Applied Catalysis A: General 489 (2015) 17–23

Contents lists available at ScienceDirect

Applied Catalysis A: General

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

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

Sanny Verma[a], Deepak Verma[b], Anil K. Sinha[b,*], Suman L. Jain[a,*]

[a] *Chemical Sciences Division, CSIR – Indian Institute of Petroleum, Mohkampur, Dehradun 248005, India*
[b] *Catalytic Conversion Process Division, CSIR – Indian Institute of Petroleum, Mohkampur, Dehradun 248005, India*

ARTICLE INFO

Article history:
Received 31 December 2013
Received in revised form 27 March 2014
Accepted 2 October 2014

Keywords:
Magnetically separable catalyst
Graphene oxide
Palladium
Esterification
Oxidation

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. $PdCl_2(CH_3CN)_2$. 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.

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 $Na_2Cr_2O_7$, $Ca(OCl)_2$, $NaBrO_3/NaHSO_3$, MnO_2, 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].

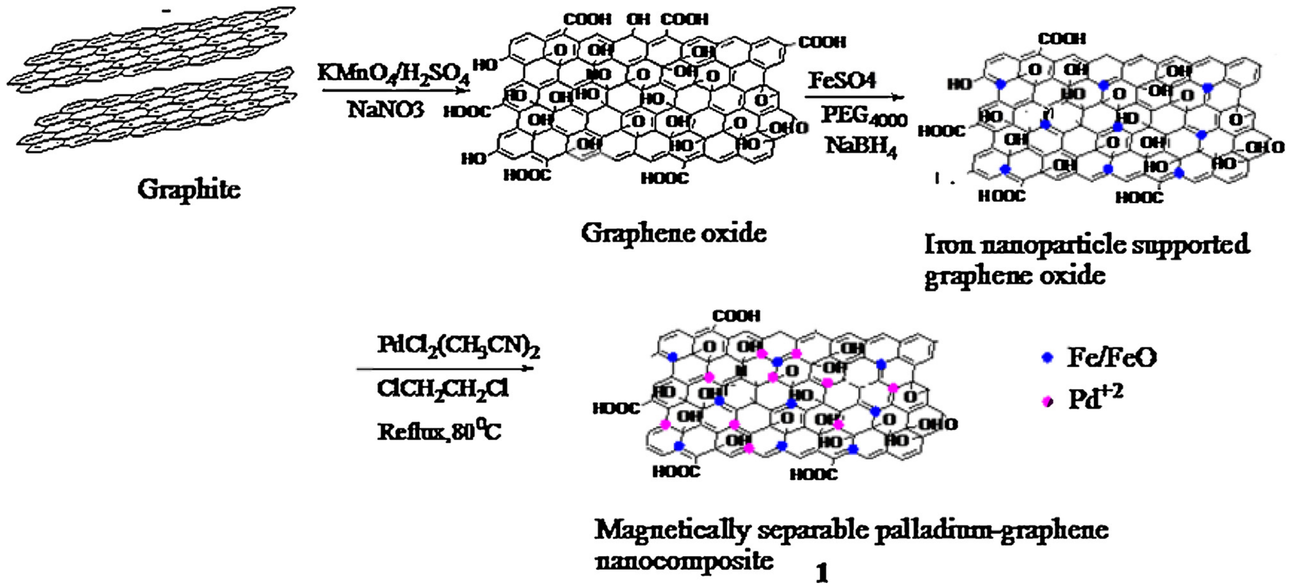
Recently, functionalized magnetic separable nanocomposite materials have emerged as viable alternatives to conventional materials for organic transformations [14–16]. Besides the facile separation of the catalyst by external magnetic field, the magnetic nanocomposite matrices act as the stabilizer of 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.

