Catalysis Communications 46 (2014) 219–223

Contents lists available at ScienceDirect

Catalysis Communications

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

Short Communication

Aqueous phase catalytic hydrodechlorination of 4-chlorophenol over palladium deposited on reduced graphene oxide

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ARTICLE INFO

Article history:
Received 29 July 2013
Received in revised form 16 December 2013
Accepted 20 December 2013
Available online 29 December 2013

Keywords:
Palladium
Graphene
Hydrodechlorination
4-Chlorophenol

ABSTRACT

Palladium/reduced graphene oxide nanocomposites (Pd/RGO) are synthesized through the impregnation of polyvinyl-pyrrolidone-stabilized palladium nanoparticles on the surface of RGO sheets prepared from the reduction of graphene oxide in the presence of hydrogen gas. The Pd/RGO nanocomposites exhibited excellent catalytic property for the hydrodechlorination of 4-chlorophenol.

1. Introduction

Chlorophenols are widely used as end products or intermediates in the production of pesticides, disinfectants, wood preservatives, and personal care formulations [1]. The residue of these compounds causes a negative effect on the environment and human beings such as the contamination of groundwater due to their acute toxicity and poor biodegradability. Among the current approaches that have been employed to deal with the wastewater containing chlorophenols, catalytic hydrodechlorination (HDC) is considered to be an environmental-friendly one by the breaking up of the C – Cl bond and thus transforming toxic substances into safe compounds or even useful materials.

Generally, the catalytic HDC is conducted under a reduction atmosphere of molecular hydrogen and by contacting with supported metallic catalysts such as Pd [2–6], Pt [7,8], and Rh [9–12]. Pd has been proven to be the most promising one due to its high activity in such degradation of chlorophenols at ambient conditions. Nevertheless, severe catalyst deactivation originated from the strong adsorption of chlorine on Pd surface [13,14], aggregation of active Pd particles [15,16] and/or carbonaceous deposited on Pd surface [17–19] have been reported in recent years. In order to improve the catalytic stability and reusability, a method based on the addition of a large amount of base to neutralize the HCl formed in the reaction process has been developed, however it calls for extra work to segregate the additives from the reaction mixtures to avoid the secondary pollution. So far, a more facile route to maintain the activity of catalysts without introduction of additives still remains as a challenging task to be fulfilled.

As one atom-thick sheet of sp^2-bonded carbon atoms, graphene has high surface area (theoretical value 2600 m^2/g), good conductivity and stability, and low cost. Therefore, graphene based materials obtained from the chemical modification have attracted intensive research interest recently. Especially, the use of RGO as a support to synthesize RGO/nanoparticles (NPs) composites from the co-reduction of GO and metal precursors was the promising one due to their versatile applications in the area of hydrogenation, Suzuki–Miyaura and Heck coupling reactions. By applying the RGO, the stability and dispersity of the NPs on the surface of RGO can be improved through the interaction of the oxygen containing groups. Meanwhile, the existence of metal/support interaction between the NPs and RGO can lead to an increased performance of the composites [20]. Thus, it is desirable to employ RGO as a support for developing new catalysts with enhanced catalytic activity and stability. As far as we are aware, no attempt has yet been exerted to apply RGO as a support of catalyst in the HDC of chlorophenols. Herein, we reported the synthesis of RGO from the reduction of GO in a mixture of ethanol and water and then used as support for depositing Pd

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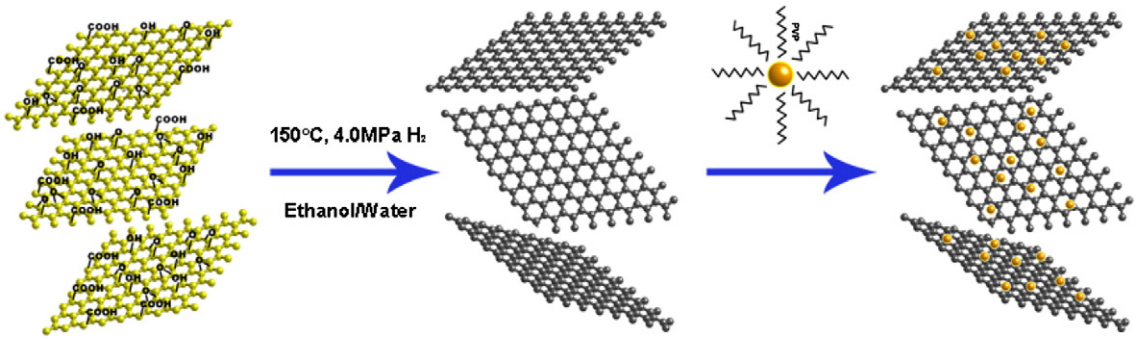
http://dx.doi.org/10.1016/j.catcom.2013.12.025



Scheme 1. Preparation of Pd NPs supported on RGO sheets.

