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ARTICLE TYPE

Synthesis and characterization of Pd (II) dispersed over Diamine functionalized graphene oxide and its scope as catalyst for selective oxidation

Surjyakanta Rana, Suresh Maddila, and Sreekantha B. Jonnalagadda*

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A protocol for synthesis of active palladium (II) over diamine functionalized graphene oxide (Pd(II)AAPTMS@GO) is described. The catalyst gave excellent 96% conversion of benzyl alcohol with 99% selectivity towards benzaldehyde. The active catalytic material was fully characterized by BET surface area analysis, X-ray diffraction (XRD), Fourier-transfer infrared spectroscopy (FTIR), Raman spectra, X-ray photoelectron spectra (XPS), Scanning electron microscope (SEM) and Transmittance electron microscopy (TEM). From FT-IR, the organic amine was successfully grafting over the graphene surface. The palladium distribution on graphene oxide surface was conformed from TEM. The catalytic activity remained unaltered in the first five cycles, but efficiency of conversion and yield dropped to 89% in the 6th cycle.

Introduction

Selective oxidation of alcohols to aldehydes or ketones is one of the important reactions in organic chemistry. Aldehydes and ketones are valuable chemicals in the dye, perfumery and agro chemical related industries.[1] The oxidation of alcohols in industry mostly has been based on the use of stoichiometric amounts of CrO_3, $K_2Cr_2O_7$, $KMnO_4$, MnO_2, etc., which are expensive and environmentally unfriendly.[2] In the past few decades, transition-metals, such as palladium, copper, rhodium, iridium, iron and gold, as catalysts have been meaningfully developed as catalysts, which have played pivot role in organic synthesis. There is a strong interest in finding better catalysts and alternative methods that are eco-friendly and economically viable. Heterogeneous catalysts remained best option due good selectivity and scope for recycling. However, not many articles with palladium as active material have been reported. Mori et al. have observed that Pd supported on Al_2O_3, SiO_2, and C as catalyst produced the aldehydes with less than 50% selectivity.[3] While Manyar et al. have reported the oxidation of alcohol using phosphomolybdic acid supported vanadium-alumina mixed oxides and toluene as solvent, [4] Shimaju et al., have reported that oxidation of benzyl alcohol over Pd/Ni-Zn catalyst gave 90 % conversion. [5] Pd/LDH catalyst has been reported by Kakiuchi et al., for oxidation of alcohol using toluene as solvent.[6] Keresszegi et al., have reported that oxidation of benzyl alcohol over Pd/Al_2O_3catalyst gave 82 % conversion by the help of cyclohexane solvent. [7] In this context, the graphene oxide and modified graphene oxide are definitely attractive as support for economically viable and easily synthesizable option.

Graphene oxide (GO) is a two-dimensional single-layer sheet of honey-comb like structure, having grander properties, such as high surface properties, high optical, electrical conductivity etc. [8-17] There are several structural models for GO and the final structure of GO would depend on the chemical oxidation process that is employed. While graphene oxide contains various functional groups like hydroxyl, epoxy and carboxylic, only epoxy and carboxylic groups would facilitate the functionalization of its surface properties by binding to some organic moiety through covalent linkage. The modified hybrid material is stable and can effectively bind a metal. Hence, graphene oxide based hybride materials have received enhanced attention as they combine the advantages of graphene oxide and other components, which have potential applications in the catalysis, sensors and energy fields. Therefore, we attempted to develop such type of new hydride material, with potential for various applications. Of the number of ways for preparation of graphene oxide reported in literature, [18-20] the modified Hummers method followed by sonication for preparation of single layer graphene oxide is adopted in the current study.

In this study, we herein reported for the first time the synthesis of palladium over diamine functionalized graphene oxide and its potential as catalyst for selective partial oxidation of benzyl alcohol with water medium.

