

# Palladium complex immobilized on graphene oxide–magnetic nanoparticle composites for ester synthesis by aerobic oxidative esterification of alcohols

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## ABSTRACT

A well dispersed magnetically separable palladium complex immobilized to magnetite–graphene oxide nanocomposite has been synthesized via solvothermal route. The successfully decorated graphene oxide sheets with the homogeneously dispersed iron nanoparticles and palladium(II) complex were proved by transmission electron microscopy. X-ray diffraction pattern of the synthesized catalyst revealed that palladium(II) complex was successfully immobilized to the support. Further, X-ray photoelectron spectroscopy confirmed that palladium is present in +2 oxidation state. The synthesized heterogeneous material was found to be an efficient catalyst for the oxidative esterification of alcohols with methanol by using molecular oxygen as oxidant. The developed catalyst was found to be more reactive than its homogeneous analog, i.e. PdCl<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>. Similarly, no reaction occurred in the presence of Pd(0)/magnetite–graphene nanocomposite catalyst. These studies confirmed that the palladium(II) ions are the main catalyst and superior reactivity of heterogeneous palladium catalyst is attributed to the promotion role of graphene support in the adsorption of reactant alcohol and oxygen. After the reaction, the catalyst was easily separated by external magnetic effect and reused for several runs with consistent catalytic activity without any detectable leaching.

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## 1. Introduction

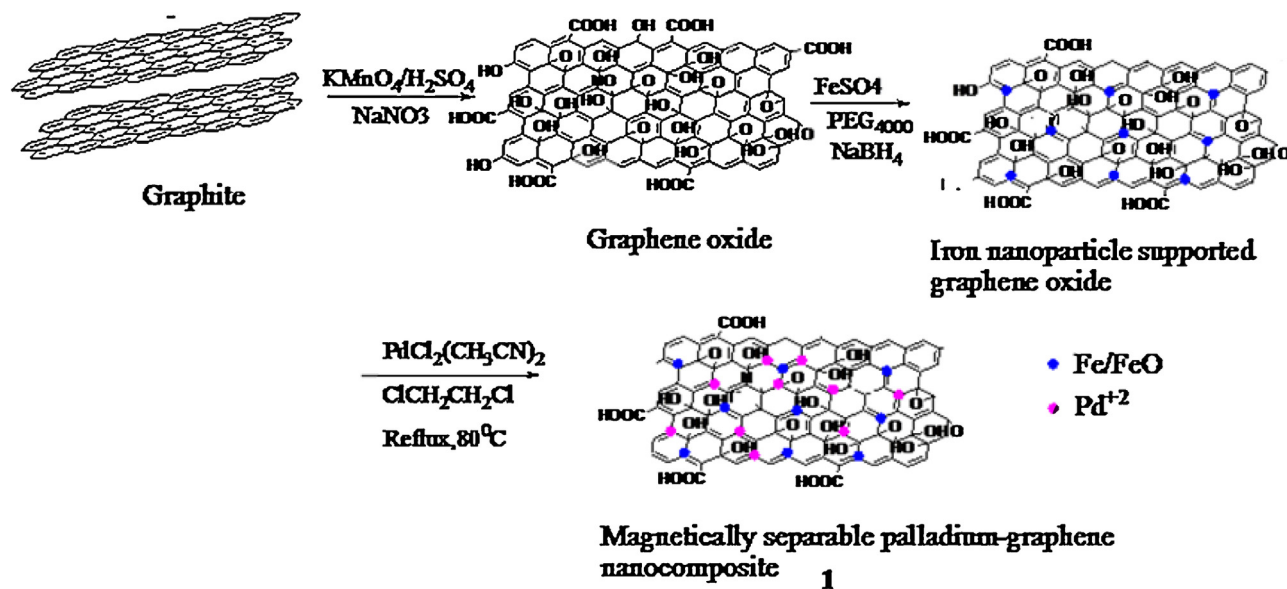
Synthesis of esters particularly, methyl esters is one of the important transformations in organic synthesis mainly due to their wide spread applications in pharmaceutical chemistry, materials science, and also as a protective group in organic synthesis [1]. The conventional synthesis of methyl esters includes the reaction of carboxylic acids or activated carboxylic acid derivatives such as acid anhydrides or acid chlorides with methanol [2–4]. Alternative simple methodologies such as direct oxidative esterification of aldehydes with alcohols by using stoichiometric amounts of strong oxidants such as Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, Ca(OCl)<sub>2</sub>, NaBrO<sub>3</sub>/NaHSO<sub>3</sub>, MnO<sub>2</sub>, and *N*-iodosuccinimide have also been reported [5,6]. From the viewpoint of green chemistry, direct oxidative esterification reactions with alcohols, using molecular oxygen, catalyzed by reusable heterogeneous catalysts is an attractive and challenging area of current research interest [7–13].

Recently, functionalized magnetic separable nanocomposite materials have emerged as viable alternatives to conventional materials for organic transformations [14–16]. Besides the facile separation of the catalyst by external magnetic field, the magnetic nanocomposite matrices act as the stabilizer of the nanoparticles and thus providing a means to prevent aggregation. In the recent years, magnetically separable palladium based nanocomposite materials have been widely used for various organic transformations including oxidation, C–C bond formation and coupling reactions [17–20]. Very recently, few reports have been published on the direct synthesis of esters via palladium catalyzed aerobic oxidative esterification of alcohols by using molecular oxygen as terminal oxidant [21–23]. However, in most of the cases difficult recovery and non-recycling ability of the homogeneous palladium catalysts make them of limited synthetic utility.