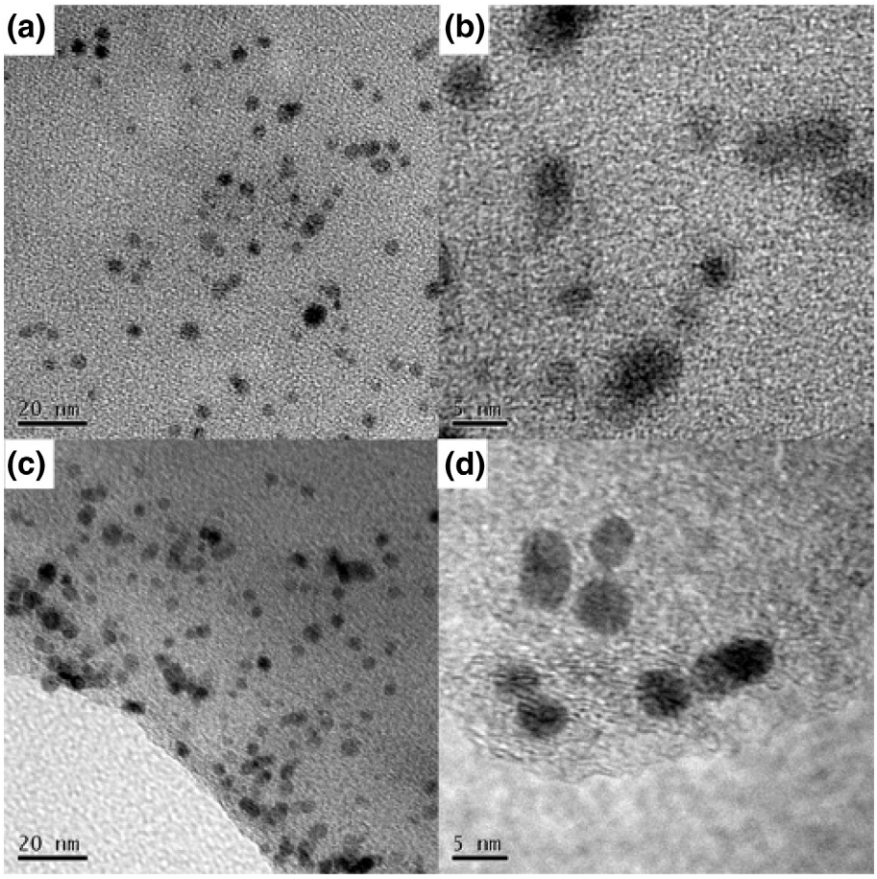


Fig. 1. TEM images of fresh Pd/RGO (a and b) and used Pd/RGO(c and d).

NPs. The as-prepared catalyst was applied for the catalytic HDC of 4-chlorophenol in aqueous phase. The Pd/RGO catalyst exhibited excellent activity as well as stability at 40 °C under ordinary pressure (hydrogen balloon) and can be reused four times.

2. Experimental

2.1. Catalyst preparation

GO was synthesized via improved synthetic method reported by Marcano et al. [21]. RGO was synthesized as follows: a mixture of GO (0.5 g), water (10 mL) and ethanol (20 mL) was transferred into an autoclave. Then the autoclave was sealed and charged with H_2 for five times to expel the air. The reaction was carried out at 4.0 MPa H_2 and 150 °C for 4 h. The generated black solid was washed with ethanol and distilled water several times and dried under vacuum at 60 °C for 12 h.

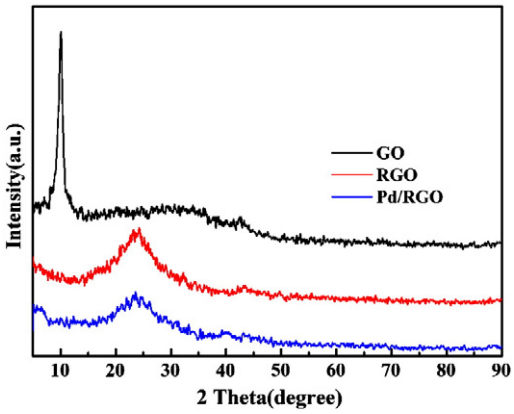


Fig. 2. XRD patterns of GO, RGO and Pd/RGO.