Experimental

Preparation of Graphene Oxide:

Initially, graphite powder (0.5 g) and $NaNO_3$ (0.5 g) were dissolved in concentrated H_2SO_4 (23 ml) with stirring for 20 min and the mixture was cooled on ice bath for 2 h. Then, the reaction mixture was put on hot plate with magnetic stirrer at 40 °C and $KMnO_4$ (6 g) crystalline powder was added slowly with continues stirring for 70 min. Next, distilled water (50 ml) was added to the mixture and stirred for further 20 min. H_2O_2 (30 %) was then added to the above mixture till the colour of the solution changed from dark brown to yellow. Upon the colour change, water (50 ml) was added, and the resulting solution was sonicated for 2 h. The solution was centrifuged, separated, filtered and washed with double distilled water several times. The product was dried in a vacuum oven at 100 ^oC overnight to obtain graphene oxide.

Preparation of metal modified amine functionalized Graphene Oxide:

GO (1 g) was dissolved in toluene (50 ml) in a conical flask and sonicated for 2 h. [3-(2-Aminoethylamino) propyl] trimethoxysilane (AAPTMS) (1.68 mmol) (Aldrich) was added to the above solution and sonicated further for 1 h. Next, palladium nitrate (0.2 mmol) was added to the mixture and stirred for 4 h. The solution was centrifuge and dried in a vacuum oven at 100 ^oC over night to obtain Pd(II)-AAPTMS@GO(Scheme-1). The amine functionalized GO (AAPTMS@GO) sheets serve to stabilize the Pd metal for several cycles. In the reaction medium, after oxidation reaction the Pd(II) converted to Pd(0). In this situation, AAPTMS@GO will supply adequate electron density to the anchored Pd(0)species to facilitate the oxidation reaction.

Characterization of Catalysts:

The powder X-ray diffraction (XRD) performed on a Bruker D8 Advance instrument, equipped with an Anton Paar XRK 900 reaction chamber, a TCU 750 temperature control unit and a CuKα radiation source with a wavelength of 1.5406 nm at 40 kV and 40 mA. Diffractograms were recorded over the range 15–90° with a step size of 0.5 per second. The TEM images were viewed on a Jeol JEM-1010 electron microscope. The images were captured and analysed by using iTEM software. The SEM measurements were carried out using a JEOL JSM-6100 microscope equipped with an energy-dispersive X-ray analyzer (EDX). Infrared spectra of the samples were recorded using Fourier transmission infrared (FTIR) spectrometer (PerkinElmer spectrum 100 series with universal ATR accessory). Raman spectra are collected on a Perkin Elmer 1200 Fourier Transform Infrared and on a DeltaNu advantage 532™ Raman Spectrometer (100 mW Nd: YAG laser with an excitation wavelength of 532 nm). The X-ray photoelectron spectra of Pd were recorded by using a KRATOS apparatus with Mg, Al and CuKα as X-ray sources.

Catalytic reaction:

Pd(II)-AAPTMS@GO catalyst (0.15 g), Benzyl alcohol (1 mmol), pyridine (5 mmol, 0.4 ml) as base, and 10 ml of water as solvent were stirred in a round bottom flask. The suspension was purged with molecular oxygen. The reaction mixture was stirred at 60 ^oC under 1 atm of O_2 for 3 h under constant stirring (Scheme-II). After completion of reaction, the catalyst was separated by centrifuge. Organic part was extracted with diethyl ether and the final product was analyzed by GC.

Results and discussion

The X-ray diffraction study of GO, and Pd(II)-AAPTMS@GO are shown in figure1. In that pattern, at 2θ approximately 10.651 and 42.91 are the characteristic diffraction peaks (002) of graphene oxide [21,22] and to the (100) plane of the hexagonal structure of carbon.[21,23.] After modification of both amine and palladium over the graphene oxide sheets, the (002) plane slightly shifted towards higher angle at 2θ≈ 11.52 due to the molecule intercalation and also sonication. The peak at 2θ≈ 40.11, 46.27 and 68.32 correspond to palladium (111), (200) and (220) plane. Hence, it was conformed that palladium modified over organo functionalized graphene oxide sheets.

