Catalysis Today xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

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

Photocatalytic C—H activation and oxidative esterification using Pd@g-C_3N_4

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ARTICLE INFO

Keywords:
C—H activation
Visible light
Heterogeneous catalysis
Oxidative esterification
Alcohols

ABSTRACT

Graphitic carbon nitride supported palladium nanoparticles, Pd@g-C_3N_4, have been synthesized and utilized for the direct oxidative esterification of alcohols using atmospheric oxygen as a co-oxidant *via* photocatalytic C—H activation.

1. Introduction

Esters are important functional groups present in natural products and pharmaceutical active scaffolds [1]. In many instances, they serve as starting materials for the synthesis of a wide range of active pharmaceutical ingredients and important polymeric compounds [2]. Methyl esters are the simplest esters [3] and have been mainly utilized as precursors in multistep organic synthesis [4]. In general, they are synthesized by the reaction of activated carboxylic acid with methanol. Methyl esters have also been accessed using acid catalyzed condensation of carboxylic acid with methanol. Although, these methods provide high yield but they demand higher temperatures or require the activation of carboxylic acid which may interfere with the sensitive functional groups present in the vicinity [5,6]. Direct synthesis of methyl esters has also been reported using oxidants such as MnO_2, $Na_2Cr_2O_7$, *etc.* [7,8]. The serious problem in these methods is the generation of a large amount of toxic waste typical of stoichiometric reactions. The growing environmental concerns in chemical research have prompted researchers worldwide to seek greener pathways for all transformations preferably deploying catalytic reactions. We focused on esterification reactions using alcohols in the direct synthesis of methyl esters where few general methods have been documented [9–14]. Lei et al. has reported the synthesis of methyl esters using palladium (Pd) catalyst under oxygen atmosphere (oxygen balloon) [15] with moderate success due to compromising yields along with the loss of precious Pd complex. Although the synthesis of esters using photoactive VO@g-C_3N_4 and hydrogen peroxide is known [16] but we envisioned that the use of air is more sustainable then hydrogen peroxide. Working towards the development of sustainable and greener protocols in organic synthesis [17–21], herein we describe a superior method which deploys air as an oxidant. Accordingly, graphitic carbon nitride supported palladium nanoparticles (Pd@g-C_3N_4) were synthesized in view of the inherent photoactivity of graphitic carbon nitride (g-C_3N_4) and their application in cascade oxidative C—H activation-esterification of alcohols is demonstrated. In Pd@g-C_3N_4, the nitrogenous framework of g-C_3N_4 provides electron rich environment for holding palladium nanoparticles and absorbs visible light, which is further dispersed in reaction media thus accomplishing aerial oxidative esterification.

2. Materials and methods

2.1. General methods

All the reactions were performed in an oven-dried apparatus in a closed box using domestic bulb (20 W), with wave length in the range of 400–700 nm and were stirred magnetically. ^1H NMR spectra were recorded at 300 MHz instrument. Chemical shifts are reported in parts per million downfield from the internal reference, tetramethylsilane (TMS).

2.2. Synthesis of materials

2.2.1. Synthesis of g-C_3N_4

The graphitic carbon nitride, g-C_3N_4, was synthesized by calcination of urea at 500 °C for 2 h [16].

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http://dx.doi.org/10.1016/j.cattod.2017.06.009
Received 14 March 2017; Received in revised form 6 May 2017; Accepted 13 June 2017
0920-5861/ Published by Elsevier B.V.

Please cite this article as: Verma, S., Catalysis Today (2017), http://dx.doi.org/10.1016/j.cattod.2017.06.009

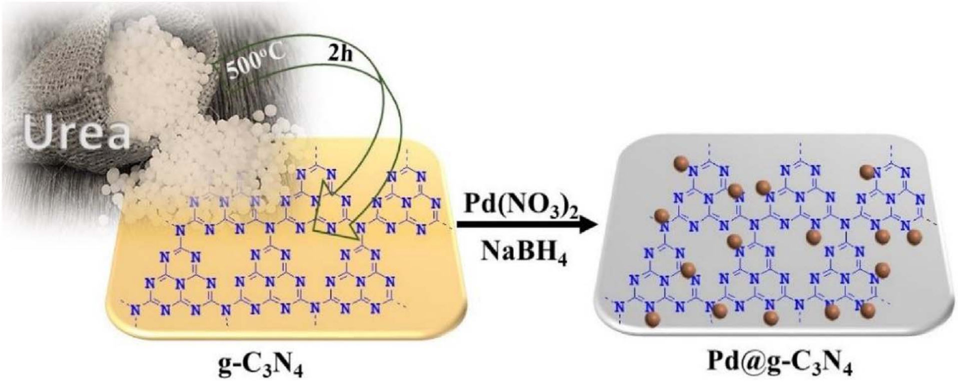

Fig. 1. Synthesis of Pd@g-C_3N_4.

2.2.2. Synthesis of Pd@g-C_3N_4 catalyst

100 mg of g-C_3N_4 was dispersed in water (500 mL) under sonication. The aqueous solution of palladium nitrate hydrate (10.82 mg of Pd $(NO_3)_2$ in 5 mL water) was added and stirred for 4 h. The reaction temperature was raised to 60 °C and the excess of sodium borohydride was added, in portion, with constant stirring. The reaction mixture becomes black after $NaBH_4$ addition. The reaction was further stirred for 4 h and cooled down to room temperature. The catalyst was centrifuged, washed with methanol and dried under vacuum at 50 °C. The Pd@g-C_3N_4 catalyst was isolated as off black powder (Fig. 1) and characterized using SEM, TEM, XRD, XPS and ICP-AES analysis.