---

* Corresponding authors. Fax: +91 135 2660202.
E-mail addresses: asinha@iip.res.in (A.K. Sinha), suman@iip.res.in (S.L. Jain).

http://dx.doi.org/10.1016/j.apcata.2014.10.004
0926-860X/



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

2. Experimental

2.1. Materials

Graphite powder and $PdCl_2$ was purchased from Sigma–Aldrich and used as received. $KMnO_4$, H_2SO_4, $NaNO_3$, HCl, NaOH, $FeCl_3$, 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, quadrapole mass analyzer, EM detector. ^1H NMR and ^{13}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), $NaNO_3$ (1.0 g) and H_2SO_4 (45 ml) were mixed in a reaction vessel on an ice bath. This is followed by gradually addition of $KMnO_4$ (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 °C using an oil bath. After another 24 h, 200 ml of water was added, followed by another addition of 30% H_2O_2 (20 ml). Finally, oxidation product was filtered and purified by rinsing with 50 ml of 5% 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 °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, $NaBH_4$ (1 g, 26 mmol) added to this reaction mixture at 80 °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 °C under vacuum.

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

A solution of homogeneous palladium complex, i.e. $PdCl_2(CH_3CN)_2$ (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 °C under stirring for 4 h. The yellowish colored heterogeneous Pd^{+2}/Fe/FeO/graphene nanocomposite was collected by magnetic separation and washed several times with water, ethanol, and acetone, respectively. Finally the sample was dried at 80 °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.

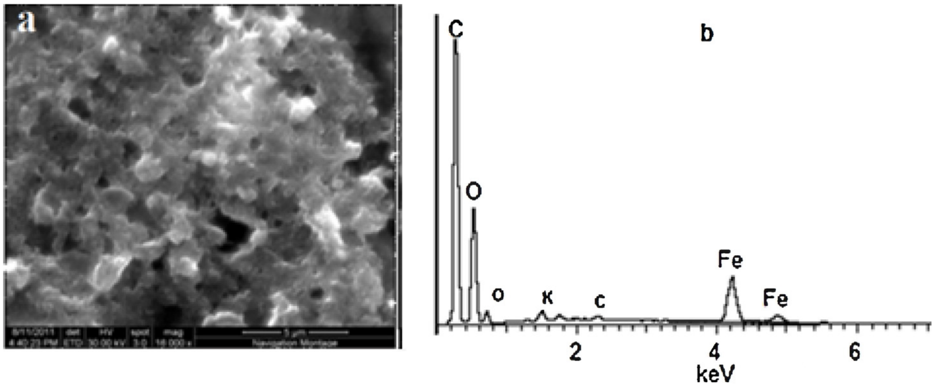


Fig. 1. SEM image of: (a) magnetite–graphene nanocomposite; (b) EDAX of magnetite–graphene nanocomposite.

Table 1
Oxidative esterification of benzyl alcohol with methanol under different reaction conditions.[a]

Entry	Solvent	Base	Catalyst	Conv./select. (%)[b]
1	MeOH	K_2CO_3	**1**	100/90
2	MeOH	Na_2CO_3	**1**	98/86
3	MeOH	Et_3N	**1**	–
4	MeOH	KOtBu	**1**	100/66[c]
5	MeOH	–	**1**	–
6	DMSO	K_2CO_3	**1**	Trace
7	THF	K_2CO_3	**1**	–
8	MeOH	K_2CO_3	Fe/FeO/GO	–
9	MeOH	K_2CO_3	$PdCl_2(CH_3CN)_2$	70/67[d]
10	MeOH	K_2CO_3	Pd(0)/Fe/FeO/GO	–

[a] Reaction condition: benzyl alcohol (1 mmol), catalyst (1 mol%), base (1.2 mmol), solvent (3 ml) at 60 °C, reaction time 6 h.

[b] Determined by GC–MS.

[c] Benzaldehyde was obtained as a by-product.

[d] Remaining was the unreacted benzyl alcohol.