The FT-IR spectra of GO and Pd(II)-AAPTMS@GO samples are shown in the figure 2. From this spectra, 3400 cm^{-1}, 1385 cm^{-1}, 1740 cm^{-1}, and 1100 cm^{-1} corresponds to O–H stretching, O-H vibration of C–OH group, C=O stretching of –COOH and epoxy vibration. The epoxy groups and the carboxyl groups vanish after modification of organo group by graphene oxide. The N-H stretching and NH_2 bending mode of free NH_2 groups correspond to 3371 cm^{-1} and 1638 cm^{-1}. The presence of 690 cm^{-1} for N-H bending vibration and 1532 cm^{-1} for -NH_2 symmetric bending vibration in the synthesized material, conformation of the organo amine is successfully linked to epoxy group and carboxyl group of graphene materials.

The Raman spectra of GO (a) and Pd (II)-AAPTMS@GO (b) are shown in figure 3. In those spectra, the entire sample exhibited in the characteristic D, and G bands. From GO spectrum [figure 3 (a)], the characteristic bands D, and G correspond to 1350 and 1590 cm^{-1}. The disorder in the sp^2-hybridized carbon atoms in graphene sheets is confirmed by the D-band of the Raman spectra, while G band corresponds to σ-sp^2 bonded C-atoms. In GO materials D band was very less i.e., negligible disorder. After modification of organic amine with palladium (Figure 3(b)), the D- band and G-band shifted towards higher wave number, which may be due to the gradually increased compressive local stress caused by molecule intercalation.

The SEM images of GO, AAPTMS@GO, Pd(II)-AAPTMS@GO and recycled catalyst are shown in Figure 4. The layer-like sheet structures were obtained for GO (Figure. 4a). The GO nano-sheets were formed due to the sonication process. The spherical palladium was present in each layer and also on the edges of the organo functionalized graphene sheet (Figure 4c). The recycled catalyst did not change its morphology after the reaction (Figure 4d).

Energy-dispersive X-ray spectroscopy gives the information about type of element present in that particular area. The EDX image of GO and Pd(II)-AAPTMS@GO is shown in the figure 5. From these spectra, only carbon was present in graphene oxide materials, but silicon, carbon, nitrogen, and palladium were present in Pd(II)-AAPTMS@GO materials.

The TEM image of GO, AAPTMS@GO, Pd(II)-AAPTMS@GO and higher magnification of Pd(II)-AAPTMS@GO are shown in the figure 6. In figure 6(a), as prepared sample is single layer graphene oxide, but after modification of organic group over the graphene oxide surface, the net like structure was formed [figure 6 (b)]. The black spots in figure 6 (c & d), show that the palladium metal particles are uniformly distributed over the organic surface. The particle size are around (4-7) nm.

XPS spectra of before and after reaction of the Pd3d region of Pd(II)-AAPTMS@GO catalyst are shown in the figure 7. The binding energy at 336.24 and 344.95 eV corresponding to $3d^{5/2}$ and $3d^{3/2}$ for the before reaction of the catalyst in figure 7(a) and the binding energy values at 337.19 eV and 345.72 due to $3d^{5/2}$

and $3d^{3/2}$ for the after reaction (filtered catalyst) respectively in Figure 7 (b). [24, 25] From the above data, we conclude that, only Pd^{2+} species exist in Pd(II)-AAPTMS@GO both before and after benzyl alcohol oxidation reaction.

Various reactions with different catalysts and catalyst-free conditions were carried out to optimize the appropriate reaction conditions to ideally maximize the product conversion at short reaction times. In our initial study, benzyl alcohol (1.0 mmol), pyridine (5 mmol, 0.4 ml) as base, bubbling molecular oxygen with water as solvent and with no catalyst, recorded no reaction. In presence of GO catalyst for 3 h, 60 °C, reaction was futile to obtain any product (Table 1, entries 1 & 2). We examined the efficiency of modified graphene and Pd/modified graphene oxide as catalysts for the reaction under similar conditions and the % conversion was 12 and 96% respectively. (Table 1, entry 3 & 4).