2.2.3. General procedure for the oxidative esterification of alcohols

A 25 mL side-armed round bottomed flask equipped with a magnetic stirring bar and a balloon filled with air was charged with alcohol (1 mmol), catalyst Pd@g-C_3N_4 (10 mg) and 5.0 mL of methanol. The reaction mixture was exposed to visible light irradiation using 20-W domestic bulb. The progress of the reaction was monitored by TLC. After the completion of the reaction, Pd@g-C_3N_4 catalyst was separated using centrifuge. The product was extracted using ethyl acetate, dried over sodium sulfate, concentrated and characterized using NMR.

2.3. Recycling of Pd@g-C_3N_4 catalyst

To establish the recyclability of the Pd@g-C_3N_4 catalyst for oxidative esterification of alcohol, a set of experiments were performed using benzyl alcohol as a substrate in methanol. After the completion of each reaction the Pd@g-C_3N_4 catalyst was recovered using a centrifuge, washed with methanol and reused for the oxidative esterification of benzyl alcohol using fresh reagents. The Pd@g-C_3N_4 catalyst could be recycled and reused up to five times without losing its activity (Fig. 2). The metal leaching of Pd@g-C_3N_4 catalyst was studied by ICP-AES analysis before and after completion of the reaction. The Pd concentrations were found to be 4.59% before the reaction and 4.58% after the 5th cycle. The ICP-AES of the mother liquor did not show the presence of palladium confirming the fact that the g-C_3N_4 holds the palladium nanoparticles tightly which minimizes the Pd leaching and supports efficient recycling.

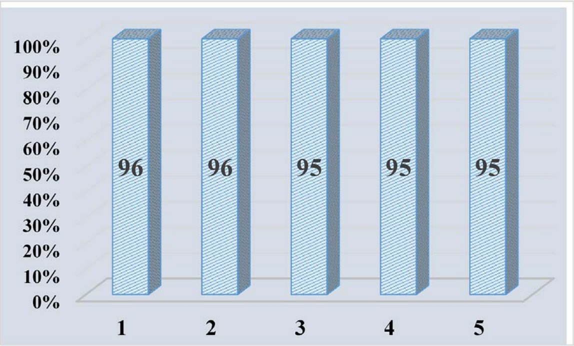

Fig. 2. Histogram for recycling experiments.

3. Result and discussion

The synthesized catalyst, Pd@g-C_3N4, was characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy and Inductive coupled plasma atomic emission spectroscopy (ICP-AES). The SEM image (Fig. 3) obtained for g-C_3N_4 and Pd@g-C_3N_4 affirms the immobilization of palladium nanoparticles with the visible difference in their morphology before and after the impregnation of nanoparticles which was further supported by TEM analysis (Fig. 4). The EDX spectrum of Pd@g-C_3N_4 (Fig. 4c) indicates the presence of palladium metal in Pd@g-C_3N_4. The XRD analysis confirmed the formation of metallic graphitic carbon nitride-Pd catalyst (Pd@g-C3N4), a peak at 27.4° is assigned to graphitic carbon nitride g-C_3N_4 (Fig. 5). The peaks at 40.1°, 46.1°, 68.2° represent the metallic Pd nanoparticles in zero oxidation state. Thus, the XRD pattern of Pd@g-C_3N_4 confirms the crystalline structure of Pd-nanoparticles over g-C_3N_4 surface and the XRD analysis was further supported by XPS analysis (Supporting Information; S1). The weight percentage of Pd (4.59%) was calculated using ICP-AES analysis.

The synthesized Pd@g-C_3N_4 catalyst was screened for the oxidative esterification of alcohols using aerial flow under visible light irradiation. We conjectured that the graphitic carbon nitride, being endowed with nitrogenous electron rich photoactive chromophore, would be a good candidate for this exploration. These conditions would help accelerate the C—H activation *via* visible light adsorption thus providing the required amount of activation energy for crossing transition barrier in the esterification of alcohols. The inherent photo active nature of g-C_3N_4 encouraged us to combine it with Pd metal which may offer synergic jump for the oxidative esterification. Palladium nanoparticles were immobilized over the surface of graphitic carbon nitride and screened for the oxidative esterification of benzyl alcohol with methanol under visible light using air (Table 1); reactions were performed with 25 mg of Pd@g-C_3N_4 bearing different Pd-loading in methanol (Table 1, entries 1–6) which was imperative for its photo-active C—H activation towards the oxidative esterification. The reaction of benzyl alcohol with Pd@g-C_3N_4 bearing about 1% Pd required 12 h to afford 47% of methyl benzoate (Table 1, entry 1). The increase in Pd concentration to 2%, 3% and 4% resulted in better yields and delivered the desired product in 67%, 73% and 87%, respectively (Table 1, entries 2–4). The Pd@g-C_3N_4 catalyst with 5% Pd-loading was most effective as it offered methyl benzoate in near quantitative yield (96%, Table 1, entry 5). Further increase in Pd concentration did not have significant impact on the progress of reaction (Table 1, entry 6). After identifying the effective Pd-loading for the catalyst it was essential to optimize the amount of the catalyst required for the oxidative esterification. Thus,