2.6. *General procedure for oxidative esterification of benzylic alcohols*

A 50 ml round bottomed flask was charged with heterogeneous Pd catalyst **1** (1 mol%), K_2CO_3 (1.2 equiv.) and methanol (3 ml). The base was soluble in the methanol and methanol acted as both reactant and reaction media for the present transformation. The resulting flask was sealed with septum, evacuated and back-filled with oxygen. After that the benzyl alcohol (1.0 equiv.) was added to the above suspension via syringe. The reaction mixture was stirred at 60 °C for the time as given in Table 1 in the presence of oxygen balloon. After completion, the mixture was cooled to room temperature and catalyst was recovered by the influence of external magnet. The crude product was dissolved in ethyl acetate and washed successively with water to remove the base. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue so obtained was purified by column chromatography using eluent ethyl acetate in hexane (20:80) to give the pure desired product. The recovered catalyst was washed with methanol, dried in vacuum and used for the subsequent runs.

3. Results and discussion

3.1. *Synthesis and characterization of the catalyst **1***

The synthetic process is indicated in Scheme 1. Graphene oxide was prepared by oxidation of graphite powder under harsh oxidizing conditions as following the literature procedure [25]. The synthesized graphene oxide was suspended into water and treated with ferrous sulphate, PEG 4000 and stirred for 24 h. The addition of $NaBH_4$ to the above suspension at 80 °C resulted in the formation of black colored graphene–magnetite nanocomposites. High specific surface area of GO along with easily accessible ample oxygen functionalities decorated on both side of GO nanosheets provided a better support for anchoring of iron nanoparticles. The SEM image of the synthesized magnetite–graphene nanocomposite (Fig. 1), indicating that the iron nanoparticles with average size of 30–40 nm were successfully combined with the graphene sheets. Further, the EDAX analysis supported the deposition of the iron nanoparticles onto the graphene surface with 8.0 wt.%. Further the addition of $PdCl_2(CH_3CN)_2$ complex into the Fe/FeO/graphene oxide suspension in dichloroethane yielded magnetically separable palladium(II) complex immobilized to graphene oxide as shown in Scheme 1.

Catalyst characterization by X-ray diffraction (XRD) (Fig. 2) and transmission electron microscopy (TEM) (Fig. 3) confirmed the successful formation of palladium/Fe/FeO/graphene oxide **1**. The X-ray diffraction pattern (Fig. 2) indicated the crystallinity of the synthesized heterogeneous material. In the XRD pattern of Fe/FeO/GO nanocomposite (Fig. 2b), the broad peak observed at the 2θ of 44.9° indicates the presence of zero-valent iron (α-Fe) crystalline phases

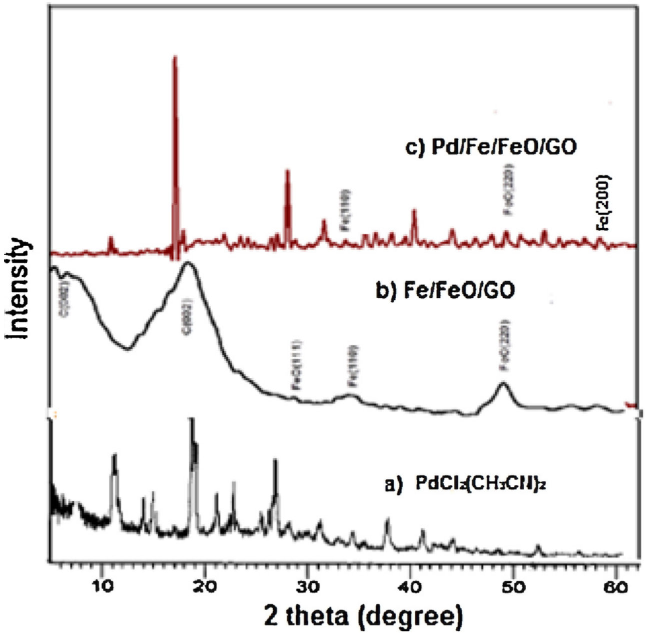


Fig. 2. XRD spectra of: (a) homogeneous $PdCl_2(CH_3CN)_2$; (b) magnetite–graphene nanocomposite; (c) magnetically separable palladium(II) complex immobilized to graphene oxide.