The probable mechanism of benzyl alcohol oxidation using O_2 over Pd (II)-AAPTMS@GO catalyst designated as Gn Pd(II) is shown in scheme-III. First step is the Pd(II) catalysed aerobic oxidation of alcohol to aldehyde, and Pd(II) reduces to Pd(0). In the second step, Pd(0) reacts with O_2 to produce palladium peroxo intermediate and the peroxo intermediate develops protonated to regenerate Pd(II).[26, 27] In the reaction medium, pyridine only promotes the rate of reaction.

To broaden the scope of the title reaction, various substituted benzyl alcohols were examined in the presence of a catalytic amount of Pd(II) substituted diamine functionalized graphene oxide for oxidation of alcohol and the results are summarized in Table 2. The derivatives of benzyl alcohol bearing electron withdrawing groups (nitro group) were less reactive towards oxidation reaction (Table 2, entry 3), but electron donating groups ($-OCH_3$) gave better conversions under wise identical conditions, (Table 2, entry 2) i.e., the % conversion increases due to its sufficient electron density in active centre, as compare to the electron withdrawing group.

Turnover frequency (TOF) totally depends on the Palladium (II) concentration, which reflects the structural development of supported palladium. Ikeda et al. reported oxidation of benzyl alcohol over Pd@*hm*C, Pd/activated carbon and Pd/*hm*C composite catalyst gives turnover frequency (TOF) = 2940 h^{-1}, TOF = 2090 h^{-1} and TOF = 1528 h^{-1}.[28] Yang et al. have observed that oxidation of benzyl alcohol over Pd/Al_2O_3 catalyst gave TOF ($3883h^{-1}$).[29] Li et al., have reported that benzyl alcohol oxidation over Pd/GO, Pd/GC, Pd/CNT and Pd/AC catalyst gave conversion less than 73%, but (TOF) 15017 mol/h, 30137 mol/h, 6910 mol/h and 11267 mol/h respectively.[30] In our study, we obtained higher conversion, better selectivity and higher TOF (24677.33 mol/h) up to five runs for benzyl alcohol oxidation in water medium over Pd(II)-AAPTMS@GO.

A comparative summary with various reported catalysts for the oxidation of benzyl alcohol is tabulated in Table 3. A perusal of the data shows that in the current study, we are getting higher selectivity and higher TOF for benzyl alcohol oxidation in water medium relative to other reported systems with Pd(II), except with Pd(II)/NiZn HTLc catalyst. Hara et al., carried out the reaction using trifluorotoluene, higher temperature and Pd(II)/NiZn HTLc as catalyst and got 99% conversion.[33] Through, they got excellent results by the help of an organic solvent, which is not so environmentally benign. Therefore the effectiveness of our new catalyst in absence of any organic solvent is ideal and opportune.

The effect of amount of Pd(II)-AAPTMS@GO catalyst loading on the benzyl alcohol conversion to benzaldehyde is illustrated in the figure 8. With the increase the catalyst amount, the % conversion increased, but the selectivity towards benzaldehyde decreased. This may be due the increase in active sites resulting from higher amount of catalyst, facilitating the further oxidation of benzaldehyde to benzoic acid.

Figure 9 shows the influence of reaction time on the conversion of benzyl alcohol and product selectivity over the Pd(II)-AAPTMS@GO catalyst. When, the reaction time is increased from 1 h to 5 h, the % conversion of benzyl alcohol too increased, but the selectivity of benzaldehyde decreased. At optimum reaction was about 3 h, when catalyst registered highest conversion (96%) with excellent selectivity (99%) towards benzaldehyde. With increase the reaction time from 3h to 5h, the conversion marginally increased from 96% to 99%, but the selectivity towards benzaldehyde dropped from 99% to 83 %, due to over oxidation of benzaldehyde to benzoic acid.

