultrasonic) were used to prepare the Pd NPs/rGO nanocomposite samples. X-ray diffraction (XRD) data were collected using a Bruker D8 Advance Theta–2theta diffractometer. Thermogravimetric analysis (TGA) was performed on a NETZSCH TG 209 F1 analyzer. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) data were acquired using a VEGA3 LMU TESCAN SEM. IR spectra were recorded from KBr disks with a Bruker Vector 22 FT-IR spectrometer. Transmission electron microscopy (TEM) images were obtained using a Zeiss em900 transmission electron microscope. Palladium content of the Pd NPs/rGO catalyst was determined using ICP-OES Varian 735 ES configuration torch redial instrument after each catalyst sample was completely dissolved in the mixture of HNO_3/HCl (1/3 ratio).

2.2. Synthesis of graphite oxide

Graphite oxide utilized in this work was synthesized according to a previously reported procedure [20].

2.3. Synthesis of palladium nanoparticles/reduced graphene oxide (Pd NPs/rGO)

Typically, 200 mg of graphite oxide powder in 800 mL of deionized water was mixed in a reaction container using bath ultrasonic with a frequency of 37 kHz for 2 h. Then 2 mL of the graphite oxide dispersion

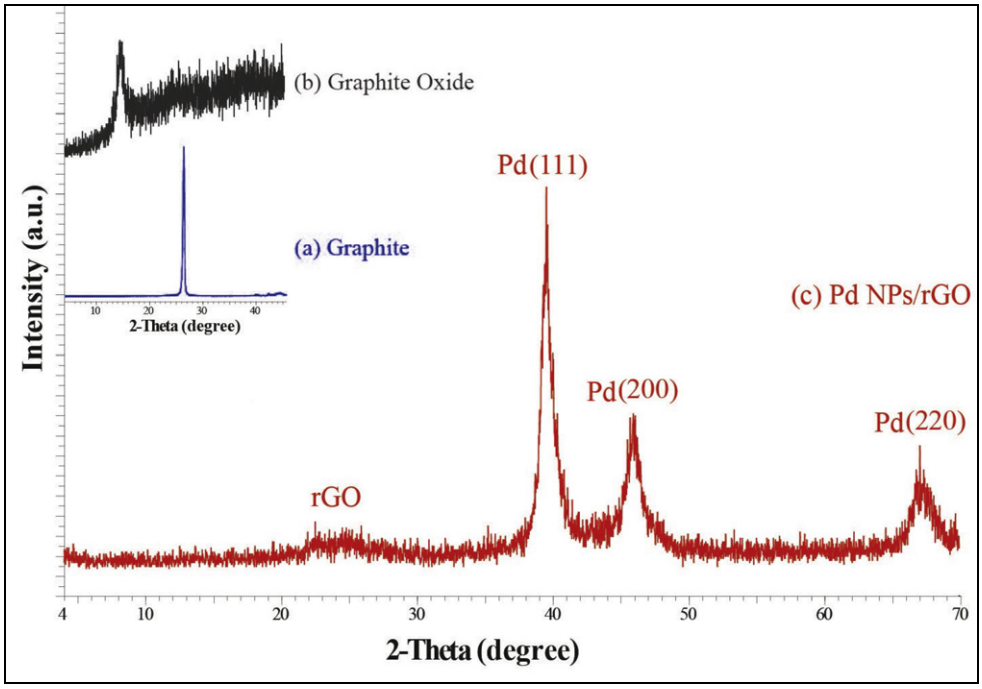


Fig. 1. XRD patterns of (a) graphite, (b) graphite oxide, and (c) Pd NPs/rGO.