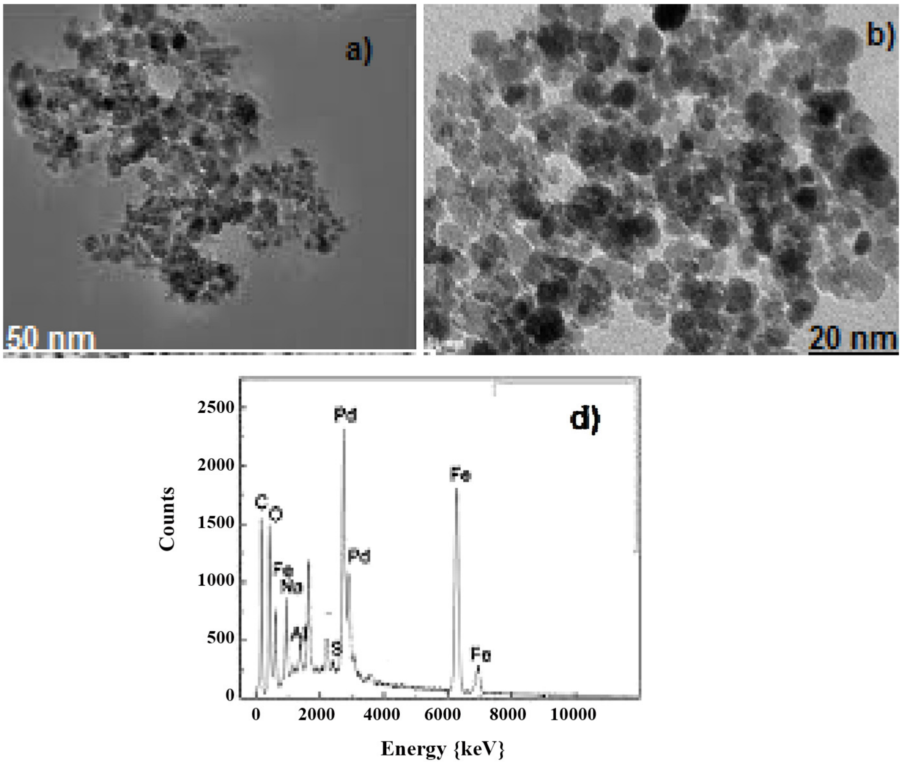


Fig. 3. TEM of magnetically separable palladium(II) complex immobilized to graphene oxide.

while small peaks at 28.9° and 35.8° attributed to FeO crystalline phase. In the XRD of Pd/Fe/FeO/GO, there is no C(002) diffraction peak, suggesting the disappearance of face-to-face stacking of graphene nanosheets. This is probably due to the presence of palladium complex and iron nanoparticles acting as a spacer to keep graphene nano-sheets isolated. Furthermore, the additional peaks at $2\theta = 18.6, 28.3, 31.2^{o}$ confirmed the presence of Pd^{2+} ions in the synthesized heterogeneous material. The XRD pattern of homogeneous Pd(II) complex, i.e. $[PdCl_2(CH_3CN)_2]$ is shown in Fig. 2a. The sharp peaks in the XRD pattern of **1** resemble well with the peaks of homogeneous palladium complex, confirming that palladium exists as Pd(II) complex in the synthesized material **1**.

The morphology and structure of Pd(II) complex immobilized to magnetite–graphene oxide nanocomposite was investigated in detail by TEM analysis. The TEM image (Fig. 3a and b) shows clearly that graphene oxide was decorated by palladium and iron nanoparticles with the diameters in the range of 30–50 nm. The distribution of magnetite as well as palladium complex on graphene sheets is uniform, and no aggregated or free particles are detected. Probably the electrostatic interaction between palladium ions and functional groups of graphene oxide provided the homogeneous distribution of the palladium complex on the surface of graphene oxide. The EDAX analysis (Fig. 3c), confirmed the presence of palladium and iron nanoparticles homogeneously distributed throughout the graphene surfaces.