To investigate the scope of recycling of heterogeneous catalyst, after completion of reaction, the catalyst was recovered by filtration, washed with water in several times and dried under vacuum at 80 °C. The recovered catalyst was repetitively used for 5 times, with no loss in catalytic activity (Figure 10). The catalytic activity decreased after 5th run, which could be due to either temporary poisoning by organic impurities, due to minor changes in the structure like coke formed or losses in recovery of the catalyst material.

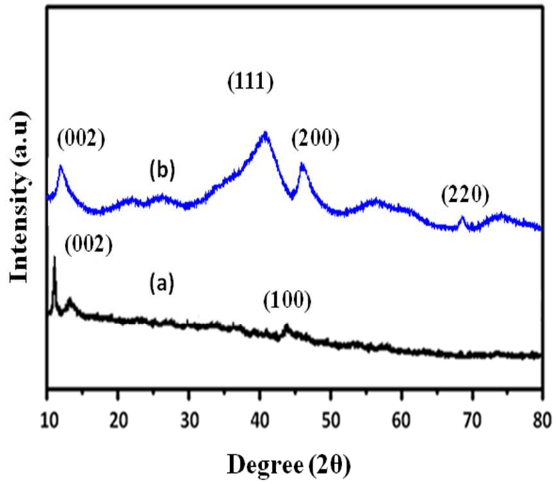


Figure 1: XRD spectra of GO (a) and Pd(II)-AAPTMS@GO(b)

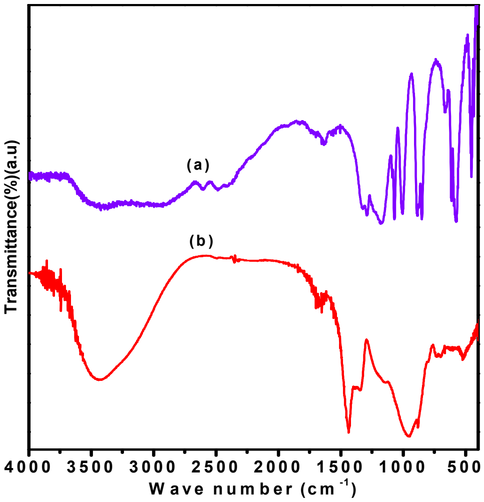


Figure 2: FT-IR spectra of GO (a) and Pd(II)-AAPTMS@GO (b) samples

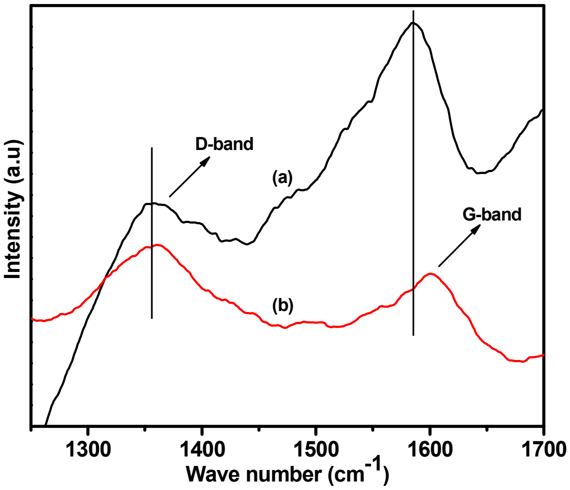


Figure 3: Raman spectra of GO and Pd(II)-AAPTMS@GO.

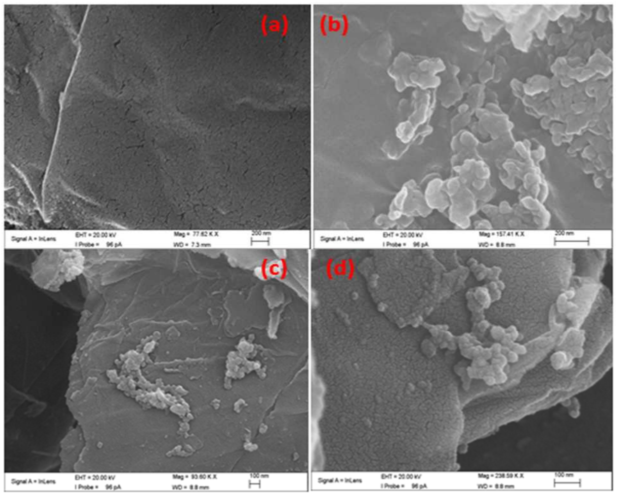


Figure 4: SEM Image of (a) GO, (b) AAPTMS@GO, (c) Pd(II)-AAPTMS@GO, and (d) SEM image of the recycled catalyst.