Herein we report the successful synthesis of magnetically separable palladium(II) complex to graphene oxide, its characterization and application in direct aerobic oxidative esterification of various alcohols with methanol (Scheme 1). To the best of our knowledge, this is the first report on heterogeneous palladium catalyst for the direct oxidative esterification of alcohols using molecular oxygen as oxidant.

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**Scheme 1.** Synthesis of magnetically separable palladium(II) complex immobilized to graphene oxide 1.

## 2. Experimental

### 2.1. Materials

Graphite powder and  $\text{PdCl}_2$  was purchased from Sigma–Aldrich and used as received.  $\text{KMnO}_4$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{NaNO}_3$ ,  $\text{HCl}$ ,  $\text{NaOH}$ ,  $\text{FeCl}_3$ , ethylene glycol, and sodium acetate were obtained from Merck (India). All the chemicals were of analytical grade and used without further purification.

### 2.2. Techniques used

Fourier transform infrared spectroscopy (FT-IR) was conducted by Perkin–Elmer spectrum RX-1 IR spectrophotometer. High resolution transmission electron microscopy (HR-TEM) and energy dispersive X-ray spectroscopy (EDAX) of the nanocomposites was executed using Phillips CM 200 operating at an acceleration voltage of 200 kV. Scanning electron microscopy (SEM) was performed by Jeol Model JSM-6340F. For FE-SEM analysis aqueous dispersions of GO and graphene–metal nanocomposites were deposited on the glass slides, while very dilute aqueous suspensions were deposited on carbon coated copper grids for HR-TEM analysis. The phase characterization was carried out by X-ray diffractometer (XRD; model No. PW1710). Sample for XRD was prepared by the deposition of well dispersed graphene–metal nanocomposite on glass slide followed by drying; the analysis was performed by using cobalt as the target material. The conversions and selectivity of the products were determined by high resolution GCMSD, EI, quadrupole mass analyzer, EM detector.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of the products were performed at 500 MHz by using Bruker Avance-II 500 MHz instrument. ICP-AES analysis was carried out by inductively coupled plasma atomic emission spectrometer (ICP-AES, PS-3000UV) by Leeman.

### 2.3. Preparation of graphene oxide (GO)

Graphene oxide (GO) was prepared by harsh oxidation of graphite powder. In a typical procedure, graphite powder (1.0 g),  $\text{NaNO}_3$  (1.0 g) and  $\text{H}_2\text{SO}_4$  (45 ml) were mixed in a reaction vessel on an ice bath. This is followed by gradually addition of  $\text{KMnO}_4$  (6.0 g) under maintained temperature and then reaction mixture

was allowed for continue stirring at room temperature for 24 h. Subsequently, 80 ml water was slowly added and temperature of reaction mixture was raised to  $98^\circ\text{C}$  using an oil bath. After another 24 h, 200 ml of water was added, followed by another addition of 30%  $\text{H}_2\text{O}_2$  (20 ml). Finally, oxidation product was filtered and purified by rinsing with 50 ml of 5%  $\text{HCl}$  solution. The filtrate cake was repeatedly washed with copious amount of HPLC grade water until the pH was about 6. This processed dark brown oxidized material was dried in oven at  $90^\circ\text{C}$ . The dried product was grounded with a mortar and pestle to the fine powder.

### 2.4. Synthesis of iron nanoparticles containing graphene–magnetite nanocomposite

In the typical synthesis, graphene oxide (200 mg) was dispersed in water (80 ml) through sonication for 30 min. The mixture of ferrous sulphate (0.5 g, 1.7 mmol), PEG 4000 (1.0 g) and double distilled water (5 ml) was added slowly in to the GO solution with vigorous stirring for 24 h. Total volume of solution was made up to approx. 1 l by adding water. After 1 h,  $\text{NaBH}_4$  (1 g, 26 mmol) added to this reaction mixture at  $80^\circ\text{C}$  and kept it for next 2 h. The black colored iron nanoparticles supported graphene oxide **2** was separated by external magnet and washed with water and dried at  $65^\circ\text{C}$  under vacuum.

### 2.5. Synthesis of magnetically separable Pd(II) complex immobilized to GO 1

A solution of homogeneous palladium complex, i.e.  $\text{PdCl}_2(\text{CH}_3\text{CN})_2$  (0.25 g, 1 mmol) in dichloroethane (10 ml) was mixed with magnetite–graphene nanocomposite (1 g) and the resulting suspension was heated at  $80^\circ\text{C}$  under stirring for 4 h. The yellowish colored heterogeneous  $\text{Pd}^{+2}/\text{Fe}/\text{FeO}/\text{graphene}$  nanocomposite was collected by magnetic separation and washed several times with water, ethanol, and acetone, respectively. Finally the sample was dried at  $80^\circ\text{C}$  for 2 h under vacuum. The catalyst was stored at room temperature without taking any precaution. The weight percentage of palladium in the final catalyst was found to be 10.23 wt% (0.96 mmol/g) as determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis.

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