FTIR spectrum [24–27] (Fig. 4) revealed the presence of various functional groups like —OH (3429 cm^{-1}), COOH (1723 cm^{-1}), C—O (1074 cm^{-1}) and C═O (1633 cm^{-1}) on the graphene oxide. The presence of these chemical functionalities makes the graphene oxide as an ideal support for anchoring of metal ions. A clear band at 582 cm^{-1} related to Fe—O suggested the successful grafting of iron nanoparticles to the graphene nanosheets. Mild reducing ability of polyethylene glycol might be responsible for the removal of some oxygenated functional groups in graphene–magnetite nanocomposite (Fig. 4).

Thermal behavior of the prepared catalyst was determined by thermogravimetric (TGA) analysis as shown in Fig. 5.

The weight percentage of palladium was found to be 10.23 wt.% as determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis.

The Pd oxidation states present in the synthesized catalyst **1** was determined by X-ray photoelectron spectroscopy (XPS) (Fig. 6). Photoelectrons with binding energies of 337.7 and 342.9 eV are observed, indicating that the Pd oxidation state in the synthesized material is +2 (Fig. 6).

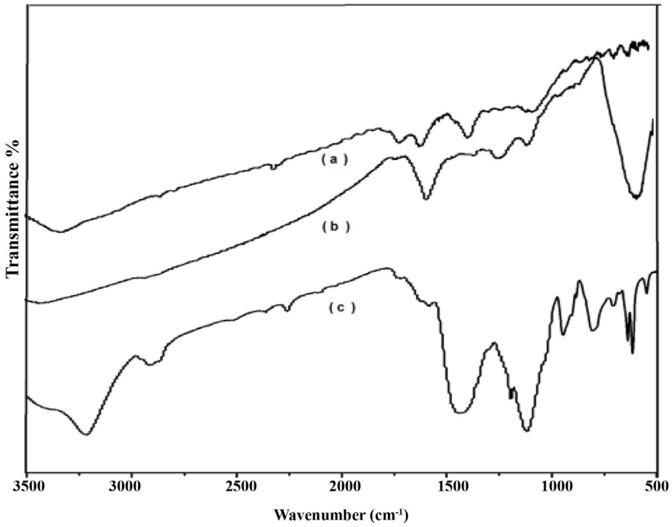
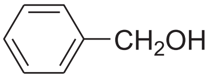
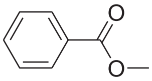
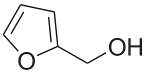
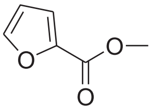
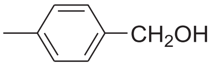
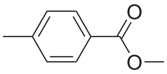
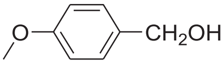
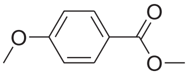
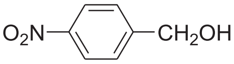
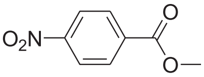
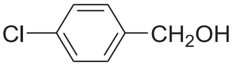
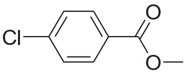
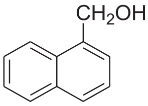
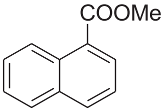
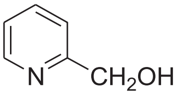
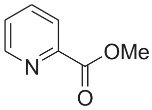
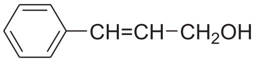
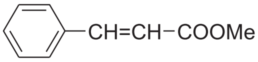
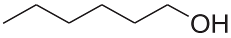
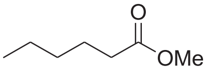
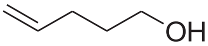
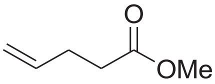


Fig. 4. FT-IR spectra of (a) graphene oxide; (b) magnetite–graphene nanocomposite; (c) Pd(II) on magnetite–graphene nanocomposite **1**.