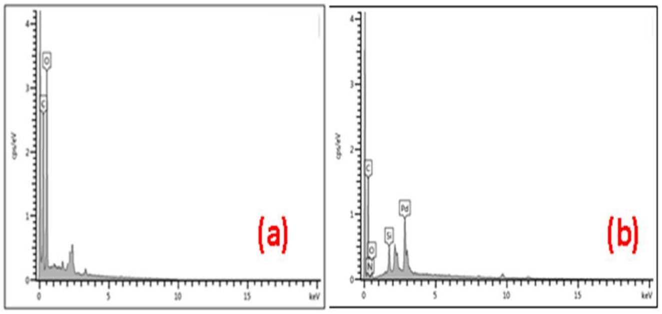


Figure 5: EDX spectra of (a) GO, and (b) Pd(II)-AAPTMS@GO catalyst.

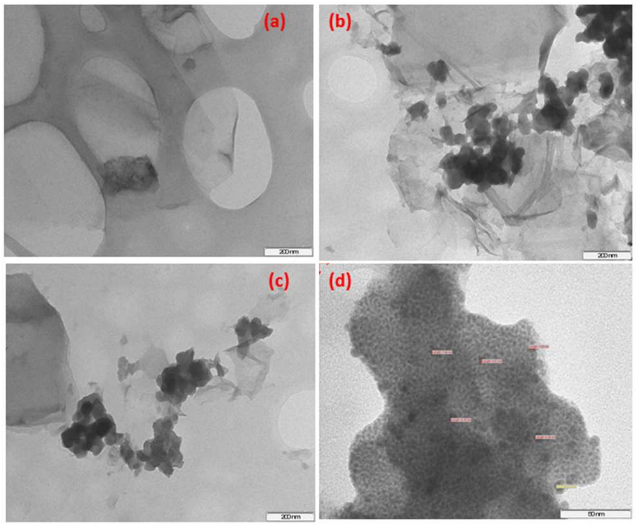


Figure 6: TEM Image of (a) GO, (b) AAPTMS@GO, (c) Pd(II)-AAPTMS@GO, and (d) Higher magnification of Pd(II)-AAPTMS@GO.

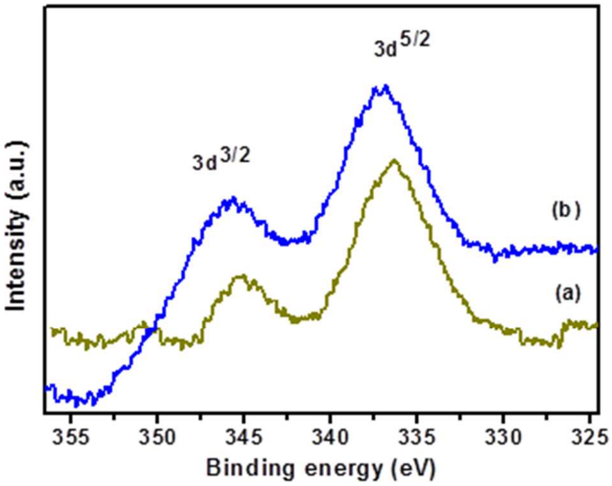


Figure 7: XPS spectra of before (a) and after reaction (b) of the Pd3d region of Pd(II)-AAPTMS@GO catalyst.