Table 2
Oxidative esterification of different alcohols with methanol.[a]

Entry	Reactant	Product	Time (h)	Conv./select. (%)[b]	Yield (%)[c]	TOF (h^{-1})
1			6	100/90	88	15
2			6	98/88	86	14.6
3			5	99/92	90	18.4
4			5	98/91	90	18.2
5			8	90/80	78	10
6			8	86/75	74	9.4
7			6	89/80	78	13.3
8			6	90/85	83	14.2
9			8	80/78	76	9.7
10			8	72/66	64	8.2
11			8	80/63	60	7.9

[a] Reaction condition: substrate (1 mmol), catalyst **1** (1 mol%), K_2CO_3 (1.2 mmol), MeOH (3 ml) at 60 °C.
[b] Determined by GCMS, remaining products were the corresponding aldehyde and unconverted alcohol.
[c] Isolated yields.

3.2. Catalytic activity

The synthesized magnetically separable palladium(II) complex immobilized on graphene oxide was tested for the oxidative esterification of alcohols with methanol in the presence of base using molecular oxygen as the oxidant (Scheme 2). Initially different bases such as Na_2CO_3, K_2CO_3, NEt_3 and KO^tBu were tested for the reaction of benzyl alcohol and methanol using molecular oxygen as oxidant. Base screening showed that the organic base such as triethylamine was found to be ineffective while a stronger base, i.e. KO^tBu gave the highest conversion albeit poor selectivity of the desired ester (Table 1, entries 1–4). Potassium carbonate (K_2CO_3) was found to be the best base from both conversion and selectivity points of view. Likewise, no reaction was observed without addition of a base (Table 1, entry 5). Solvent effect was also investigated: using MeOH as solvent as well as reactant afforded the best result. Other solvents such as acetonitrile, DMSO, THF were found to be ineffective for the reaction of benzyl alcohol with methanol under similar experimental conditions (Table 1, entries 6–7). We also performed the oxidative esterification of benzyl alcohol in the presence of Fe/FeO/GO nanocomposite without palladium under identical experimental conditions. The reaction did not proceed and original substrates were obtained at the end of the reaction (Table 1, entry 8). Homogeneous palladium complex, i.e. $PdCl_2(CH_3CN)_2$ was found to be efficient but provided poor product yield as compared to the heterogeneous catalyst (Table 1, entry 9). The superior reactivity of magnetically separable palladium(II) complex immobilized to graphene oxide may be attributed to the promoting role of graphene support in the adsorption of reactant alcohol and oxygen. Characterization of the catalyst **1**, suggested that the palladium(II) complex was the real catalyst for the present transformation. To verify this, we prepared magnetically separable graphene oxide containing palladium (0) nanoparticles and studied the oxidative esterification of benzyl alcohol under described experimental conditions. The reaction did not proceed and original substrates were recovered at the end (Table 1, entry 10).

Further, we extended the reaction to a range of various aromatic and aliphatic alcohols (Table 2) under described experimental conditions. All the aromatic alcohols (Table 2, entries 1–8) with electron releasing and withdrawing substituents underwent oxidative methyl esterification in excellent yields. Benzylic alcohol substituted with the strongly electron-withdrawing group such as

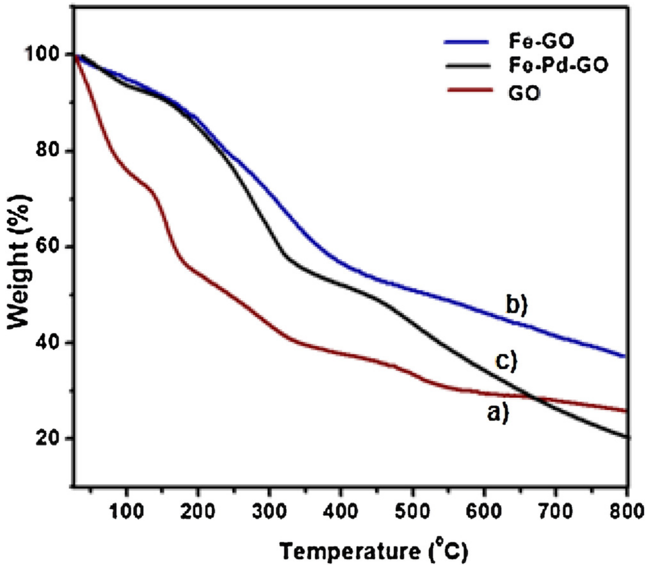


Fig. 5. TGA of (a) graphene oxide; (b) magnetite–graphene nanocomposite; (c) Pd(II) on magnetite–graphene nanocomposite **1**.