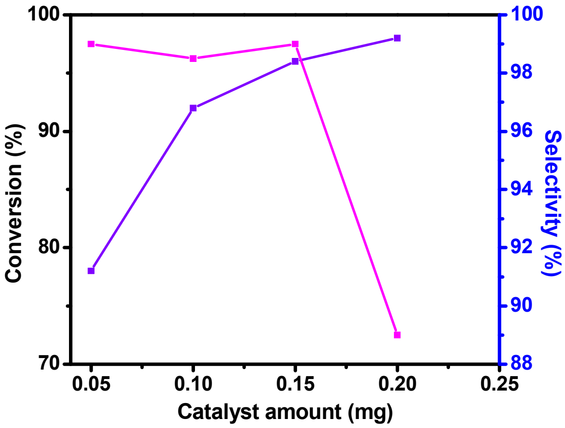


Figure 8: Effect of catalyst amount on the conversion of benzyl alcohol and selectivity of benzaldehyde over Pd (II)AAPTMS@GO Catalyst.

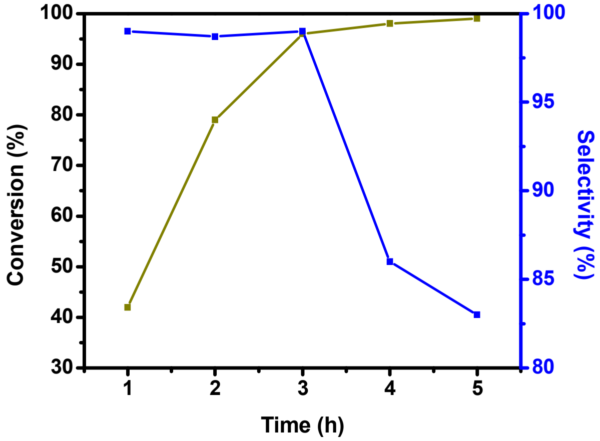


Figure 9: Effect of time on the conversion of benzyl alcohol and selectivity of benzaldehyde over Pd(II)AAPTMS@GO Catalyst

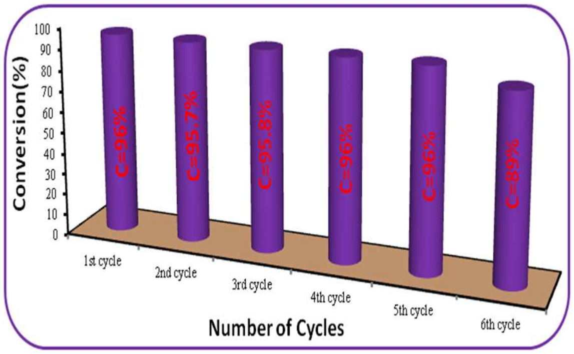
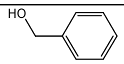
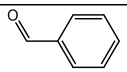
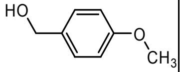
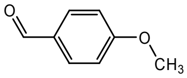
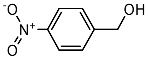
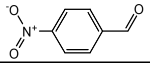


Figure 10: Reusability of catalyst (Pd(II)AAPTMS@GO).

Table 1. Activity of Various Catalysts toward oxidation reaction

S.1	Catalyst	conversion	Selectivity (%)	
			Benzaldehyde	Benzoic acid
1	Without catalyst	0		
2	GO	Tracer	-	-
3	AAPTMS@GO	12	59	41
4	Pd(II)AAPTMS@GO	96	99	1

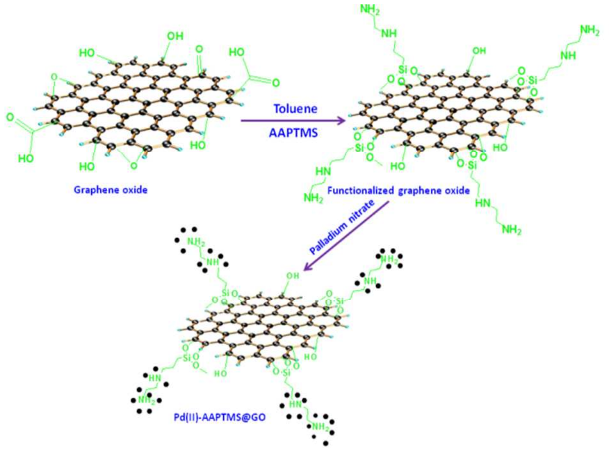
Table 2: Effect of substrate on oxidation reaction[a].