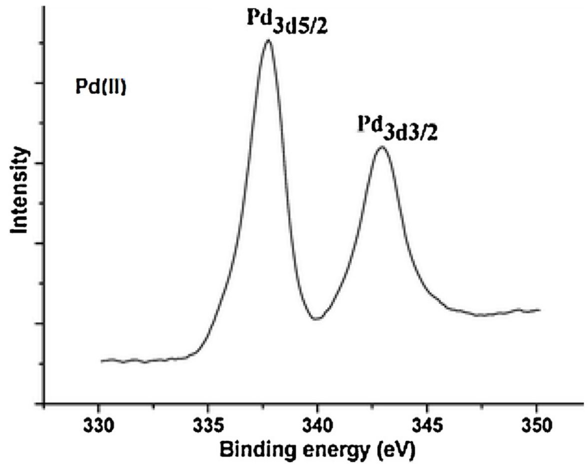
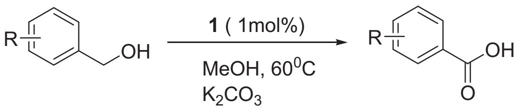


Fig. 6. XPS of Pd(II) complex immobilized to magnetite–graphene nanocomposite **1**.



Scheme 2. Oxidative esterification of alcohols with methanol.

p-NO_2, was found to be equally reactive and afforded 78% yield of the desired ester (entry 5). Finally, 2-pyridyl methanol (entry 8) and cinnamyl alcohol (entry 9) were also transformed to the corresponding esters in high yields. However, aliphatic alcohols were found to be less reactive and afforded poor yield of the desired ester (Table 2, entries 10–13). All the products were confirmed by comparing with their ^1H, ^{13}C NMR spectra with those of previously known compounds.

Next we checked the stability and recycling of the heterogeneous catalyst by using the benzyl alcohol as the representative example. The reaction was stopped after 3 h and catalyst was recovered by the effect of external magnet and washed with methanol, dried and reused for subsequent reaction. The recovered catalyst was tested for six subsequent runs by stopping the reaction before completion (Table 3). The reaction mixture was analyzed by GCMS, in all cases the conversion of the benzyl alcohol to methyl benzoate was found to be almost similar (54.1–53.8%) indicating that the prepared catalyst was quite stable and efficiently recyclable with consistent catalytic activity. Hot filtration test was performed in the oxidative esterification of benzyl alcohol to confirm that no leaching had occurred. The catalyst was refluxed in methanol for 3 h and then was separated by the filtration of hot reaction mixture. The solvent was then charged with substrate and allowed the oxidation under oxygen atmosphere for 10 h under identical reaction conditions. GC analysis of the catalyst-free reaction indicated that no oxidation of the substrate had occurred under these conditions. The absence of palladium in the filtrate solution was further confirmed by ICP-AES analysis, which indicated no detectable content of the Pd in the filtrate. Furthermore, the palladium content in the recovered catalyst (10.21 wt%) was found to be same as in the fresh one (10.23 wt%), indicating that the developed catalyst did not show any leaching and the reaction was truly heterogeneous in nature.

Table 3
Recycling of the heterogeneous Pd(II) catalyst.[a]

Run	1	2	3	4	5	6
Yield (%)[b]	54	54	54.1	53.8	53.8	53.8

[a] Reaction condition: benzyl alcohol (1 mmol), catalyst 1 (1 mol%), K_2CO_3 (1.2 mmol), MeOH (3 ml) at 60 °C, reaction time 3 h.
[b] Reaction was stopped before the completion and the reaction mixture was analyzed by GC–MS.

4. Conclusion

In conclusion, we described the first report on the use of magnetically separable palladium(II) complex immobilized to graphene oxide as catalyst for the direct aerobic oxidative esterification of alcohols with methanol. The developed method has been successfully applied to a range of substrates to give their corresponding methyl esters in moderate to high yields. Furthermore, the use of efficiently recyclable heterogeneous catalyst in conjunction with molecular oxygen as the oxidant represents a step toward an environmentally benign and sustainable process.

Acknowledgments

We are thankful to Director IIP, for his kind permission to publish these results. SV and DV acknowledge CSIR, New Delhi and UGC, New Delhi, respectively for their research fellowships.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2014.10.004.

References

[1] J. Otera, Esterification: Methods, Reactions, and Applications, Wiley-VCH, Weinheim, 2003.
[2] R.C. Larock, Comprehensive Organic Transformations: A Guide to Functional Group Preparations, 2nd ed., Wiley-VCH, New York, 1999.
[3] C.E. Rehberg, C.H. Fisher, J. Am. Chem. Soc. 66 (1944) 1203–1207.
[4] M. Hudlicky, Oxidations in Organic Chemistry, American Chemical Society, Washington, DC, 1990.
[5] R. Gopinath, B.K. Patel, Org. Lett. 2 (2000) 577–579.
[6] K. Ekoue-Kovi, C. Wolf, Chem. Eur. J. 14 (2008) 6302–6315.
[7] W.-J. Yoo, C.-J. Li, Tetrahedron Lett. 48 (2007) 1033–1035.
[8] W.-J. Yoo, C.-J. Li, J. Org. Chem. 71 (2006) 6266–6268.
[9] B. Xu, X. Liu, J. Haubrich, C.M. Friend, Nat. Chem. 2 (2010) 61–65.
[10] K. Takase, H. Masuda, O. Kai, Y. Nishiyama, S. Sakaguchi, Y. Ishii, Chem. Lett. (1995) 871–872.

[11] S.O. Nwaukwa, P.M. Keehn, Tetrahedron Lett. 23 (1982) 35–38.
[12] B.R. Travis, M. Sivakumar, G.O. Hollist, B. Borhan, Org. Lett. 5 (2003) 1031–1034.
[13] B.E. Maki, K.A. Scheidt, Org. Lett. 10 (2008) 4331–4334.
[14] R.L. Oliveira, P.K. Kiyohara, L.M. Rossi, Green Chem. 11 (2009) 1366–1370.
[15] H. Miyamura, T. Yasukawa, S. Kobayashi, Green Chem. 12 (2010) 776–778.
[16] Y. Hao, Y. Chong, S. Li, H. Yang, J. Phys. Chem. C 116 (2012) 6512–6519.
[17] S. Chandra, S. Bag, P. Das, D. Bhattacharya, P. Pramanik, Chem. Phys. Lett. 519 (2012) 59–63.
[18] V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara, J.-M. Basset, Chem. Rev. 111 (2011) 3036–3075.
[19] R.B.N. Baig Rajender, S. Varma, Catal. Commun. 49 (2013) 752–770.
[20] V. Polshettiwar, R.S. Varma, Org. Biomol. Chem. 7 (2009) 37–40.
[21] C. Liu, J. Wang, L. Meng, Y. Deng, Y. Li, A. Lei, Angew. Chem. Int. Ed. 50 (2011) 5144–5148.
[22] C. Liu, S. Tangza, A. Lei, Chem. Commun. 49 (2013) 1324–1326.
[23] S. Gowrisankar, H. Neumann, M. Beller, Angew. Chem. Int. Ed. 50 (2011) 5139–5143.
[24] H.A. Becerril, J. Mao, Z. Liu, R.M. Stoltenberg, Z. Bao, Y. Chen, ACS Nano 2 (2008) 463–470.
[25] W.S. Hummers, R.E. Offeman, J. Am. Chem. Soc. 80 (1958), 1339–1339.
[26] D.R. Dreyer, S. Park, C.W. Bielawski, R.S. Rouff, Chem. Soc. Rev. 39 (2010) 228–240.
[27] O.C. Compton, S.T. Nguyen, Small 6 (2010) 711–723.