SL	Reactant	Product	Conversion (%)	Selectivity (%)
1			96	99
2			97	99
3			82	99

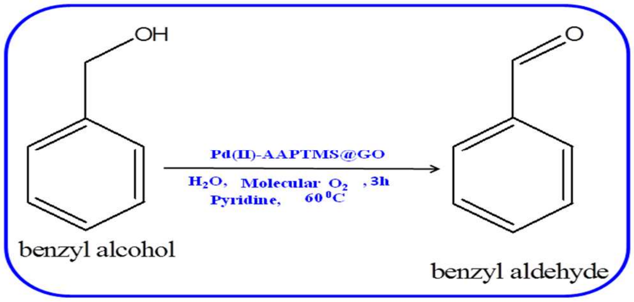
[a] Reaction conditions: catalyst (0.15 g), Benzyl alcohol (1 mmol), pyridine (5 mmol, 0.4 ml), and solvent (water, 10 ml), Temperature (60 °C) under 1 atm of O_2 for 3 h.

Table 3: Oxidation of benzyl alcohol catalyzed by Pd(II) in a variety supported catalysts

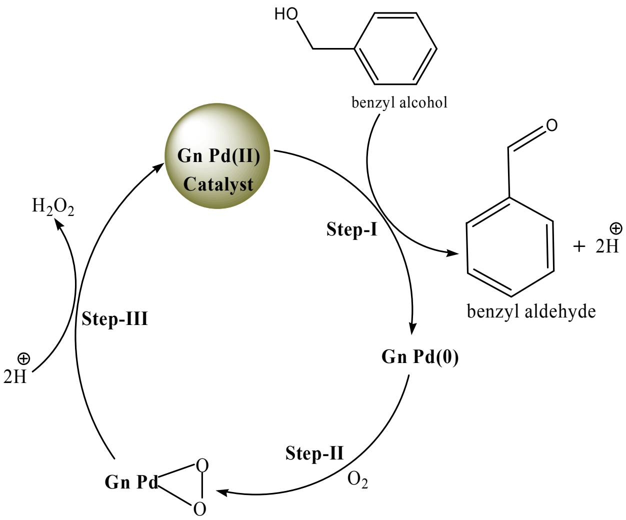
Catalyst	Solvent	Temperature (°C)	Time (h)	Conv. (%)	Reference
Pd(II)-AAPTMS@GO	Water	60	3	96	Present work
Pd(II)-HTLc	Toluene	80	2	74	31
Pd/Fe@C	Acetonitrile	80	25	96	32
Pd/Fe@C	Water	80	25	63	32
Pd(II)/NiZn HTLc	Trifluoro Toluene	80	1	99	33



Scheme 1: Preparation of Pd(II)-AAPTMS@GO catalyst.



Scheme II: Catalytic reaction path of benzyl alcohol to benzaldehyde.



Scheme III: Mechanism of oxidation of benzyl alcohol over Pd(II)-AAPTMS@GO catalyst.

Conclusions

In conclusion, we report an efficient protocol for oxidation of alcohol derivatives using Pd (II) substituted diamine functionalized graphene oxide as catalyst in aqueous media. The Raman study revealed that the prepared carbon based catalyst has lesser defect in structure. The binding of organic group covalently onto graphene oxide layer was confirmed by the FTIR and TEM analysis. We have developed simple, highly efficient and recyclable heterogeneous catalyst for partial oxidation of benzyl alcohol derivatives.

Notes and references

[a] *School of Chemistry & Physics, University of KwaZulu-Natal,Durban-4000, South Africa. Fax: +27 31 260 3091; Tel: +27 31 260 7325/3090; E-mail: jonnalagaddas@ukzn.ac